

## DEVELOPMENT OF LOW SURFACE AREA CHAR FOR CLEANUP OF INCINERATOR FLUE GAS

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### INTRODUCTION

Carbon-based systems for cleanup of flue gas have been installed on commercial medical, hazardous and municipal waste incinerators throughout Europe. The activated carbon technology is given preference over other alternatives because of its high removal efficiency for sulfur oxides, dioxins, furans, mercury, heavy metals and other air toxics. Typically, flue gases pass through an activated carbon filter at temperatures between 100 and 150°C. In the process developed by STEAG Aktiengesellschaft [1], known as the /a/c/t<sup>TM</sup>-process, a three layer moving bed of carbon separates and treats selectively pollutants in each layer. The spent carbon is returned to the incinerator where the adsorbed contaminants are either destroyed or released again for ultimate removal in a wet scrubber system situated upstream of the carbon filter. Operating results show that current European emission requirements are met with this type of system. Availability of this proven technology in the U.S. could prompt legislation to set incinerator emissions limits low enough to make incinerators acceptable to the American public. The potential market for activated char in the U.S. is estimated to be 80,000 tons/year, assuming 10% of U.S. incinerators adopt this technology to meet needs emanating from anticipated regulation of emissions from existing incinerators. A domestic source of low cost activated carbon is needed for such processes soon to be installed on U.S. waste incinerators. The carbon used by STEAG (or so-called "Herdofenkoks") is made from German lignite and has a relatively low surface area (< 270 m<sup>2</sup>/g) and price (< \$300/ton). The Illinois State Geological Survey (ISGS) has an ongoing program to develop new markets for high sulfur Illinois coal [1-9]. The specific goals of the present study [8,9] were to design and engineer a low cost char from Illinois coal suitable for cleanup of incinerator flue gas, scale up the char production process, and test the char under representative flue gas conditions.

### EXPERIMENTAL

A 1500 pound sample of size-graded (1x5 mm) Colchester (Illinois No. 2) hvC bituminous coal was used as feedstock for production of activated char. The coal has a free swelling index of 4.5. Char production runs were performed at the ISGS using a 2 in. ID horizontal tube furnace (HTF), 4 in. ID, 4 ft. (heated zone) continuous feed rotary tube kiln (RTK), and continuous feed charring oven (CFCO). Allis Mineral Systems (AMS) provided facilities for large scale production of activated char that included a 20 in. ID, 4 ft. batch RTK, an 8 in. ID, 4 ft. continuous RTK, and an externally fired, 18 in. ID, 10 ft. RTK. Details of the procedures and conditions used in production runs performed at the ISGS and AMS are given elsewhere [8,9]. The SO<sub>2</sub> adsorption capacity of a char was determined using a Cahn TG-131 thermogravimetric analyzer (2500 ppm SO<sub>2</sub>, 5% O<sub>2</sub>, 7% H<sub>2</sub>O, balance N<sub>2</sub>). Single point N<sub>2</sub> BET surface areas were determined at 77 K using a Monosorb flow apparatus (Quantachrome Corporation).

### RESULTS AND DISCUSSION

The caking properties of the Illinois coal were detrimental to surface area development. Various strategies were devised to produce a char with a surface area of 150-300 m<sup>2</sup>/g at a cost comparable to that of the German Herdofenkoks (activated carbon based on lignite). Table 1 summarizes the char production experiments performed in this study. Initial runs (samples 1-10) involved two step processes, either pyrolysis/activation or preoxidation/activation. A staged heating method used in a previous study [10] to prevent agglomeration of Illinois coal in a

fluidized bed produced a coke-like material of limited surface area (samples 1 and 2). A two step process involving activation in air at 435°C produced chars with surface areas of 150 m<sup>2</sup>/g (samples 3-5). However, air activation is not practical when manufacturing ton quantities of activated carbon due to problems that may arise with spontaneous ignition of the carbon bed. Furthermore, it has been recently shown that the SO<sub>2</sub> adsorption capacity of coal char oxidized in air is significantly less than that of one activated in H<sub>2</sub>O [2,3,11]. A two step process involving preoxidation in air at 250-350°C and activation in CO<sub>2</sub> at 850°C produced chars with surface areas of up to 200 m<sup>2</sup>/g (samples 7-10). The surface area of the char is seen to be dependent on preoxidation time and temperature. A preoxidation temperature of 250°C was deemed appropriate for the charring equipment made available at the AMS facility. A preoxidation time of 4 h was used for sample 9, but this tended to significantly decrease both the mechanical strength and yield of the final char product, which would add significantly to final production cost.

To minimize preoxidation time and improve char quality, a three step process was devised which included preoxidation, activation and an intermediate pyrolysis step. Recent work by Sun [12] had suggested that such an intermediate step could be used to enhance surface area development of Illinois coal char. Table 1 shows that chars (samples 11-16) of suitable surface area (151-237 m<sup>2</sup>/g) were produced using this three step process and preoxidation times as low as 0.5 h. The use of an intermediate pyrolysis step shortens considerably the preoxidation time needed to produce a char of adequate surface area (e.g., compare samples 9 and 12), and may decrease the activation time to achieve a given surface area. Heat treatment of preoxidized coal at some intermediate temperature (400-450°C) slows down the devolatilization process enough to allow adsorbed oxygen to cross link and prevent further rearrangement of the coal structure (melting), thus increasing the surface area of the resultant char. It is interesting to note that the char used in the STEAG /a/c/t<sup>TM</sup>-process is made from German lignite in a one step process (950°C, 0.75 h). Attempts have been made by others to produce a similar material from U.S. lignite; however, the final product typically lacks mechanical strength, and thus cannot be used in the STEAG /a/c/t<sup>TM</sup>-process nor in any other fixed-bed technology.

Based on the results presented in Table 1 (samples 11-16) and on those from several preliminary runs performed in a 20 in. ID batch and 8 in. ID continuous feed RTK at AMS [8,9], 610 pounds of activated char were produced from 1280 pounds of coal (48% yield) in the 18 in. ID, 10 ft. RTK. The three steps, preoxidation, pyrolysis and activation were done consecutively in three passes through the kiln. The initial coal feed rate during preoxidation was set at 50 lb/h to maintain a 2 h residence time at 250°C. The feed rate was decreased to 40 lb/h to increase residence time and extent of oxidation in the kiln. (A reactor that provides better gas-solid contact, e.g., fluidized bed, would probably be a more effective way to preoxidize the coal [9].) The second step, pyrolysis, was done in flowing N<sub>2</sub> (8 L/min) at a temperature between 410 and 425°C and a coal feed rate of 65 lb/h. Char activation was done in flowing CO<sub>2</sub> (6 L/min) with a char feed rate of 50 lb/h, residence time of 2 h, and a temperature between 870 and 920°C. The physical and chemical properties of the final product are compared to those of the German Herdofenkoks in Table 2. Although the surface area of ISGS char was only 110 m<sup>2</sup>/g, it adsorbed significantly more SO<sub>2</sub> than the German Herdofenkoks after 4 h adsorption time. Compared to

surface area, the SO<sub>2</sub> adsorption capacity of the char is actually the best indicator of how it will perform in the commercial unit [8,9].

Commercial activated carbons available in the U.S. today are believed to be too reactive due to their relatively high surface area (> 600 m<sup>2</sup>/g) and propensity to adsorb and react with NO<sub>x</sub>. The reaction of carbon with adsorbed NO<sub>x</sub> is exothermic and can ignite the carbon bed under certain conditions, e.g., in the absence of gas flow. Thus, the STEAG /a/c/t<sup>TM</sup>-process requires the use of a low activity char having a surface area less than 300 m<sup>2</sup>/g. Five hundred and fifty pounds of the activated char produced in this study was shipped to Essen, Germany where it was installed in a pilot plant unit and subjected to a NO<sub>x</sub> self heating test. This involved adsorbing NO<sub>x</sub> on the carbon until saturated, shutting off the flow of gas to the adsorber, and measuring the temperature rise of the char bed. The ISGS char is the only U.S. material known to have passed this NO<sub>x</sub> self heating test. The test unit containing ISGS char was then installed on a slip stream of flue gas from a waste incinerator located in Germany. Flue gas velocity through the char bed (800 mm) was 0.15 m/s. The ISGS activated char was effective in removing more than 99.7% of the dioxins and furans from the incinerator flue gas (Table 3). Also, the mercury, which was present in the inlet gas, was not detected in the exit gas. The removal efficiencies of ISGS char were at least as good as those achieved with the char presently used by STEAG /a/c/t<sup>TM</sup> processes in Europe. The two-week test, however, was not of ample duration to observe complete breakthrough of the pollutants listed in Table 3, so there is no information on capacity. Typically, other pollutants do not breakthrough the bed before SO<sub>2</sub> in these types of tests; thus the SO<sub>2</sub> capacity of the char is considered a good measure of the total adsorption capacity of the char.

#### CONCLUSIONS

Conditions were established to produce a low surface area activated char from Illinois coal of with properties suitable for cleanup of incinerator flue gas. The production steps were carried through two levels of scale up, culminating in the production of 610 pounds of activated char in an 18 in. ID, 10 ft. rotary tube kiln. A three step process, which included preoxidation, pyrolysis and activation was used to produce an activated char with a N<sub>2</sub> BET surface area of 110 m<sup>2</sup>/g and an SO<sub>2</sub> adsorption capacity of 5% by weight, the latter being almost twice that of the char used in the STEAG /a/c/t<sup>TM</sup>-process. The char was effective in removing more

than 99.7% of the mercury, dioxins and furans from an incinerator flue gas. An economic analysis of the char production process developed in this study indicates that it would cost between \$325 and \$400 to produce one ton of activated char with a plant designed and constructed to produce 80,000 tons/year activated char assuming a 20% rate of return on initial investment.

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Table 1. Summary of Char Preparation Experiments.

Sample	Preoxidation	Pyrolysis	Activation	Yield (%)	Surface Area (m <sup>2</sup> /g)
1	----	HTF, N <sub>2</sub> , 350°C, 0.75 h, 375°C, 0.75 h	HTF, CO <sub>2</sub> , 850°C, 1 h	---	2
2	----	HTF, Air, 350°C, 0.75 h, 375°C, 0.75 h, 410°C, 0.3 h	HTF, CO <sub>2</sub> , 850°C, 1 h	---	116
3	----	CFCO, 7% O <sub>2</sub> , 575°C, 0.2 h	RTK, Air, 435°C, 0.5 h	---	144
4	----	CFCO, 7% O <sub>2</sub> , 575°C, 0.2 h	RTK, Air, 435°C, 0.6 h	---	152
5	----	CFCO, 7% O <sub>2</sub> , 575°C, 0.2 h	RTK, Air, 435°C, 0.9 h	---	164
6	RTK, Air, 160°C, 0.3 h	----	HTF, CO <sub>2</sub> , 850°C, 0.75 h	59	55
7	HTF, Air, 325°C, 1 h	----	HTF, CO <sub>2</sub> , 850°C, 0.75 h	51	179
8	HTF, Air, 350°C, 1.5 h	----	HTF, CO <sub>2</sub> , 850°C, 0.75 h	52	200
9	HTF, Air, 250°C, 4 h	----	HTF, CO <sub>2</sub> , 850°C, 1 h	---	189
10	HTF, Air, 350°C, 3 h	----	HTF, CO <sub>2</sub> , 850°C, 1 h	30	179
11	HTF, Air, 300°C, 2 h	HTF, CO <sub>2</sub> , 450°C, 1 h	HTF, CO <sub>2</sub> , 850°C, 1 h	55	235
12	RTK, Air, 280°C, 0.5 h	RTK, N <sub>2</sub> , 410°C, 0.5 h	HTF, CO <sub>2</sub> , 850°C, 1 h	---	151
13	RTK, Air, 330°C, 0.75 h	HTF, CO <sub>2</sub> , 475°C, 1 h	HTF, CO <sub>2</sub> , 850°C, 1 h	---	236
14	RTK, Air, 220°C, 0.75 h	HTF, CO <sub>2</sub> , 475°C, 1 h	RTK, CO <sub>2</sub> , 850°C, 1 h	---	179
15	RTK, Air, 220°C, 1.5 h	CFCO, N <sub>2</sub> , 475°C, 0.75 h	RTK, CO <sub>2</sub> , 850°C, 0.75 h	---	230
16	RTK, Air, 220°C, 0.75 h	CFCO, N <sub>2</sub> , 475°C, 0.75 h	RTK, CO <sub>2</sub> , 850°C, 0.75 h	---	180

Table 2. Comparison of German Herdofenkoks and ISGS char.

Char Property	German Herdofenkoks	ISGS char
N <sub>2</sub> BET Surface Area (m <sup>2</sup> /g)	275	110
SO <sub>2</sub> Capacity (wt. %, 120°C, 4 h)	3	5
Bulk Density (lb/ft <sup>3</sup> )	29.8	23.8
Carbon (wt. %)	83.1	87.0
Volatile Matter (wt. %)	7.7	4.7
Ash (wt. %)	8.7	8.3

Table 3. Summary of Test Results

Contaminant in Flue Gas	Removal Efficiency
Polychlorodibenzofuran/Polychlorobenzodioxin	99.72% - 99.99%
Cadmium/Titanium	81% - 92%
Mercury	Below Detection
Antimony/Arsenic/Lead/Chromium/Cobalt/ Copper/Manganese/Nickel/Vanadium/Tin	57% - 72%