

APPLICATION OF THERMAL ANALYSIS TECHNIQUES IN ACTIVATED CARBON PRODUCTION

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INTRODUCTION

Several current research programs at the Illinois State Geological Survey (ISGS) relate to the development of activated carbons from Illinois coal, fly ash, and scrap tires [1-5]. Preparation of activated carbons involves thermal processing steps that include preoxidation, pyrolysis and activation. Reaction time, temperature and gas composition during these processing steps ultimately determine the nature of the activated carbon produced. Thermal analysis plays a significant role in developing carbons by providing fundamental and engineering data that are useful in carbon production and characterization for process development.

EXPERIMENTAL

Thermal analysis instruments and their applications are useful for characterizing activated carbon precursors and intermediate and final products. Instruments available in the Thermal Analysis Laboratory at the ISGS include both atmospheric (Cahn TG-131) and high pressure (SRE Model TL-TGA 1900/600) thermogravimetric analyzers (TGA and PTGA). Evolved gases from a controlled fixed-bed thermal reactor are monitored by non-dispersive infrared CO and CO₂ analyzers (Rosemount model 880) and a quadrupole mass spectrometer (Fisons model MMP300-D). All instruments are computer interfaced to allow data collection and rapid data reduction and analysis.

Proximate analysis is performed in the TGA to determine the amounts of moisture, volatile matter, fixed carbon and ash content in activated carbons. In a typical analysis, 50 mg of sample is heated in a platinum pan at 50°C/min to 950°C in N₂ flowing at 75 cc/min (STP). The temperature is held constant at 950°C for 10 minutes, then reduced to 750°C. Air is introduced at 750°C until the oxidation reaction is complete and no further weight loss is observed.

Activation studies are done in the TGA to determine appropriate conditions for activation of carbon samples in larger scale test facilities [6]. Reactivity is determined in the TGA using air at 380-500°C, CO₂ at 920-1000°C, or steam at 860-960°C. Typically, 2-10 mg of sample is heated in N₂ to a predetermined reaction temperature. Once the temperature and weight stabilize, appropriate reaction gas is substituted for the N₂ and weight loss is monitored as a function of time.

SO₂ removal efficiencies from simulated combustion flue gas by activated carbons is determined in the TGA [7]. In a typical run, 30-50 mg of sample is heated at 20°C/min in flowing N₂ to 360°C to remove surface impurities. The sample is then cooled to 120°C in N₂ and the gas stream is switched to a mixture of 5% O₂, 7% H₂O, balance N₂. Because at this temperature O₂ and H₂O are adsorbed onto the carbon, the sample weight is allowed to stabilize before SO₂ (2500 ppmv) is introduced into the TGA. Uptake of SO₂ is monitored for up to 60 h.

Methane adsorption capacities of activated carbons are determined using the PTGA [2]. The samples are degassed at 150°C for 3 h in N₂ prior to adsorption of methane. Adsorption of methane is done at 25°C at pressures of 0, 100, 200, 300, 400 and 500 psig. The rate of methane uptake and the adsorption capacity (g methane/g char) are recorded by a computerized data acquisition system.

The nature and extent of oxygen functional groups on the carbon surface are determined by temperature programmed desorption (TPD) [8]. TPD experiments are performed in a 2.5 cm ID stainless steel fixed-bed reactor system. In a typical run, 0.5 g of sample is heated at 5°C/min to 1000°C in N₂ flowing at 0.5 L/min. Temperature is held at 1000°C until evolved CO and CO₂ return to baseline concentrations, indicating complete desorption. Concentrations (ppm) of CO and CO₂, time and temperature are recorded by a computerized data acquisition system. The areas under the CO and CO₂ curves are converted to the amount of oxygen present on the carbon surface.

RESULTS AND DISCUSSION

Carbon production

Partial gasification during activation serves to develop surface area and porosity in char. The overall surface area and type of pore structure of the activated carbon may be controlled by the rate and

extent of gasification during activation. Chars may be activated with oxygen, steam, CO₂, or a mixture of these gases. At a given temperature, the relative rates of reaction for these gases range over several orders of magnitude, with O₂ > steam > CO₂. Thermogravimetry (TG) provides a method for directly monitoring both the rate and extent of activation as the reaction proceeds. This allows for good control of process conditions when preparing an activated carbon with characteristics needed for a particular application. Figure 1 shows the activation profile of a carbon prepared from a utility fly ash. Initial activation was done at 950°C in CO₂ for 1 hour, with a weight loss of only 5%. Surface areas of activated carbons, not corrected for ash content, generally increase monotonically during activation up to about 80% weight loss (conversion) [9]. After 1 h, the gas composition was changed to 50% steam/50% CO₂, which resulted in a total weight loss of 30% in 2 h. Using the data from Figure 1, a larger sample was prepared in a horizontal tube furnace that had surface area and adsorption properties similar to the sample prepared in the TGA.

Carbon Characterization

Carbons with a variety of surface areas and pore size distributions have been developed at the ISGS for various applications. One such application is the removal of contaminants from flue gas streams of waste incinerators [10]. STEAG, of Essen, Germany, has developed a process in which a bed of low surface area, low cost carbon is used to remove contaminants such as particulate matter, dioxins, furans, mercury, SO₂, other acid gases and heavy metals from flue gas. The ISGS was asked to prepare a low surface area, low cost activated carbon from Illinois coal for testing in the STEAG a/cTM process. Process variables, developed to prepare gram quantities of carbons in the laboratory, were used ultimately to prepare 500 pounds of activated carbon for tests in STEAG's pilot plant [11]. STEAG believes that the SO₂ adsorption behavior of a carbon is indicative of its ability to remove other contaminants from flue gas streams using their process [12]. Surface area and SO₂ adsorption behavior of the activated carbons prepared in each stage of scale up were used as guides to ensure that a carbon was produced with desired properties for the STEAG process. TG provided a rapid method for determining the relative rates of SO₂ adsorption and equilibrium SO₂ adsorption capacity of a carbon using only milligram quantities of sample. Figure 2 shows the kinetics of SO₂ adsorption in a simulated flue gas for the ISGS carbon and the carbon STEAG currently uses in their process (Herdofenkoks). Although the surface area of the Herdofenkoks was nearly three times that of the ISGS carbon, the initial rate of SO₂ adsorption was much greater for the ISGS carbon. This carbon has proven effective in STEAG's process during pilot plant tests.

TG has been used to study the effect of adsorption temperatures, gas compositions and carbon characteristics on SO₂ adsorption by carbons [13]. Figure 3 shows SO₂ adsorption by an air activated carbon heated to different temperatures in inert gas after activation. These carbons all had surface areas of about 300 m²/g, suggesting that surface area is not a good indicator of SO₂ adsorption [13]. Corresponding TPD profiles for the air activated carbons show that as the parent carbon was heated to higher temperatures, less oxygen was present on the surface of the carbon (Figure 4). These results suggest that SO₂ capacity is inversely related to the amount of oxygen on the surface of the carbon. Similar data have been found for other carbons. These results were used to propose a new mechanism for SO₂ adsorption on activated carbons [14].

TG also permits rapid evaluation of the thermal regeneration of carbons, and may be used to predict the life cycle of adsorbents in different applications. Adsorption/desorption cycles were performed in the TGA to determine regenerative properties of an activated carbon prepared from Illinois coal by steam activation, followed by HNO₃-treatment and thermal desorption at 925°C [4]. After initial SO₂ adsorption, the carbon was regenerated in the TGA by heating to 360°C. Regeneration of the carbon in this manner resulted in a significant decrease in the SO₂ adsorbed in subsequent adsorption/desorption cycles (Figure 5). These results have been explained by the formation of stable oxygen complexes on the surface of the carbon that inhibit adsorption of SO₂ [4]. It is thought that regeneration of this carbon at higher temperatures would restore its original SO₂ capacity, but this remains to be determined.

Carbons prepared from different precursors such as coal, fly ash and tires may have different adsorption properties not only because of their structure, but also due to different composition. A significant portion of the carbonaceous material is lost during pyrolysis and activation, and non-volatile mineral matter present in the precursor is concentrated in the remaining carbon product. Proximate analysis of activated carbons can be done rapidly with TG to provide information on the moisture, volatile matter, fixed carbon, and mineral matter present in the carbon. Figure 6 shows proximate analyses for a fly ash carbon and three steam activated chars made from Illinois coal.

Activated carbon may be used for onboard methane storage in natural gas vehicles. This storage technology is less expensive, occupies less space and costs less to refuel than compressed natural gas storage, and may result in vehicles that are lighter and have much greater storage density at low

pressure (< 35 atm). Activated carbons that might be suitable for this application have been prepared at the ISGS from both Illinois coal and scrap tires [2]. Pressurized TGA allows methane adsorption isotherms to be measured for small quantities of sample as shown in Figure 7. Shown for comparison is the isotherm for a commercial activated carbon Calgon BPL. Activated carbons prepared from scrap tires exhibit a wide range of adsorption capacities. Methane adsorption capacities (g methane/g char) of some tire-derived carbons were within 10% of the BPL carbon.

SUMMARY

Thermal analysis techniques have been used at the ISGS as an aid in the development and characterization of carbon adsorbents. Promising adsorbents from fly ash, tires, and Illinois coals have been produced for various applications. Process conditions determined in the preparation of gram quantities of carbons were used as guides in the preparation of larger samples. TG techniques developed to characterize the carbon adsorbents included the measurement of the kinetics of SO₂ adsorption, the performance of rapid proximate analyses, and the determination of equilibrium methane adsorption capacities. Thermal regeneration of carbons was assessed by TG to predict the life cycle of carbon adsorbents in different applications. TPD was used to determine the nature of surface functional groups and their effect on a carbon's adsorption properties.

REFERENCES

1. Lizzio, A.A. and Rostam-Abadi, M., "Production of Carbon Molecular Sieves from Illinois Coal," *Fuel Processing Technology*, 34, pp 97-122, 1993.
2. Brady, T.A., "Adsorbent Carbons from Waste Tires for Natural Gas Storage," M.S. Thesis in Environmental Engineering in Civil Engineering, University of Illinois at Urbana-Champaign, 1996.
3. Sun, J., Rood, M.J., Rostam-Abadi, M., Lizzio, A.A., "Natural Gas Storage with Activated Carbon from a Bituminous Coal," special issue of *Gas Separation and Purification*, in press.
4. Lizzio, A.A., DeBarr, J.A., Donnals, G.L., Kruse, C.W., Rood, M.J., Gangwal, S.K., "Production and Use of Activated Char for Combined SO₂/NO_x Removal," Final Technical Report, Illinois Clean Coal Institute, Carterville, Illinois, 1995.
5. DeBarr, J.A., Rapp, D.M., Rostam-Abadi, M., Lytle, J.M., Rood, M.J., "Valuable Products from Utility Fly Ash," First Quarterly Technical Report, Illinois Clean Coal Institute, Carterville, Illinois, 1995.
6. Lizzio, A.A., DeBarr, J.A., Donnals, G.L., Kruse, C.W., Rood, M.J., Gangwal, S.K., "Production and Use of Activated Char for Combined SO₂/NO_x Removal," Third Quarterly Technical Report, Illinois Clean Coal Institute, Carterville, Illinois, 1994.
7. DeBarr, J.A., Lizzio, A.A., Daley, M.A., "Adsorption of SO₂ on Bituminous Coal Char and Activated Carbon Fibers from Phenol Formaldehyde," ACS preprints, Fuel Chemistry Division, 1996.
8. DeBarr, J.A., Lizzio, A.A., "New Insights on the Mechanism of SO₂ Removal by Carbon," Proceedings of the 22nd Biennial Conference on Carbon, San Diego, CA, July 1995.
9. Lizzio, A.A. and Radovic, L.R., "On the Usefulness of Total Surface Area for Predicting Carbon Gasification Reactivity Profiles", 19th Biennial Conference on Carbon, University Park, PA, 1989.
10. Brueggendick, H. And Pohl, F.G., "Operating Experience with STEAG's Activated Carbon Process-a/c/tTM in European Waste Incineration Plants," Proceedings of Tenth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, 1993.
11. Lizzio, A.A., DeBarr, J.A., Kruse, C.W., "Development of Low Surface Area Char for Cleanup of Incinerator Flue Gas," Proceedings of the 22nd Biennial Conference on Carbon, San Diego, CA, July 1995.
12. Rummenhol, V., Presentation to Illinois Coal Development Board, Illinois Clean Coal Institute and Illinois State Geological Survey, Champaign, IL, March 2, 1994.
13. DeBarr, J.A., "The Role of Free Sites in the Removal of SO₂ from Simulated Flue Gases by Activated Char," M.S. Thesis in Environmental Science, University of Illinois at Urbana-Champaign, 1995.
14. Lizzio, A.A., DeBarr, J.A., "The Mechanism of SO₂ Removal by Carbon," ACS preprints, Fuel Chemistry Division, 1996.

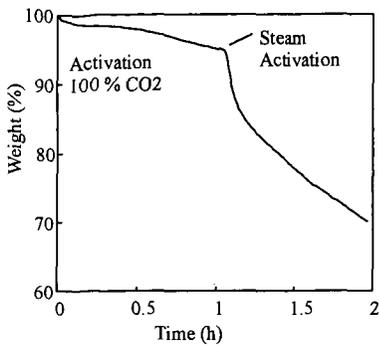


Figure 1. Activation profile of carbon prepared from a utility flyash.

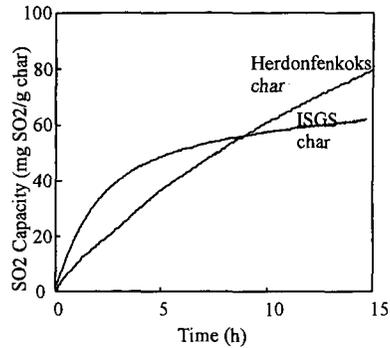


Figure 2. SO₂ adsorption of IGS and Herdonfenkoks chars.

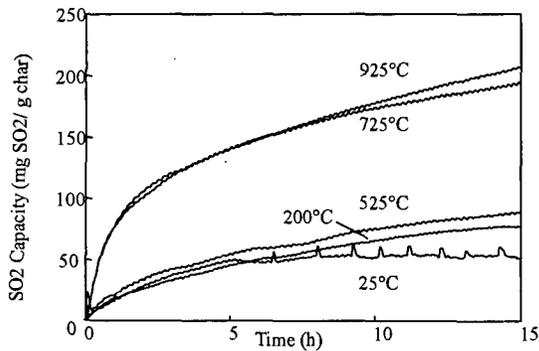


Figure 3. SO₂ adsorption profiles of air activated carbons heated to different temperatures.

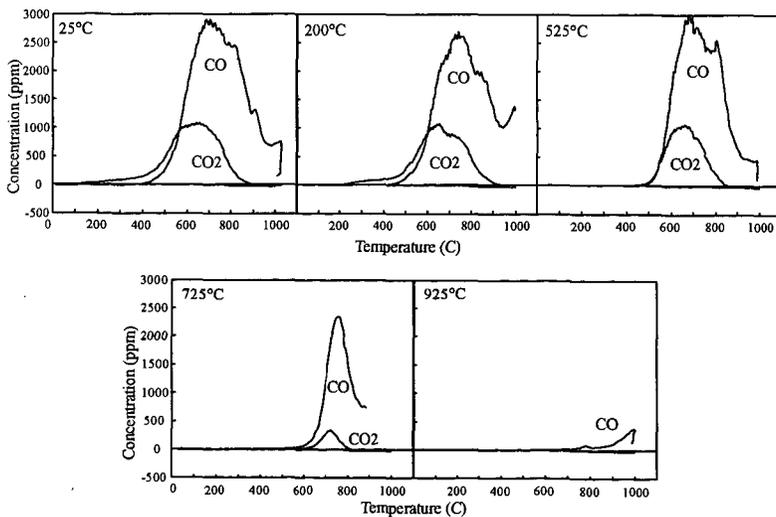


Figure 4. TPD profiles of air activated carbons heated to different temperatures.

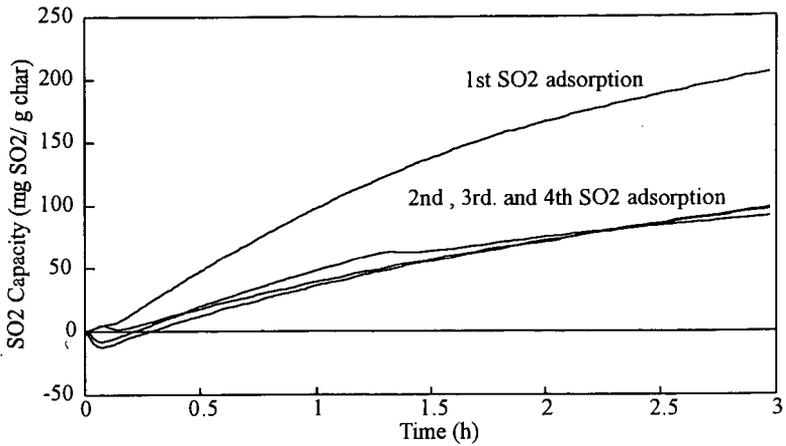


Figure 5. Thermal regeneration of nitric acid treated IBC-102 char.

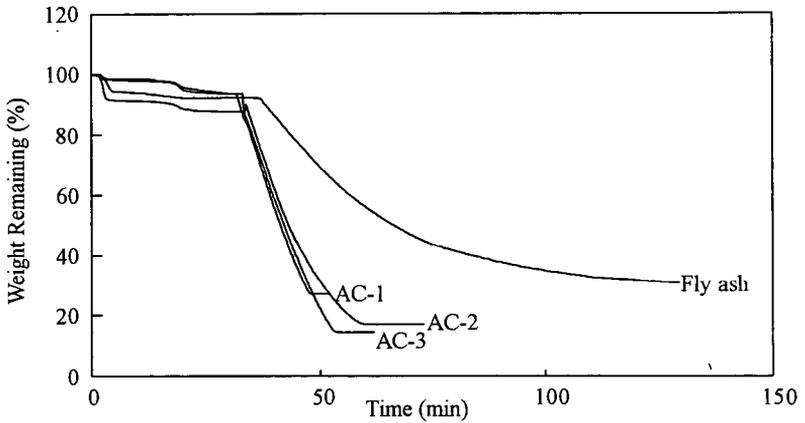


Figure 6. Proximate analysis of activated carbons.

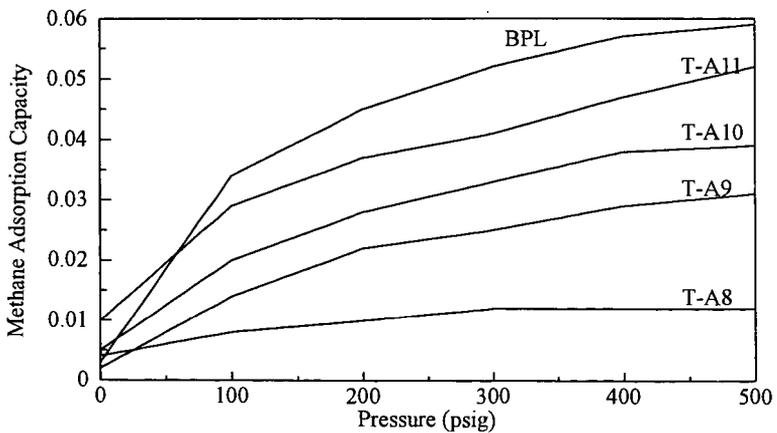


Figure 7. Methane adsorption capacity for carbons (g methane/g char at 298K).