

THE PRODUCTION OF ACTIVATED CARBON FROM A BITUMINOUS COAL

BILAL A. AKASH

Department of Mechanical Engineering, Applied Science University, Amman 11931, Jordan

AND

WILLIAM S. O'BRIEN

Department of Mechanical Engineering and Energy Processes, Southern Illinois University, Carbondale, IL62901, USA

SUMMARY

Devolatilization of an Illinois-basin coal was carried out under a nitrogen atmosphere in the temperature range 600 to 900°C. A vertical heated-wall fixed-bed furnace reactor was used. Char produced was activated in the presence and absence of steam using the same furnace setup. The surface area of the activated carbon produced was found to be equal to 54.4 m²g⁻¹ when steam was absent and 226.2 m²g⁻¹ when steam was present using the same process and conditions of activation. Breakthrough curves for the adsorption of toluene in water activated carbons prepared from that coal were obtained. They were compared with a commercially available activated carbon. On one hand, poor adsorptive properties were obtained for coal-carbons produced by the process of activation under oxygen-nitrogen gas atmospheres. On the other hand, it was found that good adsorption characteristics were obtained by using a steam-oxygen-nitrogen gas mixture. Following the preparation of activated carbon, it was necessary to treat the carbon produced in boiling distilled water. Boiling carbon in water for a short period of time (about 30 min), effectively improves the adsorption performance.

KEY WORDS: bituminous coal; activated carbon; devolatilization; activation; breakthrough adsorption test

1. INTRODUCTION

Activated carbon is prepared from naturally occurring carbonaceous materials such as coal, petroleum, coconut husks, peat and many more (Hassler, 1974). Activation involves mild oxidation of the solid in such a way that small voids are formed by removal of a portion of the solid. These voids are called pores. The carbonaceous substances have to go through two stages. The first stage is carbonization (devolatilization), followed by a second stage of activation. A simultaneous devolatilization and activation can be obtained chemically by impregnation with dehydrating agents such as phosphoric acid and zinc chloride (Kirubakan *et al.*, 1991). The adsorptive properties of activated carbon vary with the source materials and the activation process. Coals are described as porous heterogeneous organic rocks that contain small amounts of mineral matter (Gorbaty *et al.*, 1986). Generally, they are considered as one of the most important precursors in the production of carbons (Wilson, 1981). Particularly, bituminous coals are the main precursor for the production of activated carbon (Walker, 1986). This study is to demonstrate that an acceptable activated carbon adsorbent can be produced from an Illinois-basin bituminous coal. The adsorbent-behaviour of that Illinois coal-carbon is then compared with the performance of a commercially available activated carbon.

The adsorption properties of the activated carbon vary with the source materials and the process of activation (Neely and Isacoff, 1982; Rivera-Utrilla *et al.*, 1991). Its high capacity for adsorption is directly related to textural and chemical properties of the solid and method of preparation (Wigmans, 1989; Ferro-Garcia *et al.*, 1990; Stoeckli, 1990). Therefore, activated carbons with a high capacity for adsorption

for a particular adsorbate can be produced by selecting the appropriate raw materials and proper treatments (Walker, 1962). Adsorption is defined as the increase in concentration of a particular component at the surface of the interface between two phases. Dubinin (1966) found that the adsorption properties of activated carbon are associated with their porous structure, the smallest pores play a major role in adsorption. He divided pores in activated carbon into macropores, transitional-pores, and micropores. Micropores in activated carbon usually account for more than 95% of the total specific surface area, so they are considered of great significance for adsorption. Adsorption is governed by the chemical nature of the aqueous phase, the solid phase, and the chemical nature of the adsorbing organic. The surface area is one of the principal characteristics affecting the adsorptive capacity of an adsorbent. Generally, the adsorptive capacity of solid adsorbents is proportional to the specific surface area. However, one should keep in mind that any interpretation of the adsorptive behaviour of activated carbon based only on the surface area is incomplete. Carbons having equal weights and equal surface areas when prepared by different methods will exhibit different adsorptive characteristics. In this investigation, the adsorptive capacity of an activated carbon prepared in our laboratories from an Illinois coal was measured using the liquid-phase adsorption of toluene in water solution. It was compared to the adsorptive capacity of a commercially available activated carbon.

2. DEVOLATILIZATION AND MILD OXIDATION IN A VERTICAL HEATED-WALL FIXED-BED FURNACE REACTOR

2.1 Experimental section

2.1.1 Materials: A bituminous coal was used. It was Illinois No. 6 Coal, mined at a Southwestern Perry County (Illinois, U.S.A.) coal mine. The coal sample was ground to pass a 10-mesh U.S. standard size (i.e. particle diameter less than 2 mm) before it was devolatilized. Sieve analysis showed that about 93% of the coal sample had a particle diameter less than 1000 micron and larger than 75 micron. Elemental and proximate analyses of the coal sample are listed in Table 1.

2.1.2 Apparatus: Figure 1 shows a schematic diagram illustrating the flow scheme of the reactor-furnace system used in this investigation. This apparatus was used for both the devolatilization of coal and activation of the char (devolatilized coal). It consists of an electrically heated furnace that can be operated at a maximum temperature of 1200°C. A reactor tube was positioned vertically through the furnace, made of nominally 2 in stainless-steel schedule 80 pipe (6.0 cm OD × 4.9 cm ID × 52.5 cm long). Packing ceramics fill the bottom 27 cm of the furnace tube to provide sufficient heating surface area for the incoming gas stream. The tube is designed so that coal or char is held in a metal-tube or wire-mesh basket hanging in an upward-flowing gas stream, referred to as hardbasket and softbasket, respectively. The hardbasket provides a slow heating rate of about 200°C min⁻¹ while the softbasket provides a much faster heating rate of about 600°C min⁻¹.

Figure 2 shows the temperature versus time graph obtained for each basket operated at furnace temperatures of 700 and 800°C. A nitrogen-purged cooling compartment is positioned at the top of the

Table 1. Analysis of Herrin No. 6 Coal

| Proximate analysis | | Ultimate analysis | |
|--------------------|------|-------------------|------|
| Moisture | 6.5 | Carbon | 80.2 |
| Volatiles | 34.1 | Hydrogen | 5.3 |
| Ash | 11.0 | Nitrogen | 1.5 |
| Fixed carbon | 48.4 | Sulfur | 3.5 |
| | | Oxygen (by diff.) | 9.5 |

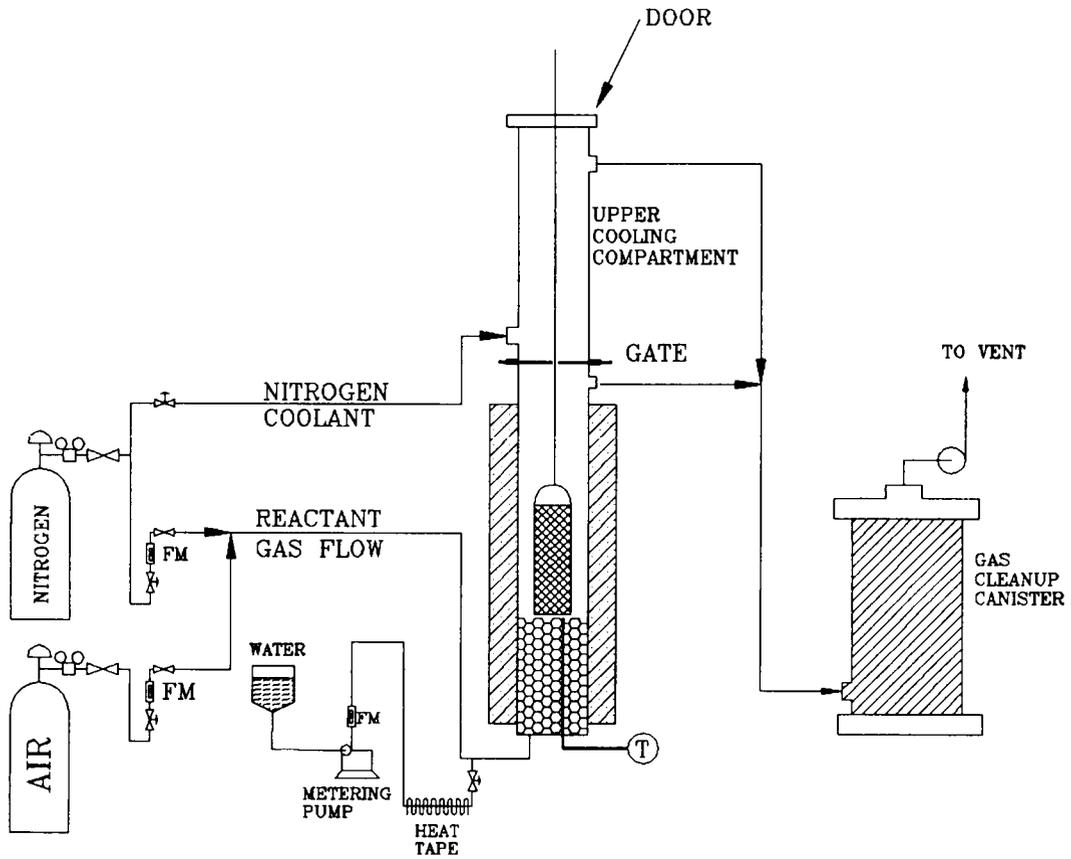


Figure 1. Schematic diagram of carbon production reaction-furnace system.

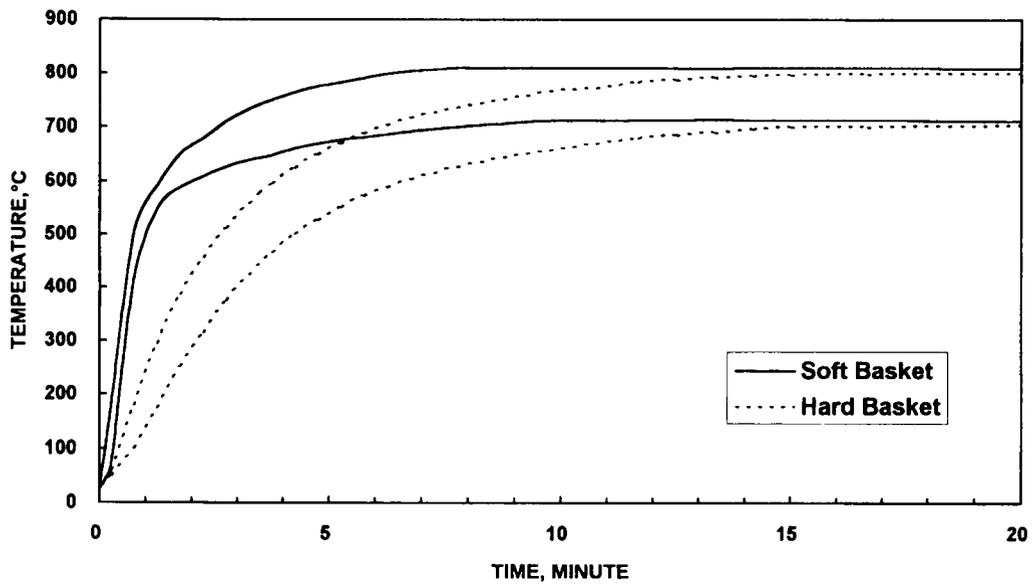


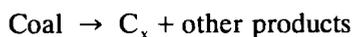
Figure 2. Temperature versus time for both baskets at furnace temperatures of 700 and 800°C.

reactor tube to allow solids and basket to be cooled in an inert atmosphere before and after heating. This reactor system could allow the carbonization of the coal and/or activation of the carbon-char to take place in controlled oxygen concentrations (air/nitrogen mixes), carbon dioxide, steam or any other reactive gas. Specific surface areas of selected samples were determined using the liquid nitrogen adsorption test. They were calculated using the BET equation.

2.2 Results and discussion

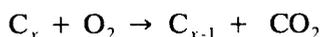
Coal is heat treated to elevated temperatures to form char. The char is then oxidized with air or steam. According to Hassler (1974), steam is preferable to carbon dioxide and much better than air. The steps that are used can be summarized by the following reaction pathways:

- (1) Devolatilization of coal in nitrogen atmosphere

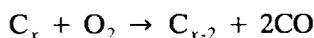


- (2) Activation of char

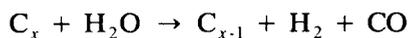
(a) with oxygen



or



(b) with steam



where C_x refers to Char, C_{x-1} and C_{x-2} refers to activated carbon.

During devolatilization process, coal loses moisture and volatile matter due to the high temperature treatment, which results in weight loss for the processed coal. The weight loss was found to be dependent on the devolatilization temperature and the type of basket used (i.e. heating rate). Figure 3 shows that larger weight losses were obtained at higher temperatures. It also shows that larger weight losses were obtained at higher heating rates for temperatures less than or equal to 800 °C. At about 900 °C, however, the weight losses obtained were approximately equal and independent of heating rate. Ash and volatile matter contents are also presented in Figure 3. It is shown that variation of ash content was minimal for the type of basket used and in the temperature range studied. Volatile matter, however, showed substantial difference between the soft and hard baskets. About 100% increase in volatile losses was obtained when the soft basket was used as compared to the hard basket. Higher devolatilization temperatures resulted in higher volatile losses.

Chars produced in the temperature range studied from 600 to 900 °C were also characterized for their elemental analysis. The results are presented in Figures 4 and 5, in which a substantial drop in oxygen and hydrogen concentrations were obtained on a dry-ash-free (d.a.f.) basis as the devolatilization temperature was increased. Oxygen and hydrogen drop was obtained when softbasket was used. Carbon content showed the opposite trend. Sulphur and nitrogen did not show any effect.

Chars prepared at 800 °C were oxidized at two oxidation temperatures of 650 and 750 °C. Three different types of oxygen concentrations in nitrogen were used; i.e. concentration of 2, 4 and 6% by volume. Different air-to-nitrogen mixes were used. Weight losses were obtained. They are presented in Figure 6. Weight loss increased with increasing oxygen concentration and increasing oxidation temperature. After 45 min of oxidation, weight loss obtained at the reaction conditions of 650 °C and 2% oxygen concentration was equal to about 6.5% of the original sample. For the same activation period and under the most severe conditions used in the study (750 °C and 6% oxygen concentration), weight loss was about 15.5%, an increase of about 150%.

Surface areas of the chars produced were determined using the BET equation. It was found that

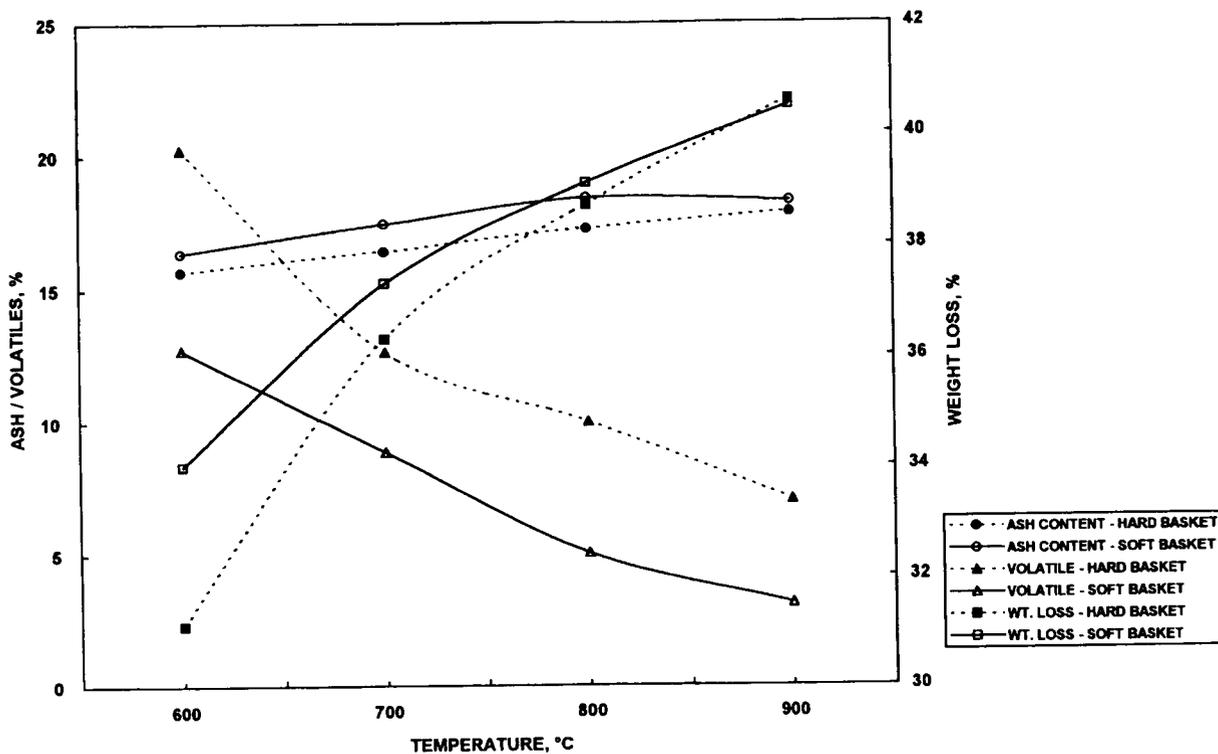


Figure 3. Ash and volatile matter contents and weight loss versus devolatilization temperature.

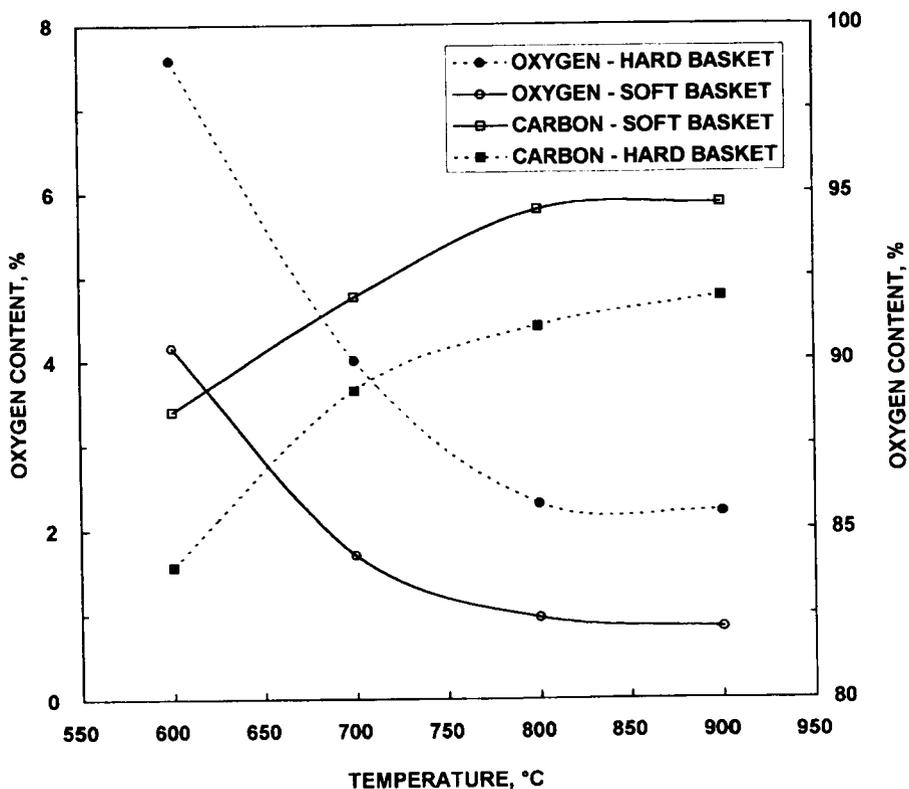


Figure 4. Oxygen and carbon contents versus devolatilization temperature

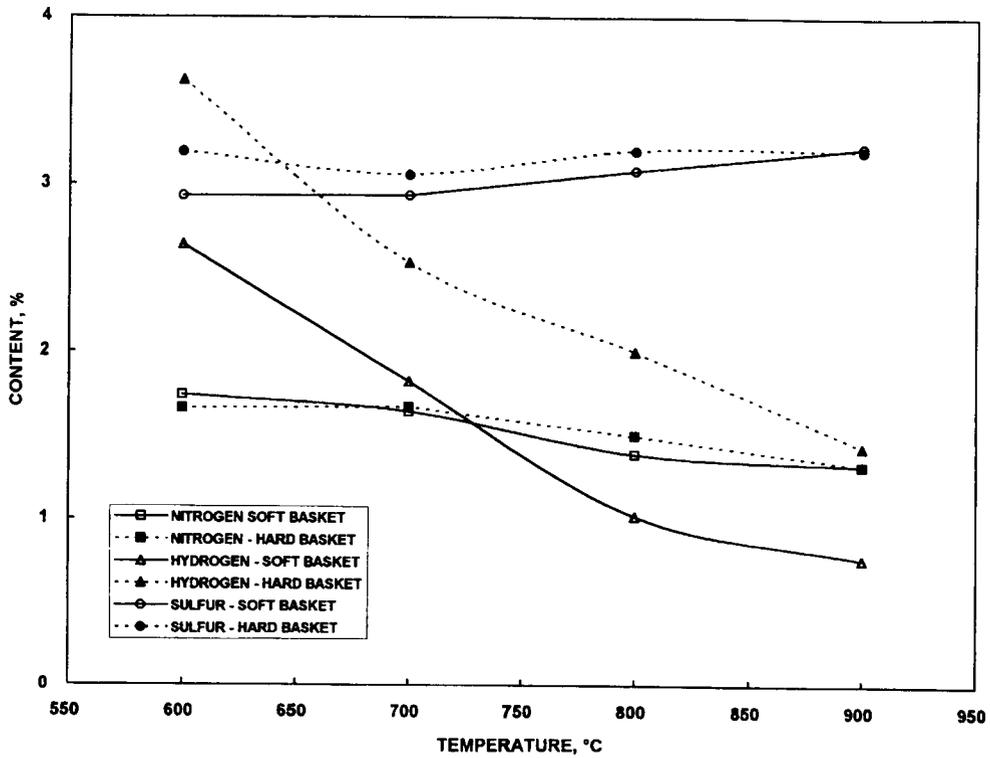


Figure 5. Sulphur, hydrogen and nitrogen contents versus devolatilization temperature

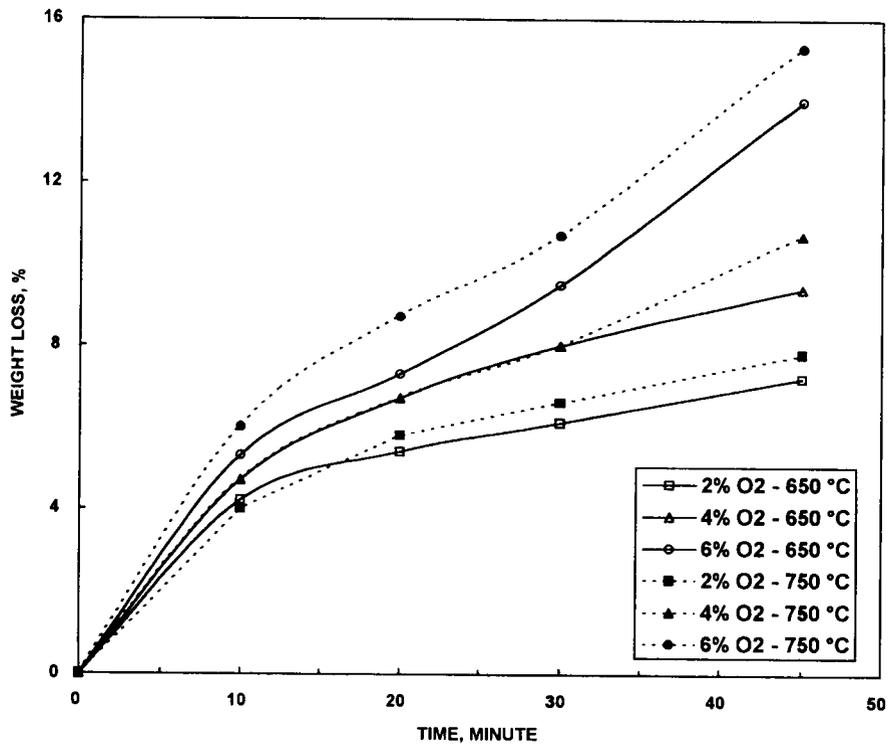


Figure 6. Weight loss versus time

carbon produced by activation with oxygen has a surface area of $54.4 \text{ m}^2 \text{ g}^{-1}$. When steam was present, and under the same reaction conditions, a four-fold increase in the surface area was obtained. The results are presented in Table 2. This indicates that steam is essential for the production of activated carbon from Illinois No. 6 coal.

3. ADSORPTION PERFORMANCE USING BREAKTHROUGH TESTS

3.1 Experimental

The liquid adsorption test was performed in the liquid phase adsorption mini-column flow system. It is illustrated in Figure 7 similar to the system described by Bilello and Beaudet (1983). The system consists of a high-pressure precision flow metering pump, a closed sample reservoir; a stainless-steel minicolumn, and a UV spectrophotometer with a flow cell that continuously measures the concentration of the effluent liquid stream leaving the column. To avoid contamination of the liquid solution, all materials contacting the sample are made of Teflon or stainless steel. The flow and concentration of the influent was kept constant throughout each run. The influent liquid solution was held in a sealed collapsible air sampling bag made of Teflon with a capacity of 2600 ml. By using this bag, the effluent end of the system was totally closed, which resulted in preventing any volatile losses or pickup of organics from the laboratory atmosphere. Activated carbon was packed in a column having an inside diameter of 4.6 mm and a length of 150 mm made of stainless-steel tubing provided with stainless-steel frits placed at both ends to act as solid filters. The frits have a pore diameter of 2 micron. Stainless-steel capillary line tubing was used having dimensions of 1.59 mm (1/16 in) outside diameter and 0.254 mm (0.01 in) inside diameter.

Two sets of experiments were conducted: first, liquid adsorption on a commercially available granular activated carbon with the commercial name 'Darco', manufactured by I.C.I. Americans, Inc., Wilmington, Delaware, U.S.A. Initially it was (-12 + 20 mesh size grade), it was then ground to allow the sample to pass through a 35-mesh grade sieve. Fines of less than 325 mesh grade were eliminated in order to avoid excessive pressure build-up in the system. Secondly, a set of experiments was performed on activated carbon produced in our laboratory from Illinois coal. During carbonization of coal at elevated temperatures, agglomeration of coal occurs which result in the production of a hard chunk of char. This char was then ground to pass a 35-mesh grade sieve. It was then activated in the presence of an activating medium such as air and/or steam. The sample was then sieved to +325-mesh grade.

3.2 Results and discussion

Adsorption of breakthrough curves for different types of activated carbon were obtained. Figure 8 shows the effluent-to-influent concentration ratio versus time breakthrough curves obtained using commercially available activated carbon (Darco), compared with two other types of carbons prepared from Illinois coal. One was activated in an oxygen-nitrogen medium, another was activated in an oxygen-nitrogen-steam medium. The breakthrough curve for Darco activated carbon is labelled 'CURVE-4'. In the case of

Table 2.

| | Surface area, ($\text{m}^2 \text{ g}^{-1}$) | Weight loss during process (%) |
|---------------------------------|---|--------------------------------|
| Coal† | 88.4 | — |
| Char devolatilized in nitrogen | 21.6 | 32 |
| Char activated in air | 54.4 | 27 |
| Char activated in air and steam | 226.2 | 29 |

†Gan *et al.*, (1972).

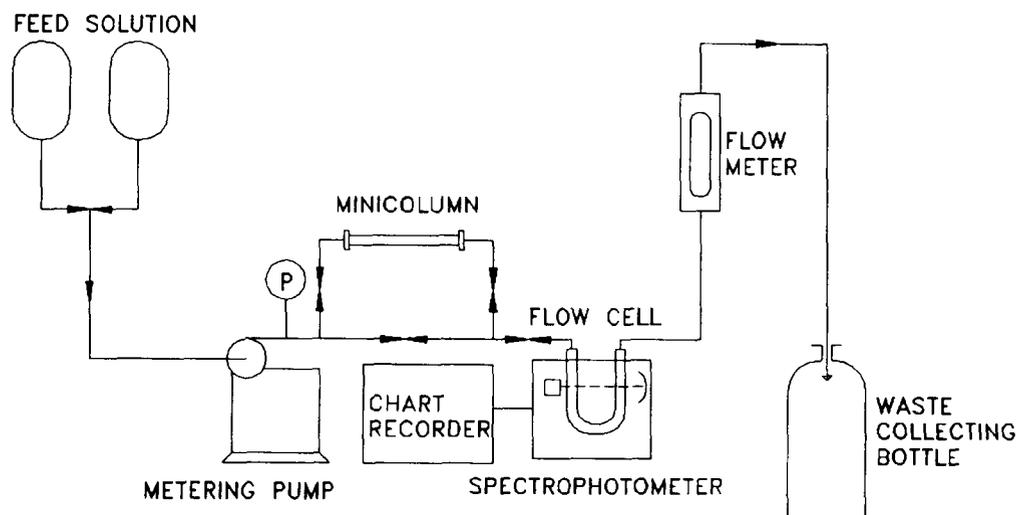


Figure 7. Schematic diagram of liquid-adsorption minicolumn flow system

breakthrough curves of carbon produced for coal. On one hand, it was found that poor adsorption properties were obtained for the coal-carbons produced by the process of activation under an oxygen-nitrogen gas atmospheres. Adsorption was negligible, which could indicate that oxygen alone is insufficient for the preparation of activated carbon suitable for water cleaning. The breakthrough curve for that carbon is labelled 'CURVE-1'. On the other hand, it was found that good adsorption characteristics were obtained by using a steam-oxygen-nitrogen gas mixture. Following the preparation of activated carbon it was necessary to treat the carbon produced in boiling distilled water for a period of time (about 30 min). The adsorption characteristics of the carbon produced were improved. It would make it more suitable for use in different applications such as water cleaning, and may also be necessary for gas cleaning. The breakthrough curve of that carbon is labelled 'CURVE-3'. Carbon produced in steam-oxygen-nitrogen activation and without treatment (not treated in boiling distilled water) produced an interesting result: adsorption, followed by desorption before beginning to adsorb again. The breakthrough curve for that carbon is labelled 'CURVE-2'.

Figure 8 shows that adsorption does exist for Illinois carbon. Nevertheless, breakthrough tests performance was slightly poorer than that obtained with Darco activated carbon, the performance has not been optimized for the char obtained from Illinois coal. An important aspect of this result is the slope of the intensity with time which indicates that activated carbon prepared from Illinois coal produces a sharper cut-off, which can be interpreted as being due to toluenes having a greater affinity for the char produced. This in turn could suggest that greater activation might result in higher adsorption capacity. This result might also indicate that char might be capable of removing toluene to a lower concentration than Darco carbon. A more sensitive detector would be required to establish the certainty of this suggestion. This is an important issue since environmental controls require removal to the specified concentration levels. It may not be possible to obtain the same or larger capacity with the char from Illinois coal as that obtained with the Darco carbon. Still, a slight improvement in capacity, along with higher char yields, could produce a competitive carbon. Since Darco carbon produced from a lignite and Illinois coal is bituminous in character the char yield should be greater.

4. CONCLUSION

An approach has been taken to produce activated carbon successfully from an Illinois coal. Results show that an acceptable carbon has been produced. Comparison of the S-shaped breakthrough curves for that carbon with a commercially available product, show that good results can be obtained.

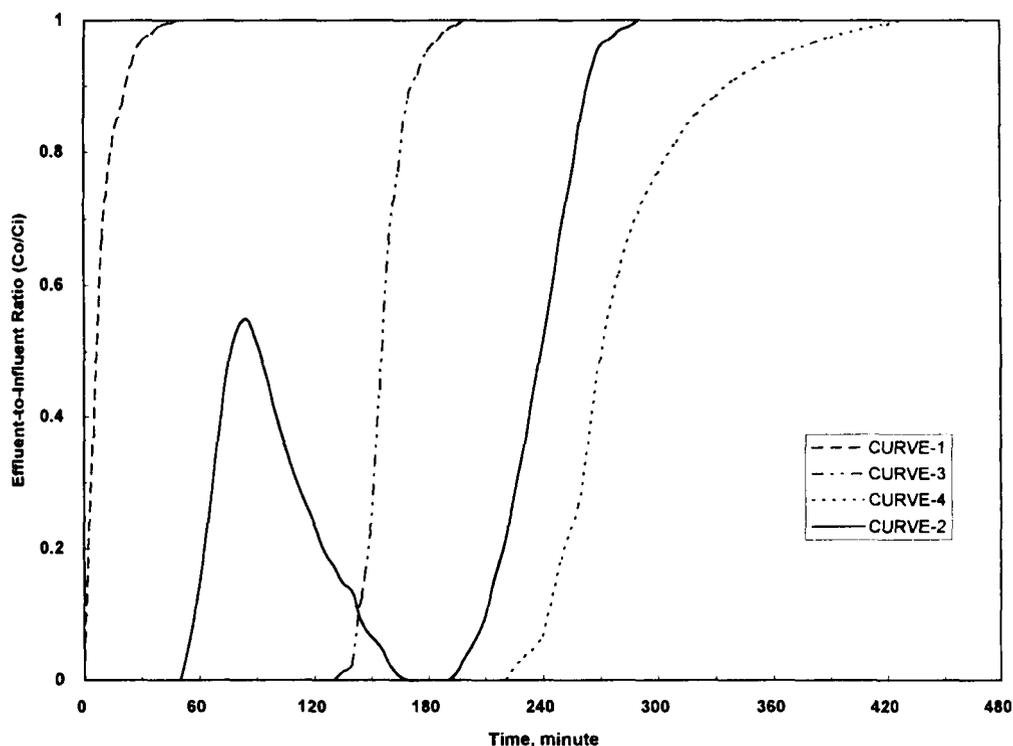


Figure 8. Breakthrough curves for adsorption of toluene from water

The findings of this experimental investigation suggest that, in order to produce quality carbon, steam was necessary for the activation of bituminous coal. Air alone was not sufficient to obtain any acceptable results.

ACKNOWLEDGEMENTS

This work was sponsored in part by the Material Technology Centre of Southern Illinois University at Carbondale. Special thanks are due to the Department of Mechanical Engineering and Energy Processes at Southern Illinois University at Carbondale, Illinois, U.S.A.

REFERENCES

- 1 Bilello, L. J. and Beudet, B. A. (1983). 'Evaluation of activated carbon by the dynamic minicolumn adsorption technique', in *Treatment of Water by Granular Activated Carbon*, M. J. McGuire and I. H. Suffet (Eds), Advances in Chemistry Series No. 202, American Chemical Society, Washington, DC, U.S.A., Chapter 10, pp 213-246
- 2 Dubinin, M. M. (1966). 'Porous structures and adsorption properties of active carbon', in *Chemistry and Physics of Carbon* P. L. Walker (Ed.), Vol 2, pp 51-120.
- 3 Ferro-Garcia, M. A., Marin, F. C., Utrilla, J. R., Hidalgo, E. and Castilla, C. M. (1990). 'The use of activated carbon columns for the removal of orthophosphate ions of aqueous solutions', *Carbon*, **28**, 91-95.
- 4 Gan, H., Nandi, S. B. and Walker, P. L. (1972). 'Nature of the porosity in American coals', *Fuel*, **51**, 272-277
- 5 Gorbaty, M. L., Mraw, S. C., Gether, J. S., and Brenner, D. (1986). 'Coal physical structure: porous rock and macromolecular network', *Fuel Processing Technology*, **12**, 31-49.
- 6 Hassler, J. W. (1974). *Purification with Activated Carbon*, Chemical Publishing, New York, U.S.A.
- 7 Kirubakaran, C. J., Krishnaiah, K. and Seshadri, S. K. (1991). 'Experimental study of the production of activated carbon from coconut shells in a fluidised bed reactor' *Ind. Eng. Chem. Res.* **30**, 2411-2416
- 8 Neely, J. W. and Isacoff, E. G. (1982). *Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters*, Dekker, New York, U.S.A.

- 9 Rivera-Utrilla, J., Hidalgo, E. U., and Garcia, M. A. (1991). 'Comparison of activated carbons prepared from agricultural raw materials and Spanish lignites', *Carbon* **29** 613-619.
- 10 Stoeckli, H. F. (1990). 'Microporous carbons and characterisation the present state of the art', *Carbon*, **28**, 1-6
- 11 Walker, P. L., J r (1986). 'Coal derived carbons', *Carbon* **24**, 379-386
- 12 Walker, P. L., J r (1962). 'Carbon - an old but new material', *American Scientist* **50**, 259-293
- 13 Wigmans, T. (1989). 'Industrial aspects of production and use of activated carbon', *Carbon*, **27**, 13-22
- 14 Wilson, J. (1981). 'Active carbon from coals', *Fuel*, **60**, 823-831