

KINETICS OF CARBON-DIOXIDE ACTIVATION OF CHARS DERIVED FROM WASTE TIRES

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Abstract

Carbon injection is a promising mercury-control method for coal-powered plants, and the use of low-cost activated carbons derived from waste tires is considered for this application. In this study, the kinetics of CO₂ activation of the tire-pyrolysis char were determined. TGA experiments were run at different temperatures, and gasification reactivities were used to prepare Arrhenius plots. The apparent activation energy in the temperature range 900–965 °C was found to be relatively independent of burn-off ($E = 220 \pm 4$ kJ/mol). In contrast, the activation energy at the low temperature range (900–917 °C) increased with burn-off from 252 kJ/mol at 5% burn-off to about 340 kJ/mol at burn-offs above 50%. This may be a result of most reactive active sites being consumed at early stages of activation and more oxidation-resistant sites being responsible for burn-off at more advanced stages. The burn-off dependence at higher temperatures (917–965 °C) was opposite, with the activation energy dropping from 211 kJ/mol at 5% burn-off to 175–185 kJ/mol at burn-offs above 60%.

Introduction

Coal combustion results in air pollution due to emissions of mercury present in coal. In view of the expected tightening of federal, state, and local regulations on heavy-metal emissions, it is imperative that effective mercury-abatement methods should be developed. Many of the currently pursued technologies for capturing mercury are based on the injection of sorbents into the flue gas (Brown *et al.* 1999), which results in the capture of mercury along with fly ash in electrostatic precipitators and baghouses. The high cost of mercury sorbents, usually activated carbons with a market price of about \$0.50/lb, is a serious drawback of this approach.

Mercury adsorption on sulfur-rich activated carbons derived from scrap tires was proposed as a way to combine good sorbent performance with low cost (Serio *et al.* 1996; Wójtowicz *et al.* 2004 and 2007). The sulfur added to tire rubber in the process of vulcanization makes the tire-derived sorbents particularly effective in mercury removal due to the high chemical affinity between mercury and sulfur. In this way, the removal of mercury from the combustion flue gas can be combined with the simultaneous utilization of solid waste (scrap tires). The objective of this work was to examine the kinetics of activation of tire-pyrolysis char using carbon dioxide.

Materials and Experimental Methods

Materials

Samples of crumb rubber were obtained from Crosston Rubber Inc. of Drummondville, Quebec. The material was derived from truck tires by cryogenic grinding to pass through an 80 mesh sieve, and the sample used in this part of the study is designated T80. The received crumb-rubber material appeared homogeneous, free of steel, fiber, and contaminants. The determination of ash and moisture contents as well as elemental composition was performed by Huffman Laboratories of Golden, Colorado. The results are: 0.25% moisture, 5.74% ash, 88.62% C, 8.01% H, 0.38% N, 2.32% S, and 0.66% O. The above values are expressed in wt% on an as-received basis for moisture, on a dry basis for ash, and on a dry, ash-free basis for carbon, hydrogen, nitrogen, sulfur, and oxygen. The oxygen content was determined by difference.

Tire-derived activated carbons were prepared by the pyrolysis of waste-tire crumb rubber, followed by char activation in a flow of carbon dioxide, as described below.

Experimental Methods

Kinetics of tire-char activation were studied using a thermogravimetric analyzer (TGA). A TGA coupled with a Fourier-Transform Infrared (FT-IR) spectrometer was used in this study, but no FT-IR analysis of evolved gases was performed. A detailed description of the TG-FTIR system, the method, and some of its applications can be found in the literature (Carangelo *et al.* 1987 and 1990; Whelan *et al.* 1988). Schematic representation of the instrument is shown in **Figure 1**.

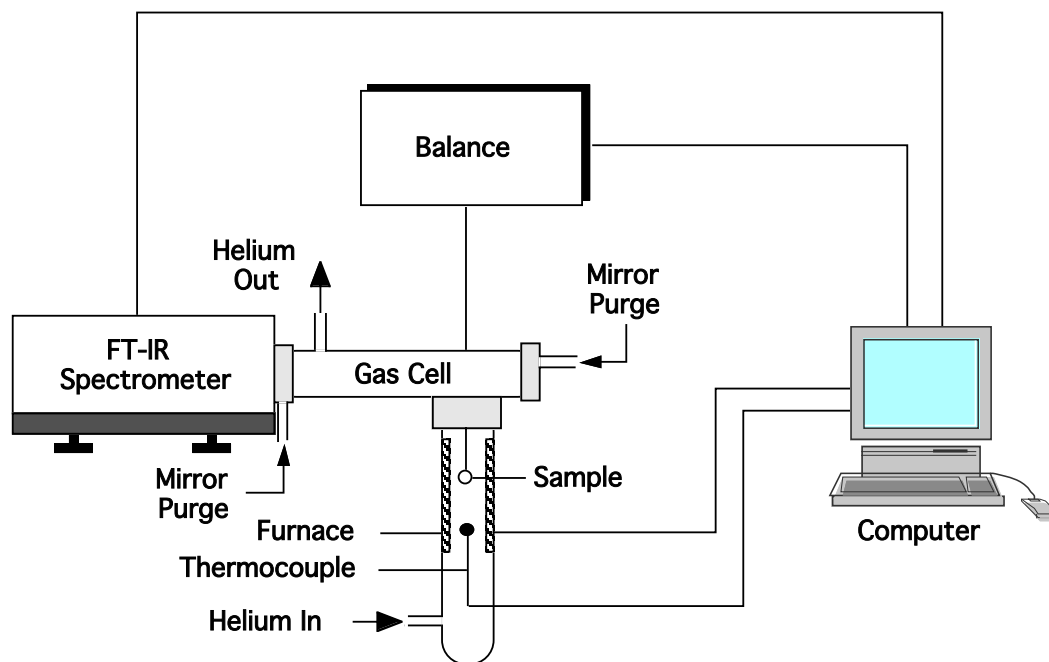


Figure 1. A schematic diagram of the TG-FTIR system.

The apparatus consists of a sample holder suspended from a balance in a stream of carrier gas. An electrically heated furnace provides temperature control in the range 20–1,000 °C. The system allows the sample to be heated on a pre-programmed temperature profile, at rates 0.3–100 °C min⁻¹, up to a temperature of about 1,000 °C. Isothermal steps with a specified hold time are also possible. In addition to temperature, the system continuously monitors the weight of the non-volatile material (residue).

In TGA experiments carried out in this project, the initial sample weight was approximately 30–45 mg, and the flow rate of the carrier gas through the TGA was 400 ml/min. TGA runs were programmed to be performed in three steps, as shown below.

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| Step 1 (drying): | Heat the sample in helium to 60 °C and hold it at this temperature for 30 min. |
| Step 2 (pyrolysis): | Heat crumb rubber in He to 900 °C at 30 K/min and hold at 900 °C for 15 min. |
| Step 3 (CO₂ activation): | Switch from He to CO ₂ , and hold at 900 °C until complete burn-out. |

Results and Discussion

TGA experiments were performed at the following temperatures: 900 °C, 917 °C, 934 °C, 950 °C, and 965 °C. The typical temperature profiles, weight loss curves, and char reactivities with respect to the initial char weight are shown in **Figure 2** and **Figure 3**. The reactivity is seen to vary as a function of burn-off due to significant changes in the pore structure that occur during activation (surface area, pore volume, pore-size distribution, etc.). The values of char reactivity normalized with respect to the initial sample weight, r^* , were determined for different levels of char burn-off, and these data were used to prepare Arrhenius plots shown in **Figure 4**.

It can be seen in **Figure 4** that char reactivity initially increases with the degree of activation up to approximately 20% burn-off, and then starts to decline as activation progresses. The initial increase in reactivity is most likely the result of rapid development of internal surface area at low burn-off.

Another observation is the fact that the data points do not fall on straight lines in the entire temperature range (900–965 °C). The slope of the Arrhenius plots seems to be steeper at 900–917 °C as compared with the slope at higher temperatures. This behavior is consistent with, and is in fact typical for, the onset of mass-transfer resistance

at elevated temperatures. Thus, intrinsic reaction kinetics are perhaps better represented in the low-temperature measurements. Unfortunately, there are only two data points in this temperature range.

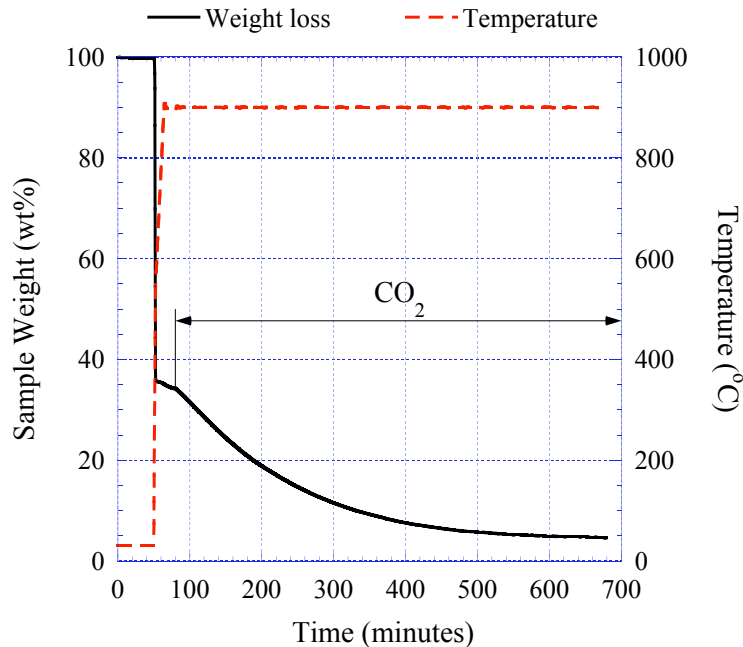


Figure 2. The temperature profile and the TGA weight-loss curve for CO₂ activation of char derived from T80 crumb rubber (truck tire, -80 mesh) at 900 °C.

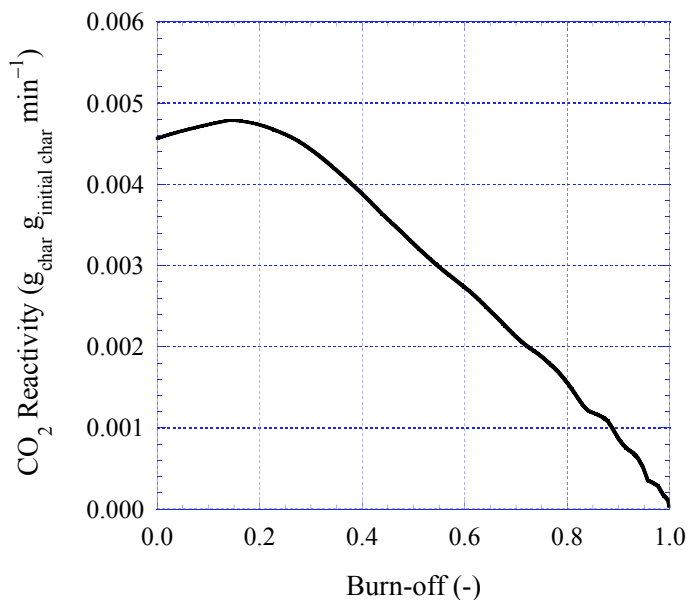


Figure 3. Char reactivity $r^*(g_{\text{char}} g_{\text{initial char}}^{-1} \text{min}^{-1})$ at 900 °C as a function of burn-off for CO₂ activation of char derived from T80 crumb rubber (truck tire, -80 mesh). Locally weighted curve fitting was performed on the data (least squares) using a 10% weight.

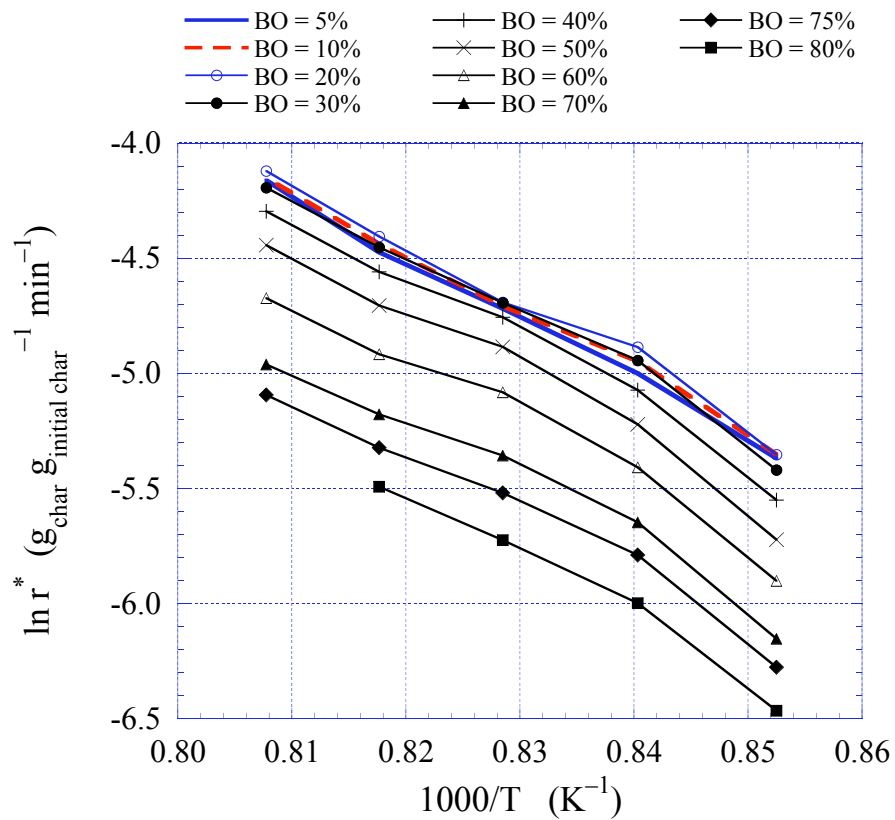


Figure 4. Arrhenius plots at different char burn-off.

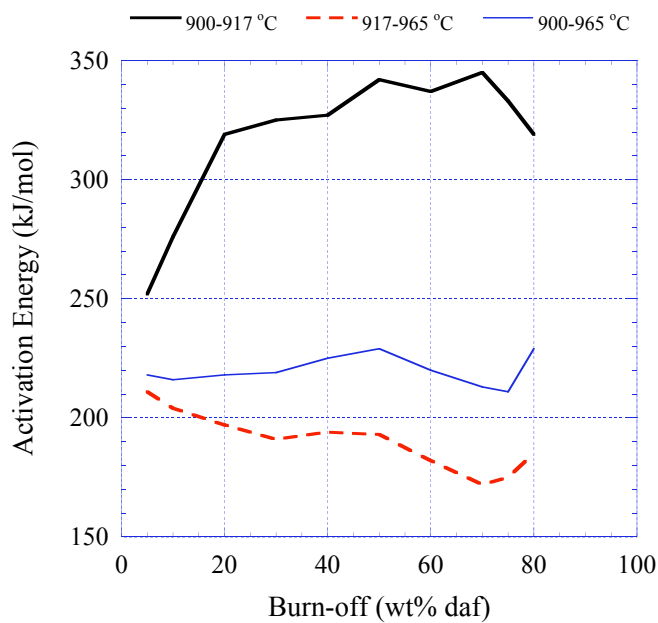


Figure 5. The dependence of activation energy, determined in different temperature ranges, on char burn-off.

Since the kinetic behavior of char oxidation seems to be different at different temperatures, the Arrhenius equation was fitted to experimental data in the following three temperature ranges: (1) 900–917 °C (low temperatures, where chemical kinetics are the rate limiting step); (2) 917–965 °C (high temperatures, where diffusion plays a role); and (3) 900–965 °C (the entire range studied). The results are summarized in **Figure 5**.

Conclusions

For the process of CO₂ activation of tire-pyrolysis char, data in **Figure 5** show that the apparent activation energy determined in the temperature range 900–965 °C is relatively independent of burn-off and is $E = 220 \pm 4$ kJ/mol (at a 95% confidence level). In contrast, the activation energy at the low temperature range (900–917 °C) increases with burn-off from 252 kJ/mol at 5% burn-off to about 340 kJ/mol at burn-offs above 50%. This may be a result of most reactive active sites being consumed at early stages of activation and more oxidation-resistant sites being responsible for burn-off at more advanced stages. The burn-off dependence at higher temperatures (917–965 °C) is opposite, with the activation energy dropping from 211 kJ/mol at 5% burn-off to about 175–185 kJ/mol at burn-offs above 60%.

Acknowledgments

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References

- Brown T. D., Smith D. N., Hargis R. A. Jr. and O'Dowd W. J. 1999. Mercury measurement and its control: What we know, have learned, and need to further investigate. *J. Air & Waste Manage. Assoc.* 1999 (June):1-97.
- Carangelo, R. M., Solomon, P. R. and Gerson, D. J. 1987. Application of TG-FTIR to study hydrocarbon structure and kinetics. *Fuel* 66:960.
- Carangelo, R. M., Solomon, P. R., Bassilakis, R., Gravel, D., Baillargeon, M., Baudais, F. and Vail, G. 1990. Applications of TG-FTIR in the analytical laboratory. *American Laboratory*, p. 51.
- Serio, M. A., Wójtowicz, M. A., Teng, H. and Solomon, P. R. 1996. Pyrolytic reprocessing of scrap tires into value-added products. Pages 105-122 in *Conversion and Utilization of Waste Materials* (M. Rashid Khan, Ed.), Taylor & Francis, Washington, DC.
- Whelan, J. K., Solomon, P. R., Deshpande, G. V. and Carangelo, R. M. 1988. Thermogravimetric Fourier Transform Infrared Spectroscopy (TG-FTIR) of petroleum source rock - initial results. *Energy & Fuels* 2:65.
- Wójtowicz, M. A., Florczak, E., Kroo, E. and Serio, M. A. 2004. Activated carbon from waste tires for mercury emissions control. *Proc. Carbon 2004 Conf.*, Brown University, Providence, Rhode Island, July 11–16, 2004.
- Wójtowicz, M. A., Florczak, E., Kroo, E., Kroo, T., Serio, M. A. and Dombrowski, K. 2007. Mercury removal from coal-combustion flue gas using activated carbon derived from waste tires. *ACS Div. of Fuel Chem. Prepr.* 52(1):157-159.