# A COMPARATIVE STUDY ON ACTIVATION RATE OF ACTIVATED CARBON FIBERS

Y. Q. Fei and F. Derbyshire

Center for Applied Energy Research, University of Kentucky,
3572 Iron Works Pike, Lexington, KY 40511, USA

## INTRODUCTION

Activated carbons fibers or ACF, with a narrow diameter (10-20 microns), allows rapid rates of adsorption and reaction, and the fibrous form offers the potential to apply them in novel processing environments in the form of fiber-containing artifacts [1,2]. The preferred precursors for ACFs are general purpose carbon fibers that are produced from isotropic pitches or polymers [1,3]. High-performance fibers from polyacrylonitrile or mesophase pitch are less desirable because of their higher cost, together with the fact that they have more ordered structure and higher temperature treatment, which confer low reactivity towards activation and difficult development of internal pore structure[4].

In this context, it is of interest to understand the kinetics of activation and the progress of porosity development with isotropic carbon fibers, and how these processes differ from those of other forms of carbon. Such studies can provide directions for the control of pore structure and surface chemistry of ACFs. The fiber with a narrow and uniform diameter is an ideal form for the investigation of reaction rates because diffusion limitations are minimal. In an earlier study, we have shown that the steam activation of isotropic carbon fibers essentially follows first order kinetics and that the reaction rates are related to both pre-carbonization and activation temperatures by the Arrhenius equation, with negative and positive activation energies, respectively [5]. In more recent research, the activation of the same carbon fiber samples has been investigated to determine the reaction kinetics and the pore structure of the activated products. The two series of experiments allow comparisons to be made between activating agents ($CO_2$ versus steam), and between fibrous and granular carbons [6,7], and kinetic factors to be taken into account at the same time.

## EXPERIMENTAL

The fiber samples (10-15 μm dia.) used in the study were the same as those in previous research [5]. Green fibers were produced by melt spinning an isotropic petroleum pitch (Aerocarb 80, Ashland Carbon Fibers Division of Ashland Inc.). The fibers were stabilized by air oxidation and then carbonized for 30 min at temperatures between 650 to 1050 °C. The pre-carbonized fibers (~ 0.5 g) were activated by heating in a horizontal tube furnace in flowing nitrogen at 20 °C/min to the activation temperature (850 to 1000 °C). The gas flow was then switched to pure $CO_2$ for reaction times from 30 to 240 min. The flow was switched back to pure nitrogen for cool down. The overall reaction rate for activation was assessed by the first order equation: $r = -(1/W_o)dW/dt = kW$, where $W_o$ is the initial mass of carbon. The rate constant, k, was obtained from the integral form of the equation, $kt = \ln(W_o/W) = \ln[1/(1-x)]$, where x is the fraction of starting material that is gasified (burn-off). Information on surface area and pore structural characteristics was obtained from nitrogen adsorption at 77K using a Coulter Omnisorp 610.

## RESULTS AND DISCUSSIONS

Figure 1 shows a plot of the kinetic parameter, $\ln[1/(1-x)]$ against reaction time at the activation temperature of 1000 °C. The straight line correlation shows that, as with steam, the overall reaction with $CO_2$ is also first order, as observed for other types of carbons of small dimensions [7,8]. The slope of the line corresponds to the rate constant, k. Similar sets of data were also obtained for different reaction conditions. Table 1 summarizes the rate constants and time to 50 % burn-off ($t_{1/2}$) for activation at several temperatures. Some data from steam activation are also listed for comparison. For both activating agents, it can be seen that the rate constants increase with reaction temperature. However, the values for steam are much higher than for $CO_2$, by approximately factor of ten. In order to achieve 50 wt% burn-off in one hour, an activation temperature of over 1000 °C is required for $CO_2$ activation, whereas in an atmosphere of 50 vol % steam, the same reaction rate can be reached at about 870 °C.

The relationship between the rate constant and activation temperature is given by the relationship, $k = A\exp(-Ea/RT)$, where A is a pre-exponential factor and Ea is the activation energy. From the Arrhenius plot, in Figure 2, the values of A and Ea can be calculated. These kinetic parameters are shown in Table 2. For both activation, the carbon fibers have higher activation energy than other forms of carbon[6,7], probably due to lower contents of the impurities in the carbon fibers which can act as catalysts for gasification. The $CO_2$

activation energy is slightly higher than for $H_2O$ with carbon fibers, as has also been observed in the activation of chars and pitch cokes [6]. However, much greater differences in activation energy are observed between carbon fibers and other forms of carbon. For chars produced from cellulose, coal and pitch, the activation energy varied from 27 - 52 kJ/mol [6,7], whereas the carbon fibers in the experiment show only 22 kJ/mol.

The experimental results also show that the rates of activation in $CO_2$ are little affected by the pre-carbonization temperature of the fibers. This finding contrasts with studies of steam activation, where it was found that an increase in 400 $^oC$ of pre-carbonization temperature could reduce the rate of activation by a factor of approximately 2/3 [5]. A possible reasons for this difference is that the slow rate of $CO_2$ activation tends to obscure the influence that prior heat treatment may have in improving the structural order of the carbon and reducing reactivity. Also, the reaction temperature regime for $CO_2$ is considerably higher than carbonization and steam activation, therefore structural and reactivity differences due to heattreatment temperature are diminished during heating, even before gasification start.

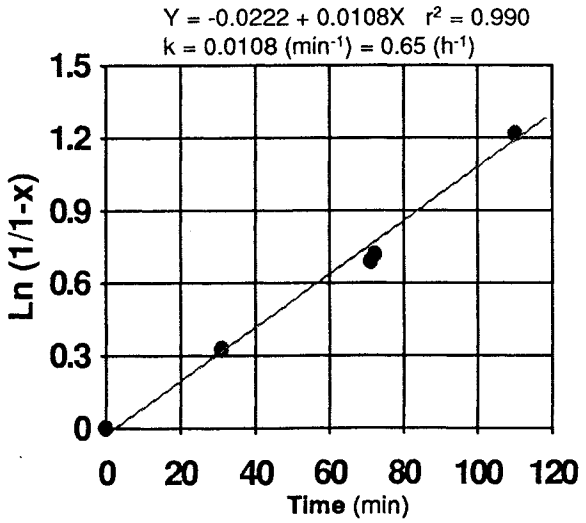


Fig. 1 Plot of a kinetic parameters against reaction time for CO2 activation of fibers carbonized at 850$^oC$.

Table 1 A comparison of rate constant and time required for 50 wt% burn-off for $CO_2$ and steam.

| Activation Temperature (°C) | Pure $CO_2$ | | 50 vol% steam | |
|---|---|---|---|---|
| | Rate ($h^{-1}$) | $T_{1/2}$ (h) | Rate ($h^{-1}$) | $T_{1/2}$ (h) |
| 850 | 0.045 | 15.4 | 0.43 | 1.6 |
| 880 | 0.083 | 8.3 | 0.86 | 0.81 |
| 950 | 0.28 | 2.5 | -- | -- |
| 1000 | 0.65 | 1.1 | -- | -- |

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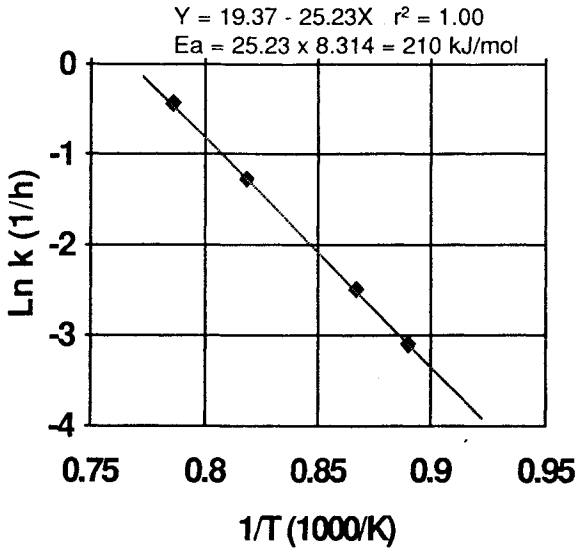


Fig. 2 Arrhenius plot of $CO_2$ activation rate of carbon fibers against activation temperature.

Table 2 Kinetic parameters for $CO_2$ and steam activation of isotropic carbon fibers

| Activating agent | 100%$CO_2$ | 50%$H_2O$ |
|---|---|---|
| Activation energy (kJ/mol) | 210 | 188 |
| Pre-exponential ( x$10^4$ $sec^{-1}$) | 7.18 | 6.80 |