

# Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation

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## Abstract

Activated carbon fibres (ACF) are obtained mainly by physical activation with steam or carbon dioxide. Additionally, there are many papers dealing with chemical activation of carbon fibres, or a polymeric raw material, with several chemical agents like for example, phosphoric acid, zinc chloride, aluminium chloride, ... Nevertheless, although it is well known that hydroxides are good activating agents, there are few papers about the activation of carbon fibres with KOH or NaOH. In the present work, ACF with high surface area are obtained by chemical activation with KOH and NaOH. Both chemical agents present different behaviour; thus, NaOH developed the highest value of porosity and KOH developed samples with narrower micropore size distribution. In order to compare the results with those obtained by physical activation, some ACF have been prepared using CO<sub>2</sub> activation. The main conclusion of this work is that by using chemical activation it is possible to obtain similar, or even higher, porosity (~1 ml/g, ~3000 m<sup>2</sup>/g) than by physical activation. However, chemical activation presents two important advantages: (1) a much higher yield (27–47% for chemical activation and 6% physical activation for ~2500 m<sup>2</sup>/g activated carbon fibres) and (2) the surface of the fibres prepared by chemical activation is less damaged than by physical activation.

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**Keywords:** A. Coal tar pitch; B. Activation; C. Adsorption; D. Carbon yield; Porosity

## 1. Introduction

Chemical activation with KOH or NaOH is an effective method to prepare activated carbon materials [1–3]. Both hydroxides are very effective activating compounds in different carbon materials: coal [1], bituminous [4], anthracite [2,3,5], nanotubes [6], etc. Chemical activation presents several advantages and disadvantages compared to physical activation. The main advantages are the higher yield, lower temperature of activation, less activation time and generally, higher development of porosity. Among the disadvantages, the activating agents are more expensive (KOH and NaOH vs. CO<sub>2</sub> and H<sub>2</sub>O) and it is also necessary an additional washing stage. Moreover, these hydroxides are very corrosive. Physical activation with carbon dioxide or steam is the usual procedure to obtain activated carbon fibres (ACF). Chemical activation of carbon fibres by ZnCl<sub>2</sub>, AlCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>BO<sub>3</sub>, ... has been reported [7]. However, the

studies on chemical activation by KOH and NaOH are scarce [8–11] and focus on PAN-based carbon fibres as precursors. Then, there are not papers dealing with activation of general purpose carbon fibres. In the present work ACF with high surface area are obtained by physical (CO<sub>2</sub>) and chemical activation (KOH and NaOH) of commercial carbon fibres from coal tar pitch.

## 2. Experimental

### 2.1. Raw material

Milled carbon fibres from an isotropic coal tar pitch precursor were used (DONACARBO-S-241, Osaka gas Co., Ltd). The mean fibre length and diameter are 0.13 mm and 13 µm respectively. The ash content for the raw material is 0.03 wt%.

### 2.2. Physical activation

A given weight of Donac carbon fibres was placed into a horizontal cylindrical furnace (65 mm i.d.) under

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flowing nitrogen (100 ml/min). For most activations, approximately 2.5 g of fibres were used; however, some activations used 3.6–5.1 g. The furnace was purged with nitrogen for 30–60 min; then, the temperature was increased at 5 °C/min under flowing nitrogen (100 ml/min) until the desired activation temperature; (from 820 to 900 °C). Once the activation temperature was reached, nitrogen flow was switched to CO<sub>2</sub> (100 ml/min). Furnace temperature and CO<sub>2</sub> flow were kept constant for the desired period of activation (from 2.5 to 26 h). At the end of the activation period, the sample was cooled under nitrogen (100 ml/min).

### 2.3. Chemical activation

Chemical activations were carried out in a horizontal furnace by physical mixing of the hydroxide (K or Na) and carbon raw material with a hydroxide/carbon ratio (wt/wt) varying from 2/1 to 8/1. The mixture was heated under nitrogen with a heating rate of 5 °C/min. The temperature used was 750 °C. Holding time at the maximum temperature was one hour. Samples were washed with 5 M HCl and vacuum filtered three times and then rinsed with hot distilled water (80 °C) and filtered until the filtrate was free of chloride ions. This washing step ensures the removal of most of the alkaline. Thus, in the most unfavourable cases (8:1 ratio), the ash content for the samples activated by KOH and NaOH were 5% and 2% respectively. The cleaned samples were dried in an oven at 120 °C for 24 h. The samples were weighed in order to know the yield in each chemical activation.

### 2.4. Characterisation of porosity

The characterisation of the porosity of the activated materials was done using physical adsorption of N<sub>2</sub> at –196 °C. (Quantachrome, Autosorb-6B). The samples were outgassed at 250 °C under vacuum for 4 h. Nitrogen adsorption results were used to determine BET surface area values and DR<sub>N2</sub> micropore volumes (i.e., Dubinin–Radushkevich micropore values). Pore size distributions are obtained applying the DFT method to the nitrogen adsorption isotherms at –196 °C, using the software supplied by Autosorb 1 (Quantachrome).

## 3. Results and discussion

### 3.1. Chemical activation

ACF prepared by chemical activation (CA) show isotherms of type I (Fig. 1). The knees of the isotherms are wider with increasing the hydroxide/carbon ratio and, therefore, the pore size distributions (PSD) are also wider as can be seen with the DFT PSD (Figs. 2 and 3).

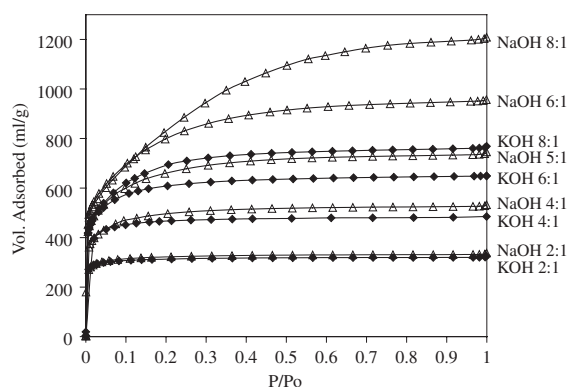


Fig. 1. N<sub>2</sub> adsorption isotherms for CA samples.

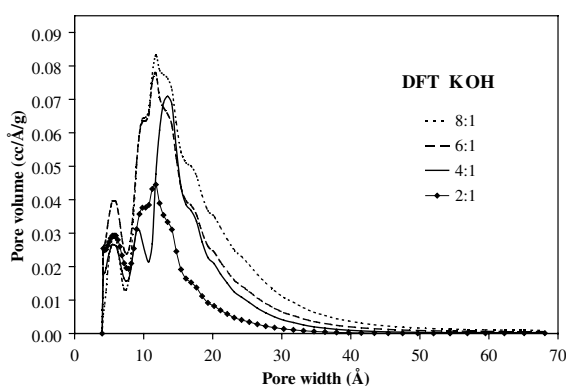


Fig. 2. DFT pore size distribution for KOH samples.

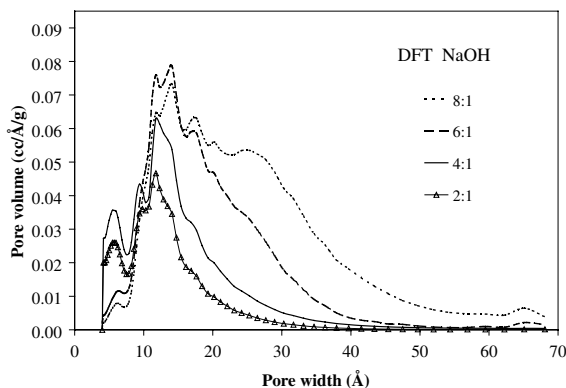


Fig. 3. DFT pore size distribution for NaOH samples.

Total pore volume also increases with the ratio showing a development of porosity (Table 1). In the case of NaOH and for high ratios (6:1 and 8:1), the adsorption capacity and the proportion of mesopores obtained are considerable. The behaviours of both activating compounds are similar, although KOH shows a better yield than NaOH. Thus at low ratio (2/1), KOH and NaOH present comparable porosities (Fig. 1) and a similar micropore size distribution (Figs. 2 and 3). However as the hydroxide/carbon fibres ratio increases, KOH and

Table 1  
Activation data

Activ. agent	Ratio (wt:wt)	<i>T</i> activ. (°C)	Time activ. (h)	Yield (%)	<i>V</i> <sub>DR</sub> (cm <sup>3</sup> /g)	<i>S</i> <sub>BET</sub> (m <sup>2</sup> /g)
KOH	2:1	750	1	78	0.49	1090
KOH	4:1	750	1	67	0.78	1635
KOH	6:1	750	1	60	0.90	2225
KOH	8:1	750	1	47	0.94	2420
NaOH	2:1	750	1	71	0.51	1130
NaOH	4:1	750	1	55	0.81	2000
NaOH	6:1	750	1	37	0.96	2541
NaOH	8:1	750	1	27	1.02	3033
CO <sub>2</sub>	—	890	3	80	0.29	644
CO <sub>2</sub>	—	890	9	45	0.64	1528
CO <sub>2</sub>	—	890	22.5	6	0.86	2487

NaOH became more different, showing NaOH better adsorption performance than KOH. In addition, NaOH develops wide micropore size distributions and even mesopores for high ratios (Figs. 2 and 3). In the case of NaOH for 8:1 ratio, the activated carbon fibres obtained present an interesting quite narrow mesopore size distribution (centered at 25 Å) and a great adsorption capacity. Contrarily KOH allows one to prepare narrower pore size distributions (Figs. 2 and 3).

### 3.2. Physical activation

ACF obtained by physical activation (PA) with carbon dioxide present nitrogen adsorption isotherms of type I (Fig. 4). The width of the knee increases strongly with burn-off as it also can be seen in the DFT plots (Fig. 5). PA shows a linear correlation between the micropore volume (Dubinin–Radushkevich) determined by N<sub>2</sub> adsorption at −196 °C and the yield (Fig. 6).

### 3.3. Chemical vs. physical activation

Comparing Figs. 1 and 4, it can be seen that samples prepared by PA always show wider pore size distributions than those prepared by KOH. Pore size distributions for NaOH and PA are quite similar, but the amount of porosity developed by NaOH is always

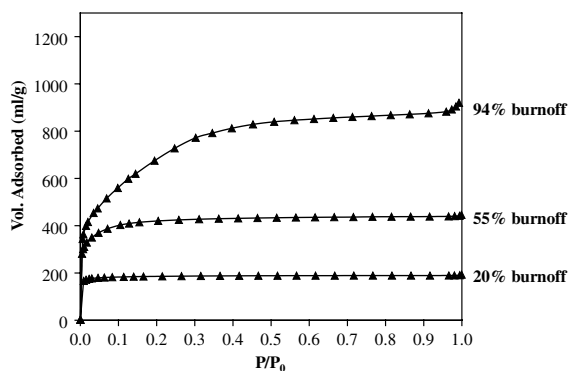


Fig. 4. N<sub>2</sub> adsorption isotherms for PA samples.

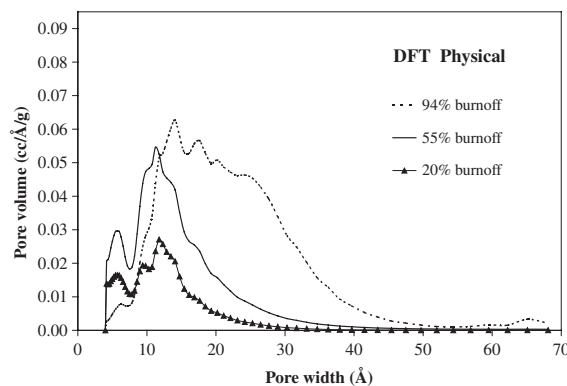


Fig. 5. DFT pore size distribution for PA samples.

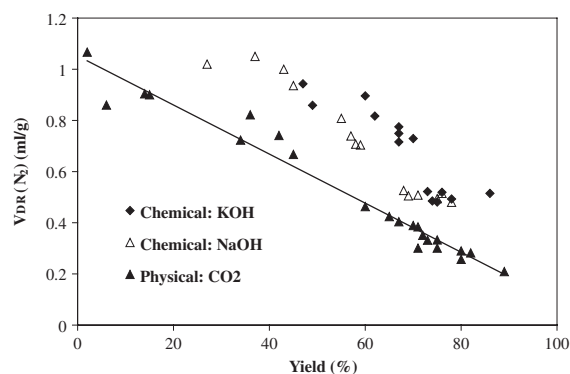


Fig. 6. Micropore volume of ACF vs. yield.

higher (Table 1). Fig. 6 presents the  $V_{DR}N_2$  of samples prepared by both methods plotted as a function of the yield. In all the range of yield the porosity developed is higher when CA is used. In other words, to reach a particular porosity development, a higher burn-off is needed for PA. Moreover, PA is not interesting from an industrial point of view to obtain high surface ACF (about 1 ml/g and,  $BET = 3000 \text{ m}^2/\text{g}$ ) because the yield is too low (less than 20%). On the contrary, these high surface ACF can be obtained by CA (KOH or NaOH) with yields higher than 40% (Table 1). It can be concluded that chemical activation is more selective than

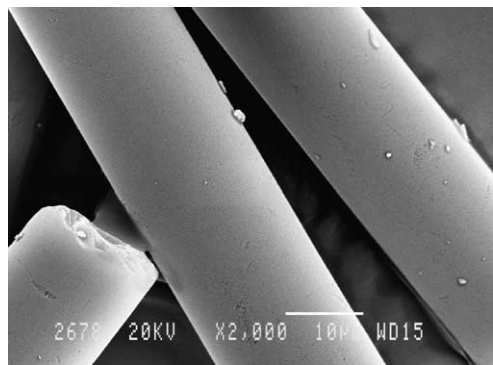


Fig. 7. SEM for a sample activated by KOH (8:1 ratio).

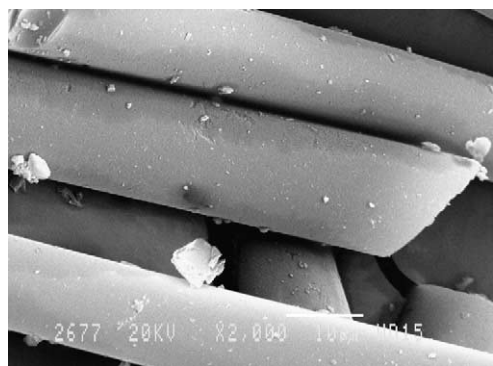


Fig. 8. SEM for a sample activated by NaOH (8:1 ratio).

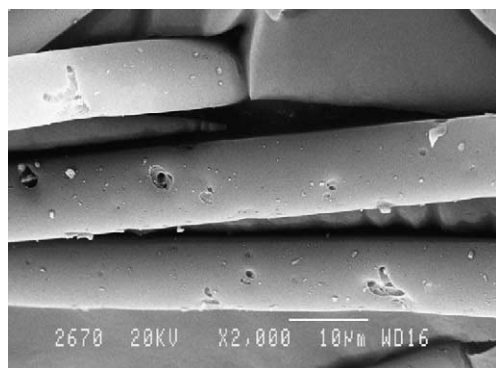


Fig. 9. SEM for a sample activated by CO<sub>2</sub> (86% burn-off).

physical activation for the materials studied. SEM examination shows that ACF prepared by chemical activation preserve the shape after activation process. The surface is not very damaged even with high ratios (8:1) of KOH (Fig. 7) or NaOH (Fig. 8). Nevertheless, a serious surface damage appears when physical activation with CO<sub>2</sub> (Fig. 9) is employed for high burn-off.

#### 4. Conclusion

Chemical activation of carbon fibres by hydroxides is more appropriate than physical activation to reach

high porosity development, maintaining the fibre morphology and a reasonable yield. In addition it is more selective than physical activation for the materials studied. Pore size distributions of the samples prepared by KOH are narrower than those obtained by NaOH. Nevertheless, NaOH develops more porosity than KOH for the same hydroxide/carbon fibres ratio. Furthermore, the surface of the fibres prepared by chemical activation is less damaged than by physical activation for a comparable high porosity development.

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