

ELABORATION OF ACTIVATED CARBONS USING T.I. FRACTION OF A240 HEAT-TREATED PITCH.

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Introduction

The general objective of this work is to study the possibility of elaborating the accurate raw precursor which will correspond after activation process, to a special microporous network for applications such as cooling by gas sorption [1]. Following this idea, we described here how the anisotropic character of the toluene insoluble fraction obtained from an heat-treated petroleum pitch [2] can induce, after carbonization and activation, the microporous properties of the resultant activated carbons. A240 petroleum pitch was used as raw precursor for its possibility to develop various isotropic or anisotropic phases, depending on the thermal or mechanical treatment applied. The great variety of possible microtextures (anisotropic or isotropic fibers, mesocarbon microbeads...) appears to be well adapted for the study of the relationship between micro- or nanotextures, composition and porosity development.

Experimental

350 g of A240 isotropic petroleum pitch were heat-treated under nitrogen in a stirred reactor at a heating rate of 2°C.min⁻¹. After a 5 hours residence time, the residual pitch was cooled to room temperature. Stirring (1000 rpm) was kept constant throughout the heat-treatment. After solidification, the obtained pitch was ground and sieved to 100 µm.

This powder was then submitted to toluene fractionation at room temperature. EP2 and EP1 extracted pitches were obtained by addition of 250ml and 150ml of toluene to two of 1g ground pitch batches. Therefore, EP2 and EP1 present decreasing toluene soluble (TS) content. After filtration (no warm drying was performed in order to avoid possible thermal effects), residual solubilities in toluene and in quinoline of the fractionated samples were determined (see Table 1).

Table 1. Some characteristics of extracted pitches.

Material	TS (%)	TI-QS (%)	QI (%)
A 240	96	4	/
400°C-5h	77	16	12
EP 1	11	67	22
EP 2	5	76	19

Stabilization treatments of extracted pitch powders EP1 and EP2 were performed under a flowing air atmosphere (0.5 l/min) in a usual horizontal furnace. The heating rate was 1°C/min up to 280°C and the residence time at stabilization temperature was 1 hour. After carbonization at 1000°C for 1 hour, samples were activated in batches of 1.6 g at 900°C in a CO₂ flow (0.5 l/h). Carbon dioxide was chosen as activating gas in order to favorise micropores [3,4] and to lower mesopores development. The activation was held for various times and activated carbons were obtained in the burn-off range from 10% up to 60%.

Adsorption properties of the different activated carbons issued from EP1 and EP2 powders were measured by nitrogen adsorption at 77 K using an automatic ASAP 2000M apparatus from Micromeretics.

Results and Discussion

Isotherms were analysed by BET method giving the surface area value and Dubinin-Radushkevich method for the estimation of the microporous volume W_0 and the average value of pore width x (Å). A typical behaviour of the microporosity properties was observed during activation from 10% up to 60% of burn-off : both BET surface and micropore volume increase with burn-off.

Table 2. Characteristics of activated carbons.

	S BET (m ² /g)	W ₀ (cm ³ /g)	x (Å)
EP1 - BO12%	138	0.07	9.2
EP1 - BO37%	290	0.14	10.6
EP1 - BO61%	541	0.23	14.4
EP2 - BO13%	350	0.17	7.1
EP2 - BO37%	565	0.28	9.3
EP2 - BO60%	932	0.46	14.5

Figure 1 shows the evolution of the pore size x (Å) average value during carbon dioxide activation at 900°C. Even if EP1 and EP2 samples come from the same heat-treated pitch, drastic differences between the two series of activated carbons are observed: EP2 activated carbons exhibit adsorption properties two times higher than EP1 ones. In the same time, pore size of EP2 is smaller than

EP1 at low burn-off. At 60% burn-off, pore sizes appear equivalent for both series. This difference in pore size evolution is illustrated by isotherms expressed in degree of filling W/W_0 as a function of relative pressure presented in figures 2 and 3. At 12% of burn-off, reduced isotherms are very different, showing a strong adsorption at low reduced pressure (i.e. adsorption in the smallest pores) for EP2 activated carbon while EP1 doesn't. At high burn-off level (here 60%), differences have disappeared and nitrogen adsorption is similar for both samples in the whole pressure range. All high burn-off EP1 and EP2 nitrogen isotherms exhibit a small hysteresis loop of H4 type (according to IUPAC classification [5]) suggesting the presence of mesopores. Thus, mesopores development seems to be due to activation process and isn't related to the precursor composition.

However, microporous adsorption of EP activated carbons are directly resulting from the precursor composition and are specially depending on residual γ resins (TS) content. Even if non-graphitizable carbon resulting from γ resins carbonization is gasified in the earlier stage of activation [6], it seems to inhibit microporosity development. A non-graphitizable matrix (with no microporous or mesoporous potential) made from γ resins surrounding, potential microporous domains (α and/or β resins) can explain these results. Thus, microporosity development and non-graphitizable matrix gasification occur in the same time : the higher γ resins content, the smaller microporosity.

Conclusions

From adsorption data, it appears that T.I. fraction of an heat-treated petroleum pitch can give, after carbonization and carbon dioxide gasification, activated carbons with high microporous characteristics. However, residual γ resins coming from unperfect extraction lead to a drastic inhibition of microporosity development.

References

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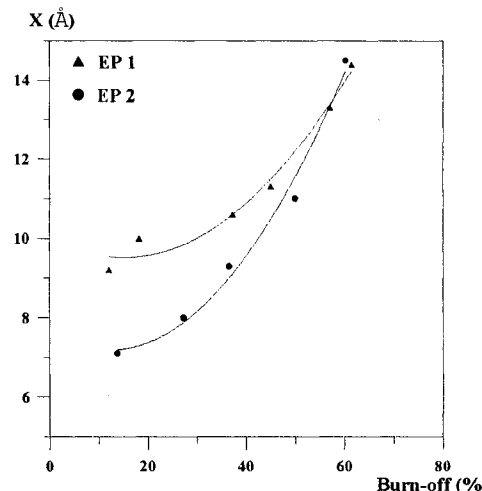


Fig. 1. Average pore size of EP1 and EP2 activated carbons.

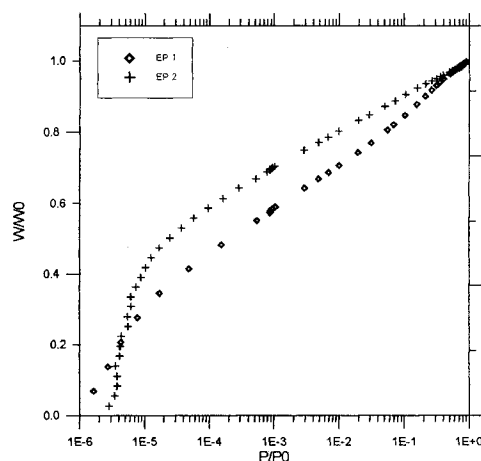


Fig. 2. Degree of filling vs relative pressure (Burn-off = 12%)

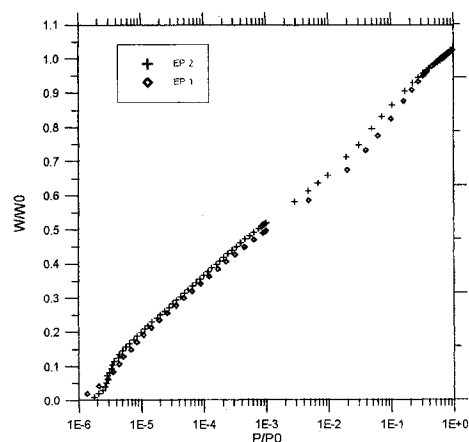


Fig. 3. Degree of filling vs relative pressure (Burn-off = 60%)