

## PREPARATION OF ACTIVATED CARBON FROM APRICOT PITS

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### Abstract

The preparation of activated carbons from an ideal precursor is described in this paper. Activation was carried out with  $H_2O$  in a rotating reactor or with a mixture of  $H_2O$  and  $CO_2$  in a fluid reactor. The use of the fluid reactor has several industrial aspects. Adsorption properties and the mesoporosity of the samples activated in the different apparatus are correlated with each other.

*Keywords:* activated carbon, activated carbon from apricot pits.

A wide variety of materials have been used as precursors of activated carbons. Beside fossil carbons, agricultural by-products are frequently used in the manufacture [1, 2]. We have prepared activated carbons from ideal raw materials (with high carbon content and low ash content) and also from non-ideal, 'waste' materials [3, 4]. The structural and adsorption properties of activated carbons, prepared from the shell of apricot stone (*Armeniaca vulgaris*) have been investigated in our laboratory since 1982 [5]. Activated carbons prepared from this raw material show a high carbon and low ash content and have a high mechanical strength. Therefore it can be considered as an ideal basic material of activated carbon. The raw material can be milled to optional particle size and no graining process is needed during the activation.

The activation of 'carbon-rich' materials is possible via chemical and physical 'routes', but recently the latter have been generally used [6]. Steam, carbon dioxide, air in very small concentration or the combination of these are used as activation agents in the physical processes. The reactions with steam or carbon dioxide lead to differences in the structural character. Notably, the smaller dimension of the  $H_2O$  molecule compared to  $CO_2$  results in the higher ratio of micropores in the whole pore volume.

In the present investigations, the activation was performed with steam in a rotating quartz reactor, and with a mixture of steam and carbon dioxide in a fluid reactor. The activated samples obtained in the two types

of reactor show different adsorption properties which will be discussed in this work.

## Experimental

### *Thermal Analysis of the Raw Material*

The dry shell was milled and the fraction with a diameter of less than 0.2 mm was analysed by using a Derivatograph Q-1500 (MOM, Budapest, Hungary). TG, DTG and DTA curves were recorded in nitrogen and air atmospheres (heating rate 10°C/min).

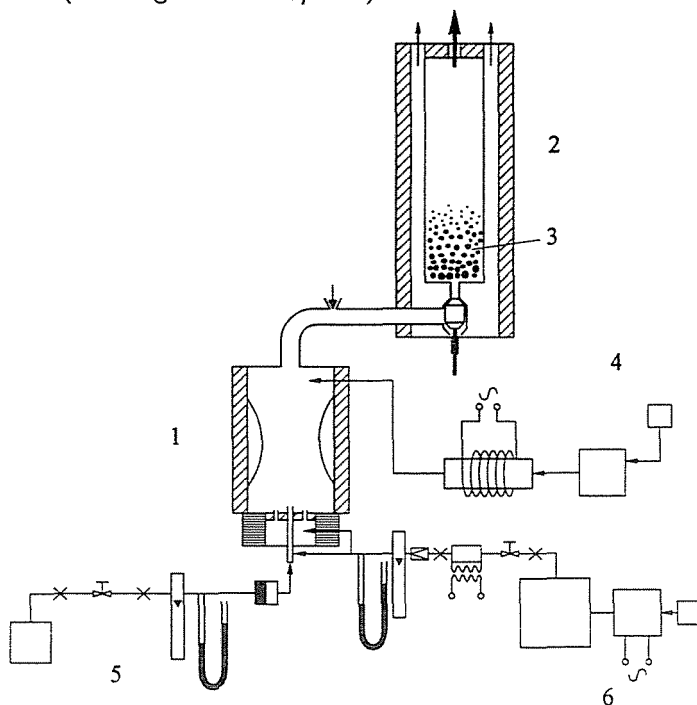


Fig. 1. Scheme of the fluid reactor, combustion zone (1), fluid reactor (2), sample in fluidized bed (3), injector for excess water (4), supply for butane (5), supply for air (6)

### *Pyrolysis*

The dry starting material was heated up to 700°C in a steel reactor flushed with 80 dm<sup>3</sup>/h nitrogen (heating rate 10°C/min) and was kept at this temperature for 30 min. This carbonized product was used for activation after sieving, without forming. The grain size was between 1.4 – 2.8 mm.

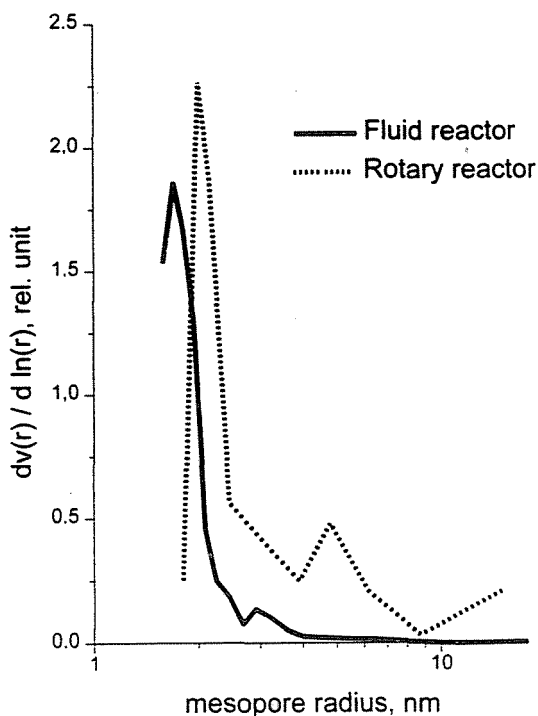


Fig. 2. Mesopore distribution of the samples activated in fluid or in rotating reactors at 20% conversion and 900°C

#### *Activation in a Rotating Reactor*

10 g carbonized sample was activated in a rotating quartz reactor at 900°C in an equimolar steam – nitrogen mixture of 50 dm<sup>3</sup>/h flow rate [7].

#### *Activation in a Fluid Reactor*

The fluid reactor was built in our laboratory. The activation was carried out by the combustion products of butane. Excess oxygen was not present during the process as controlled by a gas analyser. The apparatus consists of two main parts:

- i) combustion zone and
- ii) activation zone (*Fig. 1*).

The pressure of the gas can be modified in the range of 0 and 0.2 bar in the combustion zone. The activation was performed by a batchwise technique. The quantity of the reactor loading is maximum 200 g. The activation

temperature can be varied in the range of 800 - - 1000°C. Besides, preheated excess steam can be injected into the reactor.

### *Adsorption of Iodine and Methylene Blue*

The adsorption properties of the active carbon were tested by the widely used iodine and methylene blue uptake [8]. The iodine number informs about the internal surface of the activated carbon. 1 mg of iodine adsorbed represents 1 m<sup>2</sup> internal surface. The methylene blue value reveals the adsorptive properties of a carbon towards large organic molecules.

### *Gas Adsorption*

Nitrogen adsorption - desorption isotherms of the active carbon samples were determined by volumetric method at 77 K using a sorptometer type Autosorb 1 (Quantachrome, Syosset, New York, USA). Samples were evacuated at 400°C for 4 - 5 days. The specific surface area, the volume of the pores and the pore size distribution were calculated from the low temperature nitrogen adsorption-desorption isotherms.

## **Results and Discussion**

After pyrolysis, the yield of the carbonized precursor was 25%. The outward appearance and the adsorption properties of the activated samples differed depending on the type of reactor. In the rotating quartz reactor the activation proved to be gentle. No significant moulding and decrease in the grain size were observed. In the fluidized bed the activation process caused much more drastic changes in the appearance and in the mechanical strength of the particles. The reaction was found to be of quasi zero order in both reactors up to a conversion of 50%. The parameters of the activation and the adsorption properties of the activated samples are listed in *Table 1*. At 900°C the rate of conversion in the fluid reactor was more than double the rate in the rotating one. The ratio of the specific surface area, indicated by the iodine number, to the weight-loss was less favourable in the fluidized bed than in the other reactor. Furthermore, in the shell region of the grains, the high burn-off level caused a decrease in the grain size. The higher conversion occurred parallel with the formation of larger pores as can be seen in the methylene blue uptake. The lower activation temperature and the higher ratio of H<sub>2</sub>O in the activation gas led to a larger volume of the micropores indicated by an increase in the iodine number and a decrease in the methylene blue uptake. These results are demonstrated at a yield of 45% in *Table 1*.

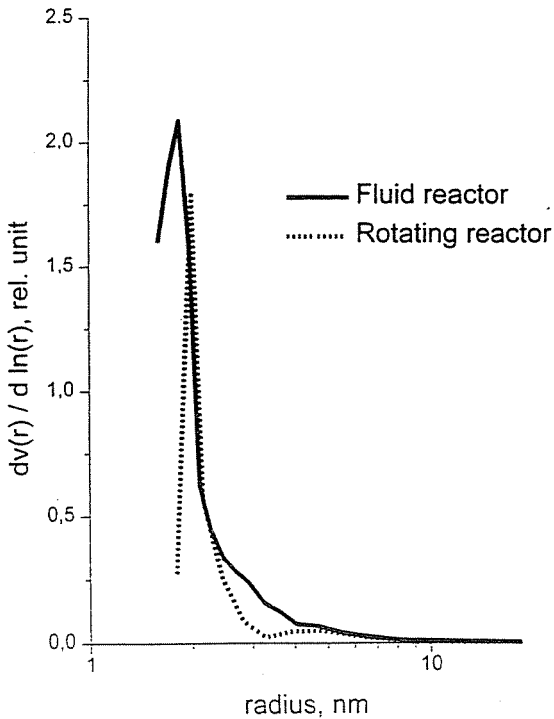


Fig. 3. Mesopore distribution of the samples activated in fluid or in rotating reactors at 50% conversion and 900°C

Table 1

Parameters of activation and adsorptive properties of activated apricot pits

Reactor	Activation agent	Temperature °C	Activation time, min	Yield %	Iodine number, mg/g	Methylene blue, g/100 g
rotating	H <sub>2</sub> O	900	30	78	750	4.0
rotating	H <sub>2</sub> O	900	60	61	1050	14.5
fluid	H <sub>2</sub> O/CO <sub>2</sub>	900	10	76	610	6.4
fluid	H <sub>2</sub> O/CO <sub>2</sub>	900	20	54	980	17.0
fluid	H <sub>2</sub> O/CO <sub>2</sub>	900	30	45	1120	25.5
fluid	H <sub>2</sub> O/CO <sub>2</sub>	900	60	21	1620	30.0
fluid	H <sub>2</sub> O/CO <sub>2</sub> + H <sub>2</sub> O	880	20	45	1270	23.5
fluid	H <sub>2</sub> O/CO <sub>2</sub> + 2H <sub>2</sub> O	880	25	31	1340	29.0

Generally, a sharp peak appears on the size distribution curves at about the 2 nm pore radius in the mesopore range for activated carbons. This

peak reflects the structural features of the matrix. The matrix of the activated apricot-coke consists of graphite-like microcrystallites and amorphous parts. For low conversion levels, the effect of the composition of the activation gas on the formation of the mesopores can be observed in *Fig. 2*. The larger molecular dimensions of the activation agent ( $\text{CO}_2$  molecules) appear in the mesopore range instead of the smaller pore dimensions. The activated carbon prepared from apricot pits consists of 4 nm crystallite clusters built up from single crystallites of 0.7 – 0.8 nm according to small and wide angle X-ray scattering measurements [9]. Presumably, the activation by carbon dioxide takes place on the outer side of the single crystallites, therefore an increase in the mesopore volume was observed. At higher conversion rates the effect of the difference of the activation agents decreased, probably because of a decrease in the difference in the diffusion rate between the water and carbon dioxide molecules in the open pore system (*Fig. 3*).

Summarizing the results, the composition of the activation gas causes differences in the adsorption properties only at low conversions. Nearly the same adsorption quality of the activated products from apricot pits can be obtained in both types of reactor at higher conversions (at about 50%).

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