Preparation and characterisation of activated carbons from pine wastes gasified in a pilot reactor

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Introduction

Activated carbon is a highly porous material which has various applications in adsorption of both gases and solutes from aqueous solution. It has been well-established the fact that activated carbons have over many years been widely used for the separation of gases, the recovery of solvents, the removal of organic pollutants from drinking water and as well as catalyst support.
Coals and ligno-cellulose materials are commonly used as the starting raw material for preparing activated carbons. Recently, numerous attempts to prepare activated carbons from solid wastes have also been undertaken [1]. The development of methods to re-use waste materials is greatly desired and the production of activated carbons from wastes offers a promising future.

Biomass wastes obtained from cleaning of forests and industrial use may play an important role in finding new alternative fuels. Biomass gasification, performed in a fluidised bed in the presence of air and steam mixtures, has proven to be a possible way of converting environmentally hazardous wastes into economically valuable products, which can be used as fuels to produce energy. Biomass gasification, using mainly pine wastes in Portugal, produces a char which has been considered an undesirable by-product. However, the characterisation of this char has shown that it could be converted into a suitable activated carbon because of its intrinsic porosity and low ash content.
As the production of an active carbon must satisfy economical viability with high performance, cheap precursor materials readily available and convertible to an active carbon using a minimum of resources could become very attractive raw materials. Among the two classical methods of preparing activated carbons, physical and chemical activation, the latter has been chosen, because it is performed in a single-step (in the presence of chemical reagents), the process normally takes place at temperature lower than that used in the physical activation process, and the yields of carbon are usually high.
Therefore, the main objectives of this work are to study the feasibility of the preparation of chemically-activated carbons from a char obtained by gasification of pine wastes and to find the optimum conditions in making activated carbons with well-developed porosity. The influence of the preparation conditions, such as, the activating agent to char ratio, and the temperature and the duration of the process have been analysed. Additionally, the design of the stainless-steel basket in which the sample to be activated is inserted, has been considered for selected cases.

Experimental

The char, obtained from pine wastes in a pilot gasifier, without any previous treatment, was physically mixed with the activating reagent (KOH), using different alkali/char ratios (from 1/1 to 4/1 in wt/wt). This mixture was then put inside into a basket made of stainless-steel net and designed specifically for this purpose. This cylinder-shaped basket has a bed in which the sample was situated, exactly, 1 cm below the reactor thermocouple. The corresponding reactor is a vertical one with a total height of 1.85 m and 0.1 m in diameter. The flow of the inert gas, N_2, was of 4 l/min, and its inlet is allowed by a gas distributor, which was a perforated plate situated at the bottom of the reactor. Previously to each run, a probe was introduced in the reactor through the upper part and the experiment was initiated when the oxygen was evacuated of the reactor. Then, the mixture was heated up to the process temperature, under N_2 flow at the rate of 10°C/min, and was held for 1 h. Other times tested were 30 min and 3 h. The process temperature was varied over the temperature range of 725-800°C. After the activation process, the sample was cooled under N_2 flow, and was washed sequentially five times with HCl 5N and finally with distilled water to remove residual chlorides. Then, the sample washed was dried at 110°C for 24 h.

The activated carbons were characterised using physical adsorption of gases (N_2 at 77K and CO_2 at 273 K). To calculate the apparent surface area and the micropore volume, (specifically micropore plus supermicropore volume), the Dubinin-Radushkevich (DR) equation was applied to N_2 isotherm data.

Results and discussion

The chemical agent to char ratio has been found to be the most important parameter in the process studied in the present work. As an example, Figure 1 demonstrates the N_2 adsorption isotherms for the different activated carbons prepared with different KOH to char ratios, ranging from 1/1 to 4/1, at 775°C. The parent char has been also included. The materials prepared have type I N_2 adsorption isotherms corresponding to essentially microporosity, as can be seen in Figure 1. Activated carbons prepared from this procedure achieve to develop very high porosity, thus improving, for all the ratios studied, the adsorption capacity of the original char. Isotherms with continuous lines correspond to mixtures activated in the stainless-steel basket with a rigid solid support (made also of stainless-steel) as bed. If this support is thrown away, and the mixture is situated directly on the net, allowing N_2 goes through the sample and improving the contact gas-solid, the adsorption capacity of the resulting activated carbon is even increased (comparing the isotherm in dashed line with the corresponding in continuous line for the ratio 3/1).

It is generally agreed among investigators that the N_2 adsorption capacity of an activated carbon largely depends on the amount of micropores that are present in the solid, hence, its measurement can be directly related to the quantity of the micropore volume in the sample. The variations in the total micropore volume (expressed per unit weight of activated carbon) with the KOH to coal ratio is shown in Figure 2. The amount of total micropore volume developed increased linearly from the original char up to a ratio of 3/1. From this point to 4/1 the enhancement is not linear because it corresponds mainly to enlargement of microporosity and not to the generation of narrow microporosity, as deduced from CO_2 isotherms (not shown).

In conclusion, the feasibility of the activated carbon obtention from char prepared by gasification of pine wastes has been proved to be a success. The micropore development depends strongly on the KOH to char ratio. The best activated carbon prepared under the conditions used has a very well developed porosity, exhibiting a total micropore volume of 0.678 cm^3/g and an apparent surface area, estimated from the DR method of 1908 m^2/g.

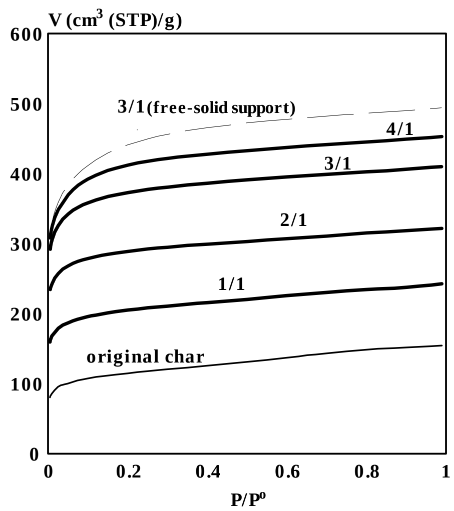

Figure 1. N_2 adsorption isotherms at 77 K.

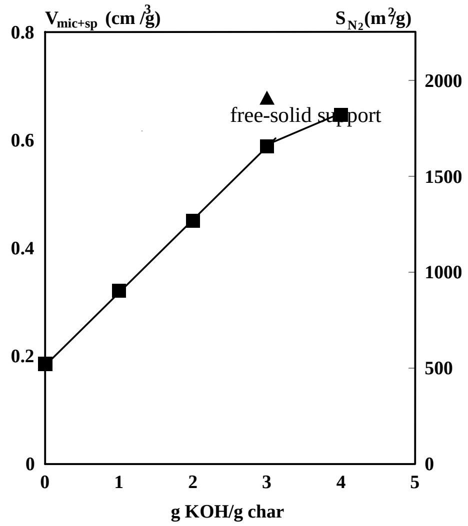

Figure 2. Effect of the KOH to char ratio on total microporosity development.

Acknowledgments

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References

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