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Proposition of a new adsorption refrigeration system using activated carbon prepared from olive stones#

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Abstract: The aim of the current paper is to propose a new solar adsorption refrigerator using a compound adsorbent fabricated from activated carbon issued from olive stones. High efficiency activated carbon (AC) with different chemical characteristic was prepared. It was established that activated carbon is obtained from carbonized olive stones in presence of argon in the temperature range from 700 to 800 °C and activated by $ZnCl_2$ and KOH. The characterization of the activated carbon samples was studied by SEM (scanning electron microscope) technique.
Keywords: *Activated carbon, olive stones, SEM, adsorptio, refrigeration system*

Introduction

In many parts of the world, the rural population lives in areas often far from the electric grid, yet its need for cooling keeps growing, mainly for food and medical product preservation. A solar refrigeration unit could be used for perishable foodstuff and as a secure store for food produce during the dry season. By using the properties of some solids to adsorb some gas at low temperature and to release it at high temperature, a thermodynamic cycle can be created to produce cold. The thermal energy can be solar because it is well adapted to the intermittency of the cycle. Adsorption solar cooling units have been widely studied in late 70s and gave rise to prototypes using the performance of mainly four pairs:

- activated carbon (AC)–methanol (Pons and Grenier, 1987), (Mhiri and golli, 1996) and (Lu et al., 2006),
- zeolite–water (Anyanwu and Ogueke, 2005) and (Schwarz, 1990)
- silicagel–water (Hildbrand et al., 2004)
- activated carbon–ammonia (Critoph, 1994), (Critoph , Metcalf et al., 2004) and (Liu and Leong, 2006)

Activated carbon obtained from olive stones and almond shells has high metal ions adsorption capacities (Ferro-García, 1988). Plum and peach stones have also been used for preparation of activated carbon (Rodríguez-Reinoso, 1985). The carbons from peach stones have also shown narrow pore size distribution and good properties as molecular sieves. The adsorbents prepared from plum stones had a better porosity compared to those prepared from peach stones. Some basic information about the adsorptive properties of activated carbon prepared from olive stones was presented by Iley and Marsh (Iley, 1973). The results obtained by them made clear that olive stones, a very abundant agricultural by-product in Mediterranean countries, could be a very adequate raw material to obtain good active carbon. The preparation of these activated carbons is economical and they have, besides some special proprieties, good adsorptive proprieties and hardness, which could be of interest in future environmental protection programs. Nearly all-inexpensive carbonaceous materials can be considered as starting materials for the production of activated carbon (Muñoz-Guillena, 1992). The starting material and the method of preparation influence the quality of the resulting activated carbon (Akash, 1994). The present work deals with preparation of carbon adsorbents from olive stones (OS), which are waste byproduct with significant amounts in the oil industry.

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Description Of The Adsorption Cycle For Refrigeration

The figure 1 represents a schematic of an intermittent solar adsorption cooling system. It consists of a copper adsorber (or a solar reactor) containing the adsorbent, which depends on the temperature and the pressure; it can be isolated and connected to the condenser or to the evaporator by a non-return valves. Theoretically, the cycle consists of two isosters and two isobars, as illustrated in the Clapeyron diagram (Fig. 2).

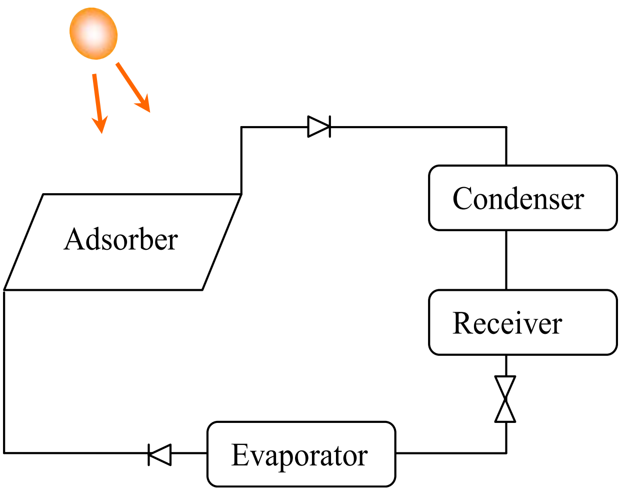


Figure 1. Schematic diagram of simple solar adsorption refrigerator

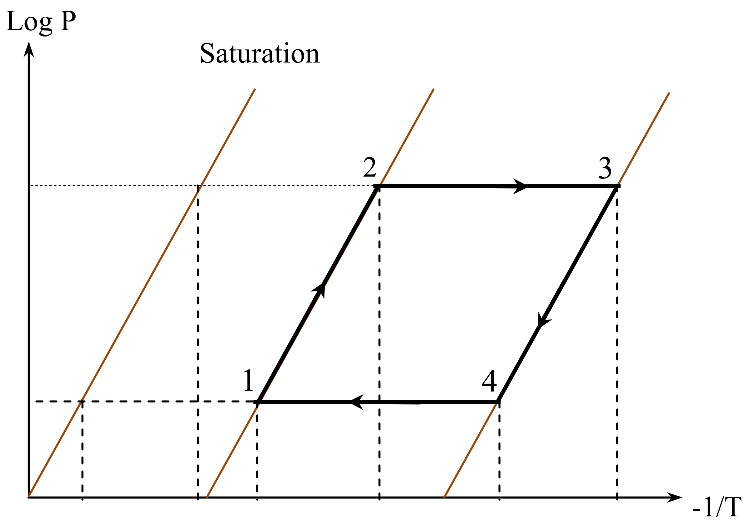


Figure 2 The ideal cycle in the Clapeyron diagram.

The basic adsorption cycle for refrigeration consists of four processes represented in Figure 1.

In the first one 1–2, the adsorbent is heated by solar energy until the pressure reaches a level that enables desorption of refrigerant (state 2). During process 2–3 addition of heat from solar energy results in desorption of vapour refrigerant, which condenses in an air-cooled condenser. At state 3, when the adsorbent reaches its maximum temperature, solar irradiance starts to decrease. The collector, cut off from the condenser, drops in temperature. Cooling of the adsorbent provokes a drop of pressure in the collector (process 3–4). Meanwhile, the liquid refrigerant is transferred into the evaporator. When the pressure reaches the value of the pressure at the evaporator temperature, the collector is connected to the evaporator (state 4).The adsorbent continues to decrease in temperature and pumps the liquid refrigerant, which evaporates and extracts heat from the evaporator (process 4–1) generating a cooling process inside the chamber. The cycle is said to be intermittent because the evaporation–cooling process happens only during the night.

Refrigerants

Adsorption technology can be used not only for air conditioning and refrigeration but also to upgrade heat with thermal transformers, and the type of refrigerant should be selected according to the application.

The requirements for a suitable refrigerant are generally as follows: (1) high latent heat of vaporization per volume unit or mass unit, (2) thermal stability, (3) environmental harmless, (4) non-flammable, (5) innoxious, (6) saturation pressure between 1 and 5 atm in the working temperatures (a perfect value would be close to 1 atm). Unfortunately, there are no refrigerants that have all the characteristics above, and the common refrigerants for adsorption refrigeration system are ammonia, water and methanol. Some physical properties of refrigerants for adsorption systems are shown in Table 1.

Table.1:Some physical properties of common refrigerants for adsorption systems

Refrigerants	Chemical formula	Normal boiling point	Molecular weight	Latent heat of vaporization L	Density ρ (kg/m3)	ρ × L (MJ/m3)
Ammonia	NH_3	−34 (°C)	17	1368 (kJ/kg)	681	932
Water	H_2O	100 (°C)	18	2258 (kJ/kg)	958	2163
Methanol	CH_3OH	65 (°C)	32	1102 (kJ/kg)	791	872
Ethanol	C_2H_5OH	79 (°C)	46	842 (kJ/kg)	789	665

Refrigerants with boiling point below −10 °C at 1 atm are positive pressure refrigerants, whereas the other ones are vacuum refrigerants. Ammonia is an example of positive pressure refrigerant, and it can be used with chlorides, activated carbon and activated carbon fibre. The saturation pressure of ethanol and methanol [39] are similar, but the latent heat of the former is about 30% lower than that of latter [40]. Methanol is normally used in association with activated carbon or activated carbon fibre. Water could be considered as a perfect refrigerant, except for its extreme low saturation pressure and for the impossibility to produce temperatures below 0 °C. Water is normally employed in pair with silica gel or zeolite.

Experimental

Preparation of activated carbon from olive stones

Olive stones freed from their fruit were obtained from the olive oil industry. They were crushed in a 10% solution of sulphuric acid and refluxed in distilled water to zero acid removal.

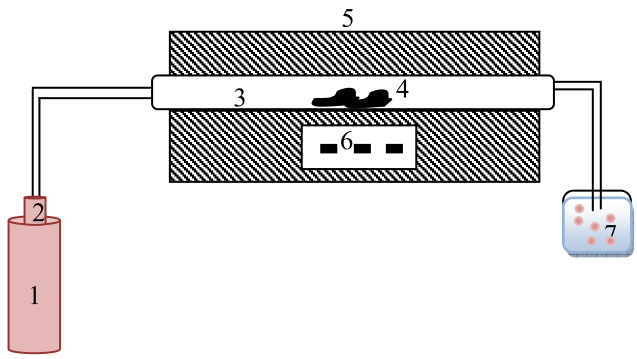


Figure 3. Schematic diagram of the apparatus (1- Argon, 2- Flow meter, 3- Quartz Tube, 4- Olive stones, 5- Tubular furnace, 6- Temperature regular device, 7- Bullor)

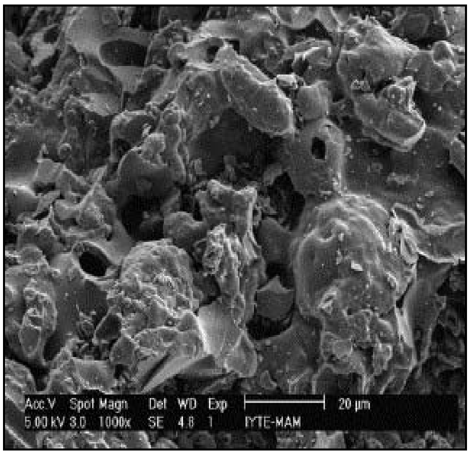
A part of the crushed olives with particle size of 0.5-1 mm diameter was impregnated with different rates of ZnCl2 and carbonized under continuous nitrogen flow at 700°C. The second part was impregnated with different rates of KOH and carbonized under continuous nitrogen flow at 800°C using a heating rate of 5°C.min-1. After the carbonization temperature was reached the sample was kept for one hour before the furnace was allowed to cool down to room temperature (Figure.3).

Results and Discussion

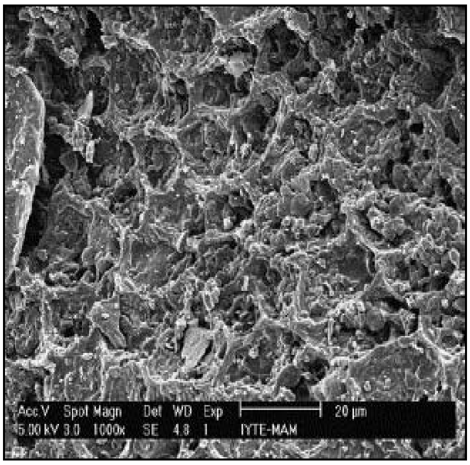
SEM analysis of the activated carbons

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the olive stone derived activated carbon. Figure 4 shows the SEM photographs of the olive stone before and after the impregnation at the optimum operating condition with 1000× magnification. It can be seen from the micrographs that the external surface of the chemically activated carbon is full of cavities, exhibiting a heterogeneous structure in terms of both size and shape. The reason for the formation of the cavities on the $ZnCl_2$ activated carbon is not clear. According to this micrograph, it seems that the cavities resulted from the evaporation of $ZnCl_2$ during carbonization, leaving the space previously occupied by the $ZnCl_2$. It can also be said that some salt particles are scattered on the surface of the activated carbon, probably due to the presence of remaining zinc chloride or other metal compounds on the activated carbon. Some particles were even trapped into the pores and could possibly block the entry of pores to some extent.

However, the impregnation by KOH shows clearly that it contributes to the development of the intern microporous cavities having for result a higher specific surface, important factor for adsorption.



a



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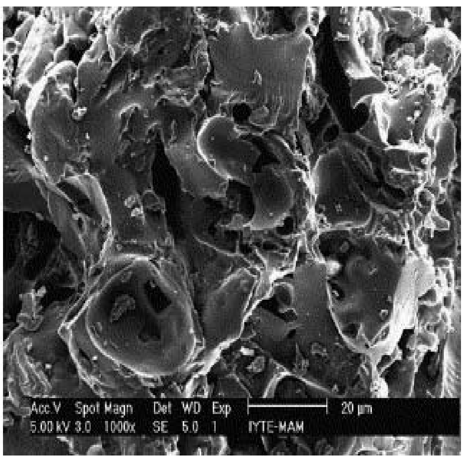

c

Fig. 4 SEMs of (a) no impregned olive stones, (b)olive stones impregned by ZnCl2 (7.35 mmol/g), (*c*) olive stones impregned by KOH (7.35 mmol/g).

Conclusion

The fabrication of the activated carbon from olive stones was successfully developed in our laboratories. We recommended using our fabricated adsorbent in a real solar adsorption refrigeration machine in order to evaluate the real comportment of the process with the new adsorbent.

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