HYDROCARBONS GAS STORAGE ON ACTIVATED CARBON PRODUCED FROM OLIVE STONES

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Introdcution

The use of gaseous hydrocarbons as energetic source in mobiles technologies (vehicles, plane, rocket…) is limited by security problems and lack of economic storage technologies offering a high energy volume density. Enhancement of storage capacity occurs with using porous materials to store the gas as adsorbed phase at relatively low pressure and near ambient temperature. Owing to their low cost and strong adsorption capacity, activated carbons are interesting media for this application [1]. A volumetric capacity exceeding 80 V/V and going up to 160 V/V at 3.5 to 4.0 MPa and near room temperature is currently reported in earlier works [2-4]. Adsorbed gas is easily desorbed by a simple relaxation or by heating. The principal goals of research in this field is the production of suitable adsorbent offering competitive and economic operating conditions.

Most early works are interested by thermodynamic studies of gas hydrocarbons adsorption whereas the dynamic of cyclic operation of charge- discharge and its performances are rarely studied despite of their importance for vehicle application.

In this work, activated carbon produced from olive stones by thermo-chemical process, is tested in his storage capacity of methane and butane gas storage at 303 K under low pressure varying between 3 to 10 bars on this activated carbons (AC). Cyclic operations of adsorption- desorption are also conducted at laboratory scale.

Experimental

The volumetric method is used to study the adsorption of methane and butane on activated carbon. Experiments are carried out in a stainless steel cell with 300 cm^3 volume (Adsorption Cell A) where 20 to 30 g of granular dried and out - gassed AC is suspended in rotate basket at low speed by magnetic stirrer drive. The temperature of the cell is controlled by inserted thermocouple and a heating mantle. A second cylindrical cell (reference cell B), with 600cm^3 volume is used as volumetric tank to control adsorbed amount and to feed the cell (A). A fixed temperature at 303 K is imposed to the two cells when adsorption isotherms are constructed. Delivered gas in desorption process is measured by water volume displacement at atmospheric pressure. To exhaust the adsorbed quantity the cell A is decompressed and heated at about 363 K.

The effective and void volume of each cell by considering piping and different accessories connections were measured by helium volumetric expansion tests.

To perform measurements of equilibrium adsorption some low quantity is withdrawn from the reference cell to the adsorption cell through the connecting valve and the system is left to reach equilibrium. Thus successive gas injections are conducted and the measured equilibrium adsorption at each injection amount gives the sorption isotherm points. For cyclic experiments at a given pressure, the progressive injection step by step is continued until saturation where no more adsorption is observed. After that, desorption is made by heating the cell to a temperature of 363 K.

Knowing the cell volumes and the sample volume, the adsorbed amount of gas in each injection is estimated from pressure decrease bye employing the real gas equation: $P_iV=Zn_iRT$, between initial and equilibrium conditions.

Activated carbon was produced in our laboratory from local olive stones, olive oil factories by –product, through a process using phosphoric acid as chemical agent in previous impregnation and thermal carbonization in nitrogen steam mixture at about 420°C. The activated carbon was analyzed in an Autosorb-AS1 C (Quantachrome, USA) through the nitrogen adsorption isotherm at 77K. This AC is essentially micro porous; the principal textural determined characteristics are shown in table1.

Table 1. Olive stones Activated carbon charateristics

Characteristic:	BET specific area	total porous volume	mean pore width(DR):	Bulk density
Value:	1260 m^2/g	0.47 cm^3/g	2.7 nm	0.426 g/cm^3

The methane gas used in this study has a purity of 99,98% and butane is a commercial bottled quality for home use.

Results and Discussion

Methane storage:

Isotherms of methane adsorption at 303K are reported in figure 1. There were carried out in three serial cycles of operation of equilibrated adsorptions separated by thermal desorption at 363K. Methane pressure is increased to about 10 bars. The adsorbed methane amounts reaches high values of about 150V/V at near 10 bars and still between 30 and 80 V/V at 4 bars.

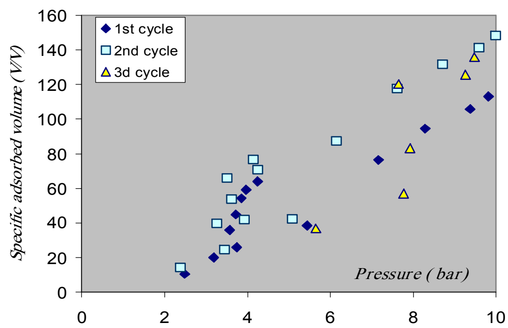

Fig. 1 Adsorption Isotherms of methane at 303K in three serial cycles.

Besides, the behavior and performance of this porous support are constants along three successive cycles. This is confirmed in a second series of experiments where the AC sample is submitted to six serial cycles of charges - discharges at two pressures: 3 and 10 bars (figure 2).

We note that the AC shows constant adsorption efficiency of methane which is kept for 6 charge-discharge cycles at two tested pressures when it is desorbed by atmospheric expansion and heating at 363K.

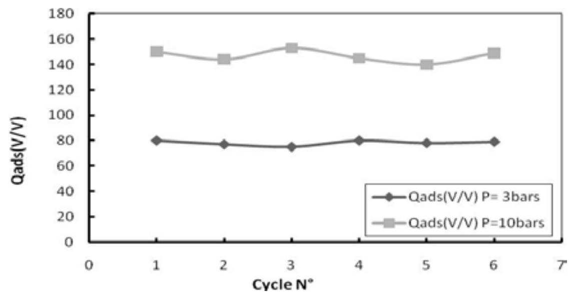

Fig. 2 Cyclic adsorption of methane on the olive stones AC at 3 and 10 bars and 303K.

Butane storage:

Commercial gaseous butane is stored in cyclic way at pressure lying between 3 and 4 bars and 303K temperature. The cyclic operation is kept until reaching a steady state of adsorption-desorption process Figure 3 resumes the specific volume amounts of adsorbed, desorbed and cumulated residual non-desorbed butane along the cyclic operation.

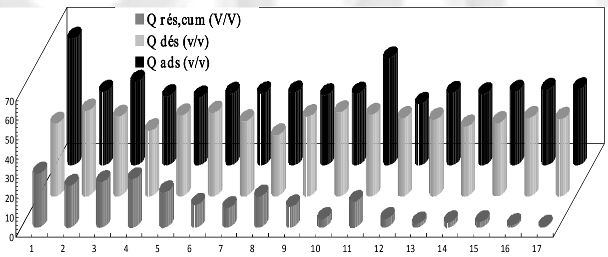

Fig. 3 Cyclic operation of butane charge-discharge on AC at 303K; support is regenerated after the 10th cycle (vacuum out -gassing at 473K)

One notes that the volumetric storage capacity reaches 65 V/V at the beginning of the operation. Quasi - steady state regime of the adsorbed and desorbed amounts is observed and values are in the range of 35-43 V/V capacity. The regeneration of AC after the 10th cycle improve its performances, in fact the residual adsorbed gas giving a desorption yield at about 100%.

Conclusions

Microporous activated carbon, generated from olive stones by wet thermo chemical process is tested for methane and butane storage. The isotherms adsorption equilibrium and cyclic charge-discharge operation confirms the opportunity of using our activated carbon for hydrocarbons gas storage application. High volumetric storage capacity of the pure methane of 150 V/V at 303K is reached 1.0 MPa pressures. Cyclic operation with butane shows interesting performances of the desorption efficiency and stable behavior along 13 serial adsorption-desorption.

References

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