International Journal of Chemical Engineering and Applications, Vol. 3, No. 3, June 2012

Hydrocarbons Gas Storage on Activated Carbons

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***Abstract*—The present study provides an experimental investigation of charge-discharge cycles of hydrocarbon gas mixture (butane and propane) in a volumetric apparatus set up filled with various activated carbons under low pressure of about 0,4MPa at 303K. This comparative study was carried out using one commercial activated carbon from NORIT company and two olive stones based activated carbons produced by chemical activation process using orthophosphoric acid with carbonization in nitrogen steam giving CAGOC and with carbonization in steam nitrogen flow giving CAGOCom. The highest storage measured capacities was about 62 V/V for the chemical activated AC, 65 V/V for the steam-nitrogen activated one and 67 V/V for Commercial AC. In spite of an efficiency fall down from the second cycle, a total desorption yield was obtained for CAGOCom with weak modifications on porous texture during cyclic operation. All these results encourage grain based activated carbons use as good candidate for gas storage to vehicular applications.**

***Index Terms*—Activated carbon, adsorption, desorption, olive stones, cyclic operation.**

I. INTRODUCTION

Nowadays, Hydrocarbons gases are considered economically attractive fuel for many applications to cover increasing energy demand. Especially for vehicle uses, gaseous light hydrocarbons being considered as an important alternative fuel due to its huge resource, relatively inexpensive price and low toxic gas emissions. However, when compared to other fuel resources, expansion of its use as vehicle fuel is limited by the storage and transportation technology. Hydrocarbons gases (H.G) stored under ambient temperature conditions are very unattractive as a transportation fuel mainly due to its limited driving range as a result of its low volumetric energy density.

The storage capacity of vehicle tanks using gas as fuel, and then vehicle's driving range, is limited essentially by the maximum storing pressure.

Using adsorbing porous solid support filling a new storage system seems to be an alternative technology to store hydrocarbons gas under convenient conditions for mobile uses. H.G stored as an adsorbed phase in porous materials is referred to as Adsorbed Natural Gas (ANG). However, currently adequate energy density comparable to that of CNG at 2400 psig can be provided by ANG at a low pressure of about 500 psig and at room temperature

The main challenge is to find adsorbents with high storage performances at low pressure and normal temperature allowing efficient desorption in simple operating conditions. Many researches are carried out in recent years in the field of gas adsorption on porous media for gas emission control and energy storage applications. Many porous solid are tested as an adsorbent for gas storage such as inorganic materials, zeolithes, silica gels, activated carbon…. A large number of papers have been published about gas adsorption at room temperatures on porous solids due to its use as a vehicular fuel [1]. Ailing Cheng and Wun- Liang Hang choose activated carbon as the best adsorbent compared to porous clay [2]. Activated carbon was recognized as best adsorbent for this purpose. Activated carbon can be based on anthracites, petroleum wastes or vegetal raw materials to be chosen as an important gas adsorbent. Precursors can be different types of vegetal grains such as olive stones [3], novel corn grain [4], anthracites [2], [5], [6], bituminous carbon [6]-[8]. Naturally, biomasses sources would be highly desirable of favorable to be converted into activated carbon used as the most important adsorbent for gas storage.

Methane adsorption on olive stones grain-based activated carbon activated by $ZnCl_2$ led to 96 V/V at 298K under 3.4MPa and to 110V/V if a physical activation with CO_2 was applied after chemical one [2]. Other study of F.Rodriguez- Rreinose et al [9] made to prepare A.C from olive stones grain to show that the best adsorption capacity is obtained with the best micro porous adsorbent.

Coconut are also used as precursor to prepare A.C [10]-[16] to reach an important capacity of about 90V/V at 298K under 4MPa near to Brazilian norm about 10V/V and far from the one fixed by energetic department of U.S about 150V/V for vehicular uses.

So the best carbonaceous adsorbents designed for gas storage should combine the highest micropore volume, the highest apparent density [17]-[19] also a high thermal conductivity of the adsorbent is required.

If we compare the different ways of carbonaceous adsorbents activation, chemical one is admitted refer to many studies as a very efficient technique to obtain a microporous activated carbon. Many advantages make it better than physical activation such as very high specific area, high micro porosity with a controlled microporosity with a controlled micropore size distribution [17].

From the chemical reagents which can be used for chemical activation like H_3PO_4, $ZnCl_2$, Alkali hydroxides seem to be those for which the microporosity of the A.C is the most developed such as sodium hydroxide chosen as the best reagent due to its low cost, simple handling and low corroding action [17] to understand chemical reaction between carbon and KOH we can say that KOH intercalates between carbon layers while NaOH reacts with the most energetic sites of the surface [17].

Manuscript received September 27, 2011; revised March 5, 2012.

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For examples wood and coconut have been used to prepare porous activated carbons.

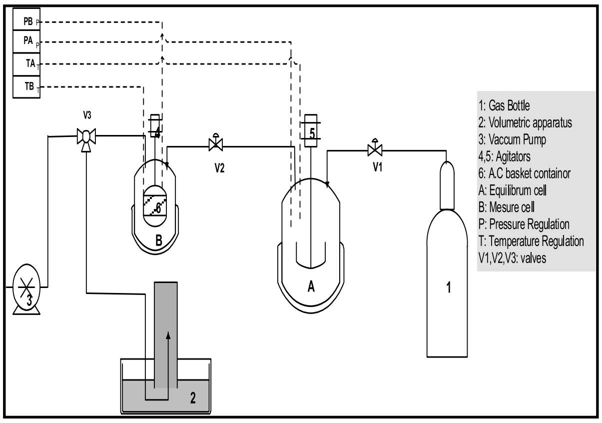
Corn stalks contain rich carbon species and the major components of cornstalks are cellulose, hemicelluloses and lignin, which can also act as a suitable precursor for the formation of porous A.C.

In the present study, olive stone grain-based activated carbon produced by chemical activation with H3PO4 and an A.C produced by Norit company are tested to store butane under low pressure about 4 bars at room temperature by a cyclic operation charge-discharge during 13 to 17 cycles.

This work has the purpose to suggest the best adsorbent with the best efficiency and the highest desorption rate for a butane- propane mixture of commercial gas in the purpose to be investigated on vehicular uses.

II. EXPERIMENTAL

A. Sorption- Desorption Apparatus



A cylindrical cell (B) (schematic diagram shown in figure 1) made of stainless steel is used to measure the gas uptake by activated carbon. The cell volume is about 308 cm^3 it can be operated up to 200 bars between 243K and 473K.

This cell contains a steel basket with 118cm^3 volume where activated carbon can be placed.

Another equilibrium cell (A) was used to measure gas amount injected into cell B.

It’s made also of stainless steel with about a 700 cm3 of volume.

Each cell is held in a metallic jacket heated by a regulation system to insure regulated heating.

To achieve good temperature stability, the jackets are insulated. Resistance probes are injected on the cells to measure gas temperatures.

B. Experimental Procedures

Firstly, activated carbon samples were kept in the oven for 24h at 383K. A known amount of activated carbon is then loaded directly into the cell B and vacuum is applied to the cell for two hours at 473K. The pressure inside the two gas cylinder A and B is measured by 2 gauges pressure transducers A and B. After injection, the system is left to equilibrate (pressure insider cell B become constant and stable for 25 min). More gas is then injected to the next desired pressure. Knowing the gas cylinder volume, initial and final pressures and atmospheric temperatures allow calculating the amount of gas injected in each step. This method was easier than disconnecting the gas cylinder and weighing it in each injection step while precise enough each equilibrium pressure and the adsorbed amount help to make the adsorption isotherm.

This adsorption- desorption cycle or charge- discharge will be repeated many times giving serial n cycles. The adsorbed amount is evaluated by volumetric method and desorbed amount is measured by volumetric method at room conditions.

The total number of (n_2 + n_3) cycles made for each adsorbent is related to its stability and efficiency, initial and final pressures and atmospheric temperature, allow calculating the amount of gas injected in each step. This is the manometric method.

$$\boldsymbol{n_{a,j} = n_{0,j} - n_{e,j} + n_{Br,j}}$$

$$= \frac{P_{A0,j} * V_A}{Z * R * T_A} - \frac{P_{e,j} * V_T}{Z * R * T_A} + \frac{P_{Br,j-1} * V_B^*}{Z * R * T_A} \text{ (mmol).}$$

$\mathbf{V^*_B = V_B - V_{C.A}}$: net volume of cell B containing Activated carbon bed.

$\mathbf{V_T = V_A + V^*_B}$ **:** total volume of gas on cell A and B

$\mathbf{V_B}$: volume of cell B

$\mathbf{V_A}$**:** volume of cell A

We deduce the total amount of gas adsorbed at the end of n_1 injections for each cycle n_a:

$$\Rightarrow \boldsymbol{n_a = \sum_{j=1}^{j=n1} n_{a,j}} \textbf{ (mmol)}$$

$$= \sum_{j=1}^{j=n1} n_{a,j} * \frac{1}{m_{CA}} * V_m * \rho_{app} \text{ (V/V)}$$

$$\Rightarrow n_a = \sum_{j=1}^{j=n1} n_{a,j} * \frac{1}{m_{CA}} * M_w \text{ (mg/g)}$$

where V_m is molar gas volume and ρ_{CA} is apparent volume mass of activated carbon.

Determination of the gaseous desorbed amount:

To measure the gas delivery the cell B was heated by an electric heater at 363K. The desorbed amount was evaluated volumetrically at room water temperature by the underwater collection method.

For each cycle l, we define the amount desorbed as follows:

$$n_d = \frac{P_{atm} * V_d}{Z * R * T_w} \text{ (mmol)} = \frac{P_{atm} * V_d}{Z * R * T_w} * \frac{1}{m_{C.A}} \text{ (mmol/g)}$$

$$= \frac{P_{atm} * V_d}{Z * R * T_w} * \frac{1}{m_{C.A}} * M_w \text{ (mg/g)}$$

$$n_d = \frac{P_{atm} * V_d}{Z * R * T_w} * \frac{1}{m_{C.A}} * V_m * \rho_{CA} \text{ (V/V)}$$

Hydrocarbon gas adsorption isotherms at 303 K for all samples were measured up to 4 bars by manometric method. The mixture desorption performances were evaluated by the underwater collection method. The experimental set up is shown schematically in figure 1 and explained next.

C. Materials

The present study deals with three activated carbons, one commercial produced and supplied by French company NORIT and two others derived from olive stones grains.

This precursor was first washed with water then impregnated (3/1 weight ratio H_3PO_4/Olive stones) with orthophosphoric acid reagent with 90% concentration for 9 hours at 383K to be pyrolysed after at 683K for 2,5 hours under nitrogen gas flow and followed by water wash to remove impurities and to reach a pH near 6 . This support chemically activated was named CAGOC. The other named CAGOCom was chemically activated also with orthophosphoric acid and carbonized in nitrogen and steam atmosphere. Before being tested in the experiments below, these supports were washed thoroughly with water. The main features of the three activated carbons namely BET, surface area, pore texture and apparent densities are given in Table I

TABLE I : ACTIVATED CARBONS CHARACTERISTICS

Activated Carbons	**S_{pBET} (m^2/g)**	**V_{pores} (cm^3/g)**	**V_{micro}(cm^3/g)**	**D pore (A°)**	**ρ app (g/cm^3)**	**ρ_{CA} (g/cm^3)**
CAGOC	1139	0.554	0.547	19.45	0.419	1.725
CAGOCom	1229	0.596	0.574	19.59	0.425	1.698
CA Norit	981	0.534	0.464	21.77	0.468	2.105

1) *Porosity characterizations*

Nitrogen isotherm at 77K were measured in a surface area analyser Quantachrome Autosorb-1MP.

Data were analyzed for BET area, total pore volume, micropore volume and average pore width. Surface areas were calculated according to BET method. Total pore volumes were directly measured at the highest relative pressure (P/P0 =1= used by the equipment. Adsorption data were analysed by the Dubinin Radushkevish equation to assess micropore volume and average pore widths were calculated based on the total pore volume and surface area.

2) *Gas Characteristics*

The hydrocarbon gas used is commercially bottled gas for domestic uses. It is a mixture of propane and butane, specification shows a major fraction of butane, Table II shows the properties of this gaseous mixture.

D. *Experimental Results and Discussion:*

1) *Gas storage on Activated Carbons*

A series of tests with butane using the three activated carbons at 303K under low pressure were conducted by cyclic operation during many cycles of adsorption-desorption.

The first n_1 cycles are carried out after preliminary discharge by applying vacuum for 2 hours at 473K. The n2 following cycles are carried out after a second regeneration at the same conditions to eliminate all impurities. The resulting adsorbed, desorbed and cumulated residual quantities along the cycles are presented in figure 2, 5 and 7 respectively for CAGOCom, CAGOC and CANorit

For each cycle residual amounts shown in Fig. 3, 6 and 8 are calculated by the following equation:

$$n_r = n_a - n_d$$: Residual amount for each cycle

2) *Gas storage on CAGOCom*

For C.AG.O.Com cyclic operation during 17 cycles of adsorption-desorption were carried out.were n_1= 10 cycles and n_2= 7 cycles after regeneration.

The evolution of the adsorbed quantities, desorbed and cumulated residual quantities along the cycles is represented on the histogram of Fig. 2.

TABLE II : GASEOUS MIXTURE PROPERTIES

Component	Molar Fraction(%)	Molair Mass(g/mol)
C2	0,145	0,04
C3	34,830	15,33
i C4	17,190	9,97
n C4	47,800	27,72
i C5	0,031	0,02
Ethyl Mercaptan(C_2H_5SH)	0,005	62,00
Mixture	100,000	53,09

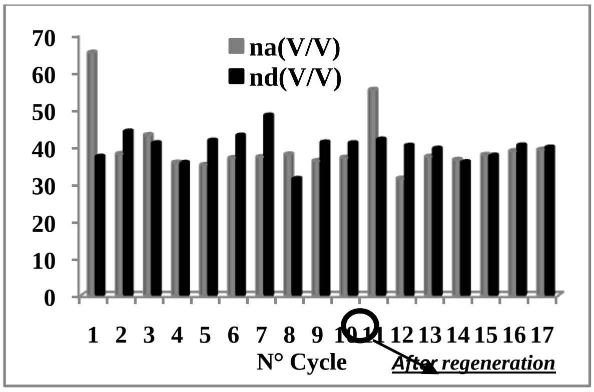


Fig. 1. Adsorbed and desorbed amounts development during cyclic operation for C.A.G.O.com

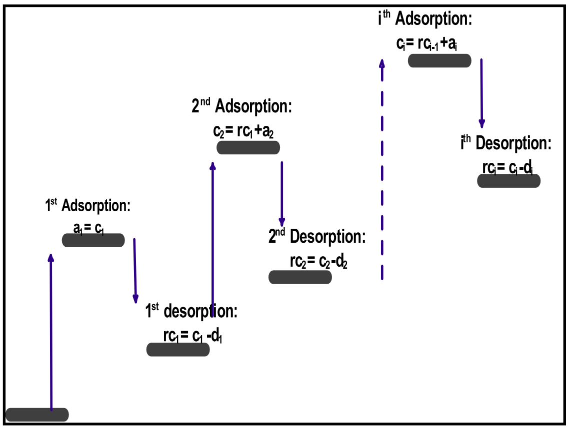


Fig. 2. Cumulated amounts within cyclic adsorption - desorption process

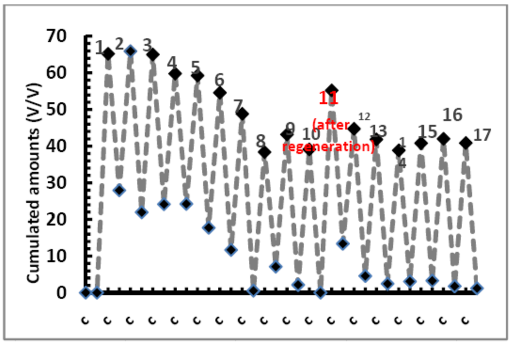


Fig. 3. Cumulated amounts evolution during cyclic operation

The amount of stored gas decrease from the second cycle (from 65 V/V to 38 V/V).

This can be due to the presence of impurities which block the pores and also due to the low desorption of the first cycle and accumulation of a gas quantity in the pores.

The low performances of CAGOCom observed from the second cycle are attributed to the presence of impurities in gas spreading in the pore spare, hence making a number of micropores unavailable for the gas.

However, within the 3rd to the 4th cycle, the amounts of butane stored become constant.

Additionally, it can be seen that going through the cycles, instability of desorbed amount are found. Consequently, it was be better to regenerate the A.C and continue cyclic operation. This regeneration induces a new adsorption capacity about 55 V/V with a loss of effectiveness of 10V/V which can be due probably to the blocked pores.

From the 13th cycle, a steady state is observed for adsorbed and desorbed amounts (38 and 39 V/V respectively). For these reasons cumulated residual quantity was null during the last 5 cycles.

Note: Cumulated and Residual cumulated amounts are calculated by the following equations:

$$n_{ci} = n_{rci\text{-}1} + n_{ai}$$

$$n_{rci} = n_{ci} - n_{di}$$

As shown in figure 2, within cycles evolution cumulated, amounts decrease to reach null amounts at the 15th cycle, where adsorbed amount is totally desorbed to have equality between cumulated and residual cumulated amounts.

Gas storage on C.A.G.O.C:

For this support, 2 series of adsorption: desorption cycles were carried out separated by regeneration after the 7th cycle to form two phases I and II. (Fig. 5 and 6)

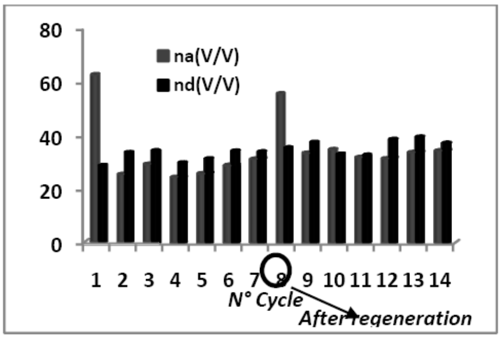


Fig. 4. Adsorbed and desorbed amounts evolution during cyclic operation for C.A.G.O.C

As seen previously for CAGOCom, we notice that gas storage on CAGOC decrease from the second cycle from an adsorption capacity of 65V/V to 30V/V.

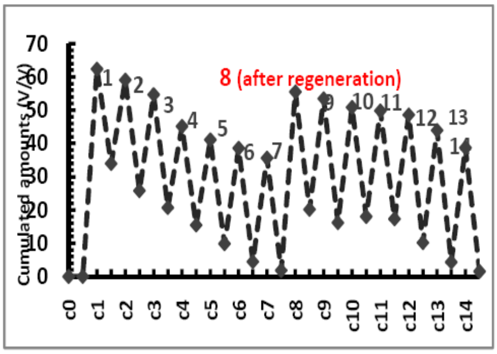


Fig. 5. Cumulated amounts for CAGOC during adsorption- desorption process

After only 2 cycles, the efficiency of the sorption process fall down by 50% and a number of 4 cycles are needed to reach a steady state where the residual cumulated quantity tends towards zero.

Gas storage on C.A Norit:

As for the previous support, for CA Norit two series of 7 adsorption- desorption cycles were carried out under 4 bars at 303K.

At the end of each cycle(figure 7) , the activated carbon is heated at 363K without vacuum to desorb gas amount. The next cycle is started after all the gas that could be desorbed was released. But for this A.C, the residual cumulated amount is not negligible and remained constant at the second phase from the 11th cycle at the range of 20V/V.

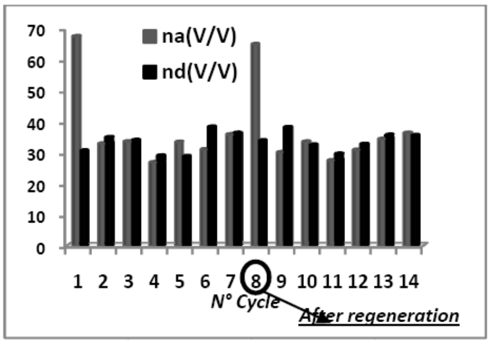


Fig. 6. Adsorbed and desorbed amounts during cyclic operation for C.A.Norit

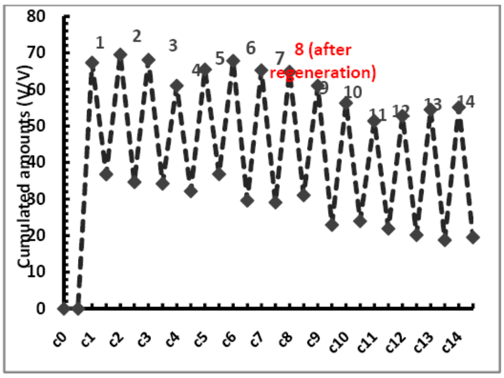


Fig. 7. Cumulated amounts during cyclic operation for CA Norit

As we can see after regeneration(figure8), CA Norit behaves with a constant state to have equal amounts of cumulated and residual cumulated amounts from 11th cycle. However this steady state the residual cumulated amount cannot be neglected since it is about 20 V/V.

Desorption Yield:

The Desorption yield of the cycle number 'i' was calculated by the following equation:

$$\boldsymbol{\varepsilon}_{\mathbf{i}} = \frac{\boldsymbol{n_{d,i}}}{\boldsymbol{n_{c,i}}}$$

From the Fig. 9, it may be seen that the desorption yield is different from one support to another.

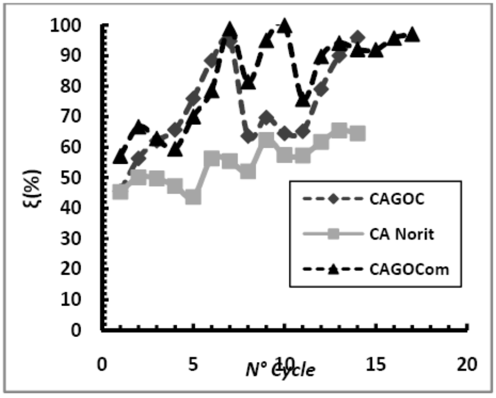


Fig. 8. Desorption yield effect on cyclic operation

For C.A.G.O.Com, desorption yield increase from 57% to 99% with the increase of cycle number. Activated carbon desorbed the total residual amount at the 12th cycle with 100% desorption yield.

As shown in figure 9, the C.A.G.O.C reach a total desorption yield at the 7th cycle.

These important results can be considered as one of the advantages that increase the chance of the activated carbon application for gas storage.

Adsorption Efficiency:

Adsorption efficiency of activated carbon can be also defined by the following equation:

$$\boldsymbol{\alpha_i} = \frac{(\boldsymbol{n_{a,i}})}{(\boldsymbol{n_{a,1}})}$$

The resulting efficiency for the three activated carbons tested is presented in figure 10.

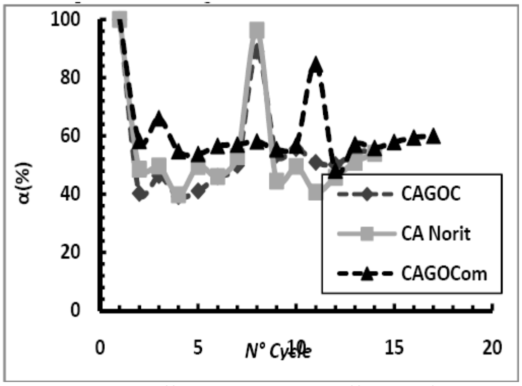


Fig. 9. Cyclic operation effect on Adsorption Efficiency for the three A.C tested

The results show that for all the three types of activated carbons, the adsorption efficiency falls down from the first cycle and remains constant at 45%.

This can be due to the blocked pores that can not realize gas impurities stored.

There is also another possibility that the impurities remain in pores and reduce adsorption capacity.

The presence of many compounds in gas, can affect the performance of the vehicle using this gas as the feed, as well as the storage capacity because these compounds slowly obstruct the adsorption sites for butane.

This could result in a reduction in the storage capacity of the activated carbon after several changes and discharges and the need for regeneration.

Texture Evolution during cyclic operation charge-discharge:

For the three activated carbons, it was observed that the efficiency of the sorption process fall down by 50% since the second cycle. This lost can be caused by textural change of activated carbon. For this reason, a several interest was given to the evolution of the support internal texture characteristics along cycles.

A.C Commercial NORIT:

In Table III, specific area of Norit activated carbon was measured during cyclic operation to see an important modification about 20% of the initial value

TABLEI: SPECIFIC AREA EVOLUTION DURING CYCLIC OPERATION FOR C. A. NORIT

State	S_{pBET} (m^2/g)
Before Adsorption	989
After the 3rd Cycle	891
After the 7th Cycle	837
After Regeneration	930
After the 10th Cycle	788
After the14th Cycle	805

TABLE II: POROUS STRUCTURE EVOLUTION DURINGCYCLIC OPERATION FOR C.A.G.O.COM

State	**S_p (m^2/g)**	**V_{pores} (cc/g)**	**$V_{micro\text{-}DR}$ (cc/g)**	**$V_{micro\text{-}DR}/V_{pores}$(%)**
Before adsorption	1421	for d<=3293A ° V_{pores} = 0,6549	0,6354	97
After the 3rd cycle	1277	for d<=2702A ° V_{pores} = 0,6093	0,5754	94,43
After the 7th cycle	1175	for d<=2825 A °V_{pores} = 0,5576	0,5295	94,42
After the 10th cycle	1282	for d<=2818,7A ° V_{pores}=0,5911	0,5649	95,56
After the 13th cycle	1140	For d<=2527 A ° V_{pores} = 0,542	0,5047	93,12
After the 17th Cycle	1362	For d<= 2713 A ° V_{pores} = 0,6074	0,5951	97,9

Thus we can confirm that cyclic operation modify A.C structure from 989 m^2/g to 805m^2/g after 14 cycles which minimizes life duration of A.C.

C.A.G.O.Com and C.A.G.O.C :

As seen previously for CA Norit, an important change in specific area was observed caused by gas adsorption phenomenon, for this reason a detailed analysis were made for olive stones based activated carbon during cyclic operation to control structural modifications using a Quantachrome Sorptiometer in Chemical Reactor and Process Control Unit Research at the national school of engineers on Gabes- Tunisia university Table IV and V show porosity modifications during cyclic operation.

TABLE III : POROUS STRUCTURE EVOLUTION DURING CYCLIC OPERATION FOR C.A.G.O.C

State	S p (m^2/g)	V pores (cc/g)	V micro (cc/g)	$V_{micro-DR}/V_{pores}$(%)
Before adsorption	1055	For d<=2338A ° V_{pores} = 0,4431	0,43	97
After the 3rd cycle	998,3	For d<= 4364A °V_{pores} = 0,6801	0,4164	61,22
After the 7th cycle	785,7	for d<=2985,5A ° V_{pores} = 0,3402	0,3266	96
After the 10th cycle	872,2	For d<=3135,6 V_{pores} = 0,3667	0,3613	98,5
After the 14th cycle	788,3	For d<=2780,9 V_{pores} = 0,3466	0,3386	97,7

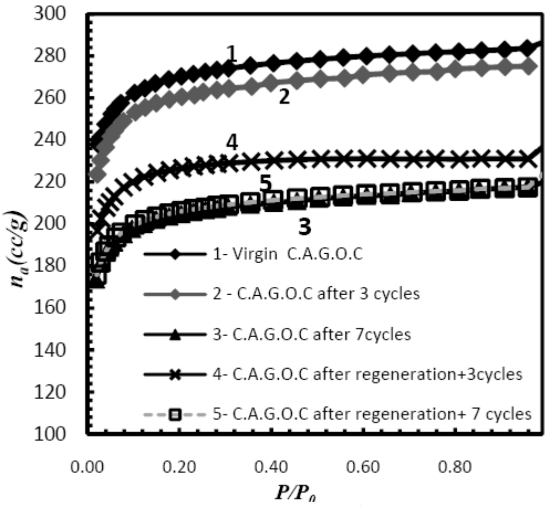


Fig. 10. Nitorgen adsorption isotherms at 77K for C.A.G.O.C during cyclic operation

However, in Table VI porous structure evolution are regrouped to conclude that after 7 cycles, C.A.G.O.C has its specific area decreasing from 1055 to 785 m^2/g with an important decrease in porous volume from 0.43 to 0.94 cc/g which explain the decrease storage efficiency. So that after these analysis we can notice clearly that cyclic operation do not affect internal structure of used supports despite blocked pores caused by accumulated impurities. We made also a detailed porosity analysis during cyclic operation to control structural modifications (Fig. 11 and 12)

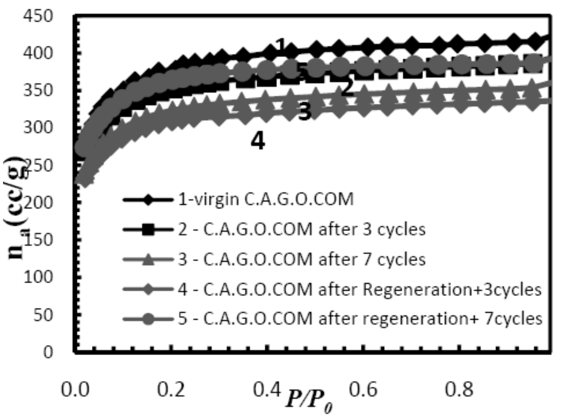


Fig. 11. Nitrogen adsorption isotherms at 77K for C.A.G.O.Com during cyclic operation

Fig. 13 shows that behavior of adsorption- desorption isotherms of nitrogen type I is kept for all A.C to conclude that cyclic operation do not deform internal texture and porous structure.

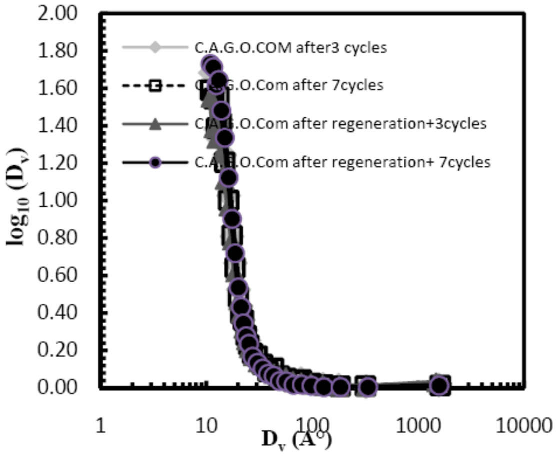


Fig. 12. Pore size distribution change during cyclic operation for C.A.G.O.Com

By examining the variation of specific surface along the cyclic operation, it is noticed that this activated carbon loses only 144 m^2/g of its surface at the end of 3 cycles but its porous volume varies slightly from 0,6549 to 0,6093 cc/g due not only to the variation of the micropores but also to the volume occupied by the meso pores. This variation in the porous structure porous due to the impurities influences the micropores and the meso pores. But after regeneration , A.C specific surface reaches 1362 m^2/g and of its microporosity towards the 17th cycle by minimizing the cumulated residual quantity which blocks the pores and damages its structure. This result insures the utility of the total desorption which is one of the performances of this activated carbon. It encourage its use for hydrocarbon gas storage and minimize the losses of effectiveness caused by impurities.

III. CONCLUSION

This work is a contribution to the development of the hydrocarbons gas storage tanks intended for vehicular uses.

This was an experimental study to choose the best activated carbon which adsorbs the maximal butane amount.

The results obtained in this study during cyclic operation charge- discharge show that for the three activated carbons investigated under low pressure about 4 bars at 303K important adsorption capacities were obtained about 65 V/V for CAGOCom, 62V/V for CAGOC and 67 V/V for CA Norit.

It was also revealed that the gas delivered from activated carbons by heating the cell at 363K can lead to an important desorption yield about 45% for CANorit and 99% for CAGOCom.

The thermal process of regeneration gives the supports in a stat very close to their initial state.

The efficiency of the Adsorbed Gas is greatly affected by cyclic operation to fall down from the second cycle to 50%.

Finally, it can be said that an important adsorbed amount close to 70V/V was obtained near room conditions for the three activated carbons tested. Such a result would be very interesting, because it is near ones obtained under high pressure about 25- 35 bars. TO conclude that olive stones based activated carbon obtained by combined process can be chosen as the best gas adsorbent.

The other conclusion of this work is that during cyclic operation charge- discharge a very weak porous textural modification was observed. It’s noted just a fall from 10 to 20% of specific area caused probably by impurities which block pores.

For these reasons, this study should be continued to elucidate the phenomenon of specific area reduction during gas adsorption- desorption and also to optimize regeneration conditions. For that purpose and due to the strategic interest of this energetic study which take place in the unit research: chemical reactors and order of the processes will be continued to chose the best gas for vehicular use by testing pure methane to optimize the best tank for adsorbed gas to vehicular uses.

IV. ABBREVIATIONS

LPG: Petroleum Liquefied Gas

NG: Natural Gas

CNG: Compressed Natural Gas

CAGOCom: Olive stones based activated carbon produced by physical and chemical ways.

CAGOC: Olive stones based activated carbon procuced by chemical atication with orthophosphoric acid

CA Norit: Activated carbon produced by NORIT company

V. NOMENCLATURE

M_{gas} : molar gaseous mass (mol/g)
$m\ CA$: activated carbon mass (g)
Mw : Molecular mass (g/mol)
$n_{a,j}$: adsorbed amount for the j^{th} injection (mmol/g or V/V or mg/g)
$n_{d,j}$: desorbed amount for the j th injection (mmol/g or V/V or mg/g)
$n_{0,j}$: the initial gaseous amount (mmol/g or V/V or mg/g)
$n_{e,j}$: gaseous amount at equilibrium state for the j^{th} injection (mmol)
n_1 : Cycle number for the first step of cyclic operation
n_2: Cycle number for the second step of cyclic operation
$n_{Br,j}$: gaseous amount residual on cell B at the end of each adsorption injection step (mmol)
$n_{c,j}$: cumulated amount for the j^{th} injection (mmol/g or V/V or mg/g)
$n_{rc,j}$: residual cumulated amount for the j^{th} injection (mmol/g or V/V or mg/g)
P_{A0} : Pressure on A at the initial state (bars)
P_e : equilibrium pressure on (A+B) for the j^{th} injection of the l^{th} cycle(bars)
P_{Br} : residual pressure on cell B (bar)
P_{atm} : atmospheric pressure (bars)
P : gas pressure (bars)
ξ_i : desorption yield for the i^{th} cycle (%)
α_i: adsorption efficiency for the i^{th} cycle (%)
R : gas constant = 0,082 l.atm/mol.K
T_A : temperature of cell A (K)
T_{ad} : adsorption temperature (K)
T_c : critic temperature (K)
T_d : desorption temperature (K)
T_w : water temperature (K)
$V_{C.A}$: the volume of the A.C bed (cm^3)
V : gas volume (cm^3)
V_A : cell A volume (cm^3)
V_B* : cell B volume with A.C (cm^3)
V_B : cell B volume (cm^3)
V_c : critic volume (cm3/mol)
V_T : total volume of the 2 cells with A.C (cm^3)
X_p : impregnation factor (g/g)
Z : compressibility factor
α_l : adsorption efficiency for the cycle l (%)
ρ_{app} : apparent density for the A.C bed (cm^3/g)
ρ_{CA} : Real activated carbon density (g/cm^3)
ρ_{gaz} : gas density (cm^3/g)

REFERENCES

[1] A. L. Cheng and W. L. Huang, ‘Selective adsorption of hydrocarbon gases on clays and organic matter,” *Organic Geochemistry*, vol. 35, pp. 413–423, 2004

[2] A. Celzard, A. Albiniak, M. J. Halat , J. F. M. Che, and G. Furdin, ‘Methane storage capacities and pore textures of active carbons undergoing mechanical densification,” *Carbon*, vol. 43, pp. 1990 – 1999, 2005.

[3] C. Almansa, M. M. Sabio, and F. R. Reinoso, “Adsorption of methane into ZnCl2-activated carbon derived discs,” *Microporous and Mesoporous Materials*, vol. 76, pp. 185 – 191, 2004.

[4] M. S. Balathanigaimani, W. G. Shim, J. W. Lee, H. Moon, “Adsorption of methane on novel corn grain-based carbon monoliths,” *Microporous and Mesoporous Materials*, vol. 119, pp. 47–52, 2009.

[5] D. L. Castello, D. C. Amoros, A. L. Solano, and D. F. Quinn, ‘Influence of pore size distribution on methane storage at relatively low pressure : preparation of activated carbon with optimum pore size,” *Carbon*, vol. 40, pp 989-1002, 2002.

[6] I. A. A. C. Esteves, M. S. S. Lopes, P. M. C. Nunes, J. P. B. Mota, “Adsorption of natural gas and biogas components on activated carbon,” *Separation and Purification Technology*, vol. 62, pp.281–296, 2008.

[7] A. M. Rubel, J. M. Stencel, “CH4 Storage on compressed carbons,” *Fuel*, vol. 79, pp. 1095-1100, 2000.

[8] M. N. Asl, M. Soltanieh, and A. Rashidi, “Modeling and preparation of activated carbon for methane storage II. Neural network modeling and experimental studies of the activated carbon preparation,” *Energy Conversion and Management,* 2008.

[9] F. R. Reinoso, Y. Nakagawa, J. S. Albero, J. M. Juárez-Galán, M. M. Sabio, “Correlation of methane uptake with microporosity and surface area of chemically activated carbons,” *Microporous and Mesoporous Materials*, 2008.

[10] F. N. Ridha, R. M. Yunus, M. Rashid, A. F. Ismail, “Dynamic delivery analysis of adsorptive natural gas storages at room temperature,” *Fuel Processing Technology*, vol. 88, pp 349-357, 2007.

[11] X. D. Yang, Q. R. Zheng, A. Z. Gu, and X. S. Lu, “Experimental studies of the performance of adsorbed natural gas storage system during discharge,” *Applied Thermal Engineering*, vol. 25, pp. 591-601, 2005.

[12] A. Perrin, A. Celzard, J. F. Marêché, and G. Furdin, “Improved methane storage capacities by sorption on wet active carbons,” *Carbon*, vol. 42, pp. 1249-1256, 2004.

[13] D. C. S. Azevedo, J. C. S. Araujo, M. B. Neto, A. E. B. Torres, E. F. Jaguaribe, C. L. Cavalcante, “Microporous activated carbon prepared from coconut Shells using Chemical activation with zinc Chloride,” *Microporous and Mesoporous Materials*, vol. 100, pp. 361-364, 2007.

[14] M. J. Prauchner and F. R. Reinoso, “Preparation of Granular activated carbons for adsorption of natural gaz,” *Microporous and Mesoporous Materials*, vol. 109, pp. 581-584, 2008.

[15] H. Najibi, A. Chapoy, and B. Tohidi, “Methane/natural gas storage and delivred capacity for activated carbons in dry and wet conditions,” *Feul*, vol. 87, pp. 7-13, 2008.

[16] F. N. Ridha, R. M. Yunus, M. Rashid, and A. F. Ismail, “Thermal analysis of adsorptive natural gas storages during dynamic charge phase at room temperature,” *Experimental Thermal and Fluid Science*, vol. 32, pp. 14-22, 2007.

[17] A. Celzard, A. Perrin, A. Albiniak, E. Broniek, and J. F. Marêché, “The effect of wetting on pore texture and methane storage ability of NaOH activated carbon,” *Fuel*, vol. 86, 2007, pp. 287-293.

[18] D. L. Castello, J. A. Monge, M. A. D. l. C. Lillo, D. C. Amoro, A. L. Solano, “Advances in the study of methane storage in porous carbonaceous materials,” *Fuel*, vol. 81, pp. 1777–1803, 2007.

[19] D. L. Castello, D. C. Amoros, A. L. Solano, and D. F. Quinn, “Influence of pore size distribution on methane storage at relatively low pressure: preparation of activated carbon with optimum pore size,” *Carbon*, vol. 40, pp. 989-1002, 2002.