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# COMPARATIVE STUDY FOR ADSORPTION OF HYDROGEN-METHANE MIXTURES ON ACTIVATED CARBON AND 5A MOLECULAR SIEVE

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**Abstract -** Equilibrium adsorption isotherms were obtained experimentally by a static method for a binary component hydrogen-methane mixture on activated carbon and 5A molecular sieve adsorbents. The temperature range 303-333 K and pressure range 0 - 4 MPa were examined. Methods for predicting gas-mixture equilibrium adsorption data from the pure-component isotherms were evaluated. Extended Langmuir model correlated the adsorption of binary mixtures fairly well. In all cases mutual interference was found, that is, the amount of a given gas adsorbed at a given partial pressure was always less in the mixture than it would have been if the other gaseous component had not been present. It was found that the amount adsorbed of gases per unit bulk volume for 5A molecular sieve was higher than for activated carbon. Furthermore, 5A molecular sieve showed better adsorption characteristics than activated carbon in mass transfer properties, affinity, selectivity and heat of adsorption.

*Keywords:* Hydrogen, Methane, Adsorption, Equilibrium, Mixture.

## INTRODUCTION

Off-gas of Iraqi north refineries usually contains large amounts of hydrogen and heavier hydrocarbons and sometimes impurities, such as sulfur compounds, water vapor and carbon dioxide. These gases are currently being burned in flare stack or as fuel, even though the fuel gas value of these streams is significantly less than the value of the hydrogen-free recoverable fuel. Also, the large demand in the refinery operations for hydrogen to desulfurize feed stocks and liquid heavy fractions make the separation of hydrogen from hydrocarbon gases an important project since upgrading of various refinery waste gases is nearly always more economical than hydrogen production by steam reforming (Gaskin, 2003).

Five types of processes were found in the literature for separation of hydrogen from gas mixtures. These processes include: condensation, absorption, diffusion, adsorption and electrochemical separation (Shindo and Nagai, 2013). The last five decades have witnessed a tremendous growth of gas adsorption processes that have made adsorption systems a key tool both for purification and for bulk separation in petroleum industries. The main advantages of

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adsorption as a separation technique, compared with the other processes, are that in many cases higher selectivity can be obtained by adsorption than by any of the other techniques, and adsorbents have a relatively high capacity for volatile materials, even at low partial pressures. The feature of higher selectivity promises more effective separations, while high adsorbent capacity allows the use of higher temperatures and lower pressures (Mohammed, 1996).

A large spectrum of inorganic (silica gels, alumina, zeolites), organic (activated carbons) and polymeric adsorbents is commercially available to carry out many separations of practical interest. These adsorbents offer a wide range of physical (micro- and macro-porosity, particle shape, size and strength) and chemical (hydrophobicity, surface polarity and ion exchangeability) characteristics to choose from. Each or all of these properties can play a role in the separation process. Activated carbon and 5A molecular sieves were selected as the best adsorbents for hydrogen recovery by adsorption processes (Teiseh and Capareda, 2010). Activated carbons contain a full range of pore sizes. Control of the pore sizes and their distribution in the manufacturing process allows a broad range of adsorbents to be available, offering widely differing selectivity. One advantage of activated carbon is that the adsorption of organic molecules tends to be non-specific. Zeolites are distinct from other adsorbents in that, for each type, there is no distribution of pore size because the crystal lattice into which the adsorbate molecules can or cannot enter is precisely uniform. For this reason zeolites are capable of separating effectively on the basis of size and they have been assigned the popular description of molecular sieves. Many zeolites are extremely polar and therefore separations may be effected using both molecular sieving and internal surface property effects (Suzuki, 1990).

Data on the adsorption of hydrogen and methane and their mixtures on activated carbon and molecular sieves are scarce in the literature. Some data have been reported for activated carbon, Linde 5A and 13X molecular sieve, where methane was found to be preferentially adsorbed on the former molecular sieve (Wakasugi et al., 1981; Ahmadpour et al., 1998; Lopes et al., 2009). Limitations are placed on the usefulness of these data for the design of commercial adsorbent-based separation systems, since a large part of these data was not ordinarily considered practical from a commercial stand point.

In the research reported herein, fundamental equilibrium adsorption data are obtained for hydrogen and methane and their mixtures on a single sample of activated carbon or 5A molecular sieve. To simulate refinery off-gas conditions, the temperature ranged from ambient to 60ºC and the pressure to 4 MPa. These data are of value in process and design studies of adsorbent-based separation systems involving the separation of hydrogen from refinery off-gases.

## EXPERIMENTAL WORK

A schematic diagram and photograph of the apparatus are shown in Figures 1 and 2, respectively. All tubing was thick wall (3.2 mm O.D. and 2.4 mm I.D.) stainless steel, to minimize the dead volume. The tubing was connected by Crawford Swagelock compression fittings. Parker CPI series severe service union bonnet valves, with a hardened ball stem tip, were chosen because of their durability under repetitive use. A metal stem tip was selected instead of a soft stem tip to avert destruction of the valve seat in the event that particulate matter should escape from the adsorption chamber, enter the valve and score the valve seat.

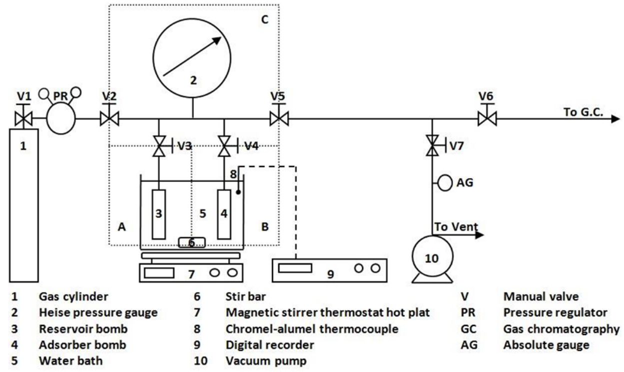

**Figure 1.** Schematic diagram of apparatus used for adsorption equilibrium measurement.

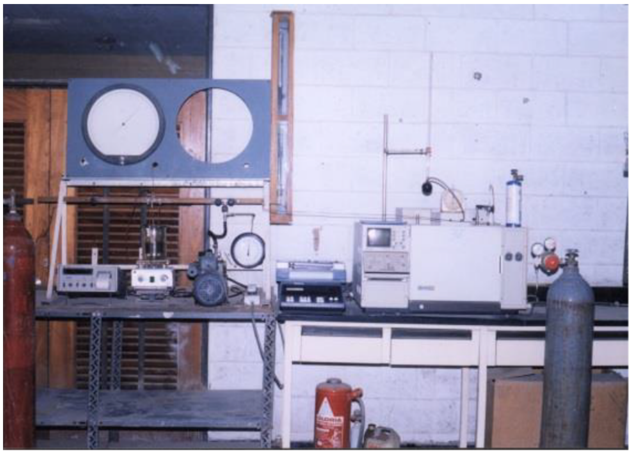

**Figure 2.** Photograph of apparatus used for adsorption equilibrium measurement.

The adsorption chamber and reservoir were approximately 20 cm$^3$ iron sample cylinders. Entrainment of adsorbent particles in the tubing and valving system was prevented by employing a dual screen method. This was accomplished by inserting Pyrex glass wool and a conical brass wire mesh screen, capable of containing particles.

The gas pressure was measured via a Heise bourdon gauge with a 430 mm diameter dial and a pressure range from zero to 6891 kPa. The accuracy of the gauge was rated at 0.1 % of the full scale and the sensitivity at 0.02 % of the full scale at all points. The pressure gauge enclosed a dead volume of approximately 30 cm$^3$.

A water bath was employed to provide a constant temperature environment up to 353 K for both the adsorber and the reservoir. The bath was thermostated and vigorously mixed by using a magnetic stirrer thermostat hot plate (Gallenkamp). The temperature of the bath was continuously measured and recorded via a digital recorder (Dacq TR-2721) and a thermocouple wire, calibrated with a mercury thermometer. The feed (hydrogen and/or methane) and carrier gas (nitrogen) supplied from cylinders were regulated by (Victory) pressure regulators.

The volume of the reservoir and the adsorber (together with the Swagelock fittings) and the other sections of the system were measured manometrically using nitrogen gas. Section C was charged with nitrogen gas to a known pressure $P_1$ = 4 MPa. Valve 5 was connected to a standard known-volume previously-evacuated cylinder vessel $V_1$ = 1 liter and opened until equilibrium was reached with a new pressure $P_2$. Then the volume of section C was determined by the equation:

$$V_C = \frac{P_2 V_1}{P_1 - P_2} \tag{1}$$

The volumes of sections A and B were determined in the same manner.

Two commercial grade adsorbents, activated carbon (supplied by Nuchar corp.) and 5A molecular sieve (supplied by Rhone Poulenc industries Ltd.), were chosen with the same cylindrical shape and to some extent with the same dimensions, in order to decrease the difference in shape factor. The average equivalent particle diameters were found to be equal to 3.971 and 3.789 mm for activated carbon and 5A molecular sieve, respectively.

Both adsorbents were regenerated with a vacuum oven (Gallenkamp) which was operated at 10 kPa pressure and 373 K temperature overnight, in order to remove previously adsorbed gases from the adsorbent surfaces. 10 g of the granular adsorbent was packed into the adsorption vessel and degassed overnight under vacuum at a pressure of less than 3 Pa to clean the adsorbent. This pretreatment enabled us to make adsorption measurements without changing the adsorbents. After the adsorbent had been regenerated, the vacuum pump was switched off. The water bath with thermostated electrical stirrer hot plate was switched on until constant temperature was reached. Through this period of time the gas chromatography unit was switched on and allowed to warm up.

The procedure for measuring equilibrium adsorption was as follow:

1. Sections A and C were pressurized with adsorbate(s), corresponding to a pressure $P_3$ . Then the number of moles of each adsorbate were estimated according to the relation:

$$n_{1i} = \frac{P_3 (V_C + V_A)}{RT} \times y_i \tag{2}$$

Passage of gas to section B was allowed until equilibrium ($\Delta P \leq 3$ kPa/h).The equilibrium pressure was recorded as $P_4$ .

2. Adsorber was isolated from the system and a sample of the gas was analyzed through valve 6 by G.C. section. The number of moles of each adsorbate were estimated according to the relation:

$$n_{2i} = \frac{P_4 (V_C + V_A + V_B)}{RT} \times y_i \tag{3}$$

The amount adsorbed of each adsorbate at partial pressure equal to ($y_i \times P_4$) is determined according to a material balance equation:

$$q_i = \frac{n_{1i} - n_{2i}}{W} \tag{4}$$

Gas-solid chromatography (Varian Vesta, 6000) was used for gas analysis in accordance with a modified standard test [ASTM D1946-90(2015)]. The GC carrier gas flow rate was measured with a soap film wet flow-meter. The chromatographic conditions for gas analysis are summarized in Table 1.

Apparent, packing or bulk density was determined according to a standard method [ASTM D2854-09(2014)]. It was found to be equal to 410 kg/m$^3$ for activated carbon and 823 kg/m$^3$ for 5A molecular sieve.

## RESULTS AND DISCUSSION

The partial pressure and temperature ranges were chosen for each component in view of the expected values in the refinery off-gas properties and component vapor pressure, which must be greater than the component partial pressure under the specified temperature, to avoid condensation of gases on the adsorbents.

The experimental results for single gas equilibrium were fitted with Langmuir and Freundlich equations. BET and other equations that represent multi-layer adsorption were excluded because it is unlikely that multi-layer adsorption could have occurred in this study where all temperatures were above the critical (Wu et al., 2007; Dąbrowski, 2001).

The Langmuir equation takes the form (Pistikopoulos et al., 2011; Yang, 1987):

$$\theta = \frac{q}{q_m} = \frac{BP}{1+BP} \tag{5}$$

The coefficients $B$ and $q_m$ depend on temperature in accordance with the following equations:

$$q_m = a_1 T^{a_2} \tag{6}$$

$$B = a_3 e^{a_4/T} \tag{7}$$

The Freundlich equation takes the form (Monemtabary et al., 2013):

$$\theta = \frac{q}{q_m} = k_F P^{n_F} \tag{8}$$

The coefficients $k_F$ and $n_F$ depend on temperature in accordance with the following equations:

$$k_F = b_1 T^{b_2} \tag{9}$$

$$n_F = b_3 + b_4/T \tag{10}$$

The objective function (average relative error) used in the minimization routine was defined as:

$$E = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\frac{q_{i,\exp} - q_{i,cal}}{q_{i,\exp}}\right)^2} \tag{11}$$

Langmuir and Freundlich adsorption parameters were determined by transforming the equations into linear forms and using the least-square method as a procedure for fitting. The calculated constants for the two model equations along with the average relative error values are presented in Tables 2 and 3. The tables show that the Langmuir equation correlates the experimental data with mean average relative error of 1.03 % versus 1.53 % for the Freundlich equation. Therefore, the best fit was achieved with Langmuir equation.

**Table 1.** Chromatographic conditions for gas analysis.

| Type of detector | TCD (Gow-Mac, TE II) |
|---|---|
| Type of chromatographic column | Parapak Q (Water Associates Inc.) |
| Nitrogen flow rate, $cm^3 min^{-1}$ | 30 |
| Injection and Oven temperature, K | 373 |
| Detector temperature, K | 473 |
| Filament temperature, K | 493 |
| Recorder voltage range, mV | 2 |

**Table 2.** Summary of single gas adsorption isotherms results, fitted with Langmuir equation.

| Adsorbate | Adsorbent | $a_1$ | $a_2$ | $a_3$ | $a_4$ | **E %** |
|---|---|---|---|---|---|---|
| $H_2$ | Activated carbon | $1.90*10^{-11}$ | 3.42 | $8.20*10^{-12}$ | 2662.61 | 1.22 |
| $CH_4$ | Activated carbon | 61.38 | -1.59 | $6.16*10^{-8}$ | 854.66 | 0.66 |
| $H_2$ | 5A Molecular sieve | $4.63*10^{-1}$ | -0.92 | $5.61*10^{-9}$ | 841.47 | 0.31 |
| $CH_4$ | 5A Molecular sieve | $8.25*10^{-1}$ | -0.99 | $3.24*10^{-7}$ | 705.96 | 0.51 |

**Table 3.** Summary of single gas adsorption isotherms results, fitted with Freundlich equation.

| Adsorbate | Adsorbent | $b_1$ | $b_2$ | $b_3$ | $b_4$ | **E %** |
|---|---|---|---|---|---|---|
| $H_2$ | Activated carbon | $2.59*10^{14}$ | -9.42 | 1.26 | -106.29 | 1.00 |
| $CH_4$ | Activated carbon | $3.22*10^{-29}$ | 9.05 | -0.32 | 277.97 | 1.12 |
| $H_2$ | 5A Molecular sieve | $9.79*10^{-3}$ | -2.79 | 0.84 | 10.46 | 0.38 |
| $CH_4$ | 5A Molecular sieve | $4.21*10^{-44}$ | 15.42 | -0.87 | 385.45 | 1.77 |

of adsorption on mass transfer properties for the two adsorbents.

The adsorption capacities of activated carbon for the two adsorbates are approximately twice that of 5A molecular sieve, as shown in Figures 3 - 6. The

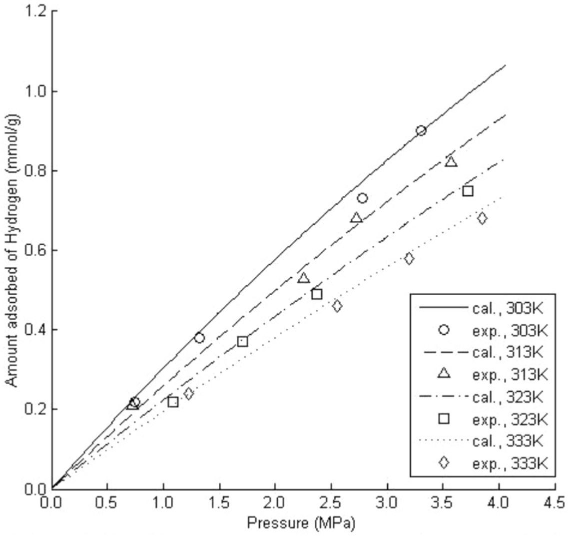

**Figure 3.** Adsorption equilibrium isotherms for the system Hydrogen-Activated Carbon correlated with Langmuir equation.

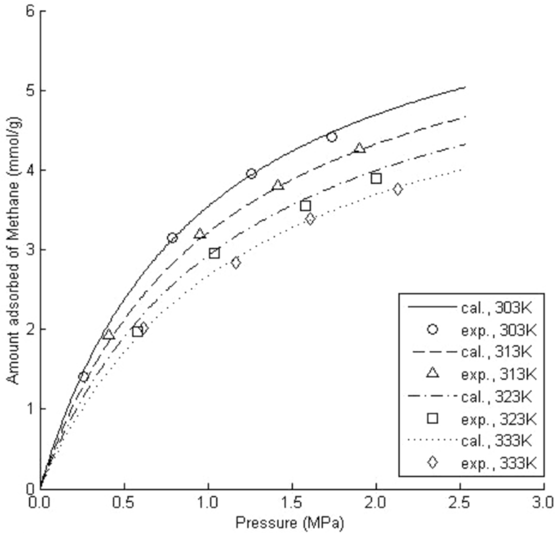

**Figure 4.** Adsorption equilibrium isotherms for the system Methane-Activated Carbon correlated with Langmuir equation.

The experimental equilibrium data were correlated by the Langmuir equation and presented in Figures 3 - 6. All curves for any specified gas on both adsorbents are similar in shape and are of the classic adsorption isotherm form.

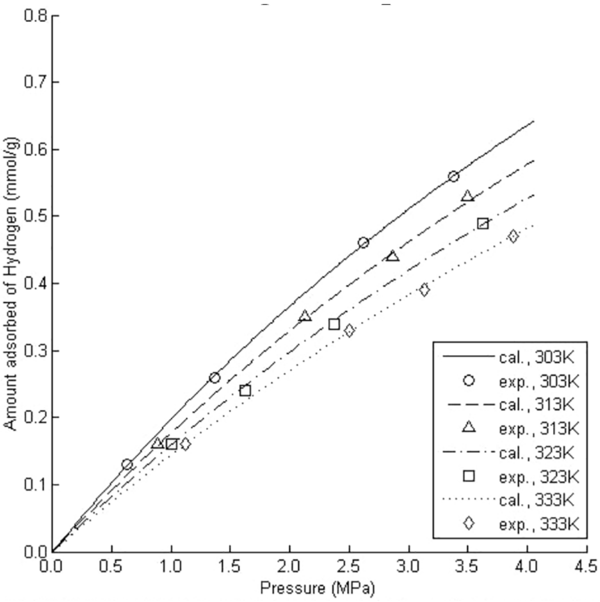

**Figure 5.** Adsorption equilibrium isotherms for the system Hydrogen-5A molecular sieve correlated with Langmuir equation.

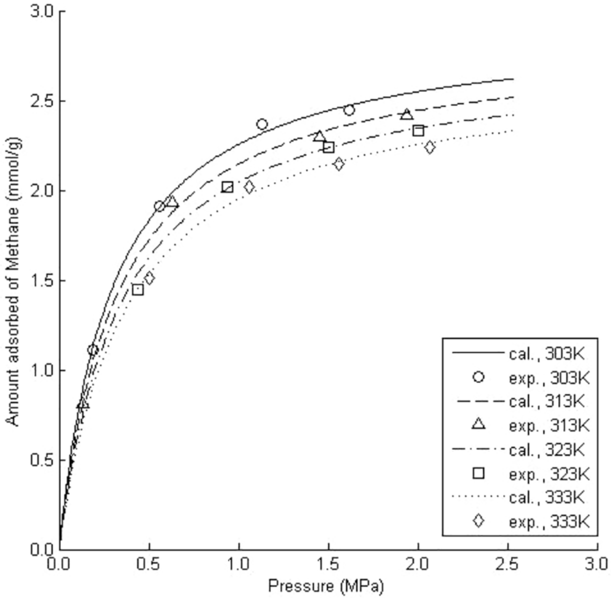

**Figure 6.** Adsorption equilibrium isotherms for the system Methane-5A molecular sieve correlated with Langmuir equation.

The adsorption equilibration times of the gases on activated carbon were usually greater than the times on 5A molecular sieve. The equilibration time is defined here as the time at which a pressure drop of ≤ 3 kPa was observed within a one hour interval. The longer equilibration times required for activated carbon compared with 5A molecular sieve resulted from slower diffusion or permeation in pores. The resistance to diffusion through a gas film is usually negligible for porous materials (Mohammed, 1996; Klaewkla et al., 2011). Table 4 shows a list of experimental equilibration times. The equilibration time data for both adsorbents were collected as average values for the selected temperatures (303, 313, 323 and 333 K) and specified pressure ranges (0 - 4 MPa for hydrogen and 0 - 2.5 MPa for methane). The experiments were as isothermal as possible to decrease the effect of heat

**Table 4.** Equilibration times of hydrogen and methane on activated carbon and 5A molecular sieve.

| Adsorbate | Adsorbent | Equilibration time*(h) |
|---|---|---|
| Hydrogen | Activated carbon | 0.5 |
| Methane | Activated carbon | 3.0 |
| Hydrogen | 5A Molecular sieve | 0.1 |
| Methane | 5A Molecular sieve | 0.5 |

(*)equilibration times were taken as an average value for different temperatures and pressures.

adsorbent capacity is defined as the specific amount adsorbed of an adsorbate at equilibrium per unit mass of adsorbent for given conditions of temperature and pressure. For practical applications involving adsorption, the important factor is the adsorption per unit bulk volume of adsorbent rather than mass of adsorbent, since bulk volume determines the size of the adsorber. The bulk volume of activated carbon is greater than that of 5A molecular sieve. Hence, the amount of gases which adsorbed per bulk volume of 5A molecular sieve is greater than for activated carbon. This observation was recognized by multiplying the $q$ axes by a factor of 2.007 for 5A molecular sieve adsorption isotherms and then compared with that for activated carbon. The factor 2.007 represents the ratio between the bulk densities of 5A molecular sieve to activated carbon. The obtained experimental results are shown in Table 5.

The results also indicate that there is fair correlation of the amount of adsorption on an adsorbent with increased adsorption for higher gas molecular weight or critical temperature. This result is in agreement with published works (Othman et al., 2004). Also, vapor pressure can be expected to be the predominant factor favoring adsorption. The much less volatile gas is more likely to condense on the surface since it has a much larger relative saturation value ($P / P^*$) than the more volatile one. This result was verified by several authors (Hyun and Danner, 1982).

The heat of adsorption ($\Delta H$) was calculated by application of the Clausius - Clapeyron equation ($^{\text{Ma, 2014}}$) at neighboring temperatures. When this equation is applied to the two phase system of gas and adsorbed component on the surface, we get:

$$\left(\frac{dP}{dT}\right)_{\theta} = \frac{\Delta H}{T(V - V_a)} \qquad (12)$$

where $V$ and $V_a$ are the volumes per mole of adsorbed component in the gas and on the surface, respectively. $V_a$ is very small and could be neglected. By assuming the ideal-gas law for $V$ we get (Monemtabary et al., 2013):

$$\Delta H = -R\left(\frac{d1nP}{d(1/T)}\right)_{\theta} \qquad (13)$$

Table 6 shows the results of this equation.

In all cases the heats of adsorption are higher than the latent heats of condensation, but are low enough to be characterized as physical adsorption. It should be noted that the heat of adsorption for activated carbon is always greater than that for 5A molecular sieve. This greater heat of adsorption results in an early and more diffuse breakthrough curve, hence worse separation would result.

Equilibrium adsorption data for hydrogen - methane mixtures on activated carbon and 5A molecular sieve are presented in the form of $x$ - $y$ diagrams at four different temperatures and shown in Figures 7 and 8, respectively.

The experimental data were compared with the theoretically predicted curves based on single gas isotherms by using the extended Langmuir isotherm equation, which takes the form (Yavary et al., 2016):

$$\theta_i = \frac{q_i}{q_{mi}} = \frac{B_i P_i}{1 + \sum_{j=1}^{n} B_j P_j} \quad i = 1,2 \qquad (14)$$

It is clearly seen from these figures that this quite simple theory provides accepted predictions for adsorption on activated carbon and 5A molecular sieve. In all cases mutual interference was found, that is, the amount of a given gas adsorbed at a given partial pressure was always less in the mixture than it would have been if the other gaseous components had not been present.

It may be recognized from Figures 7 and 8 that 5A molecular sieve has a stronger affinity for methane than activated carbon since at any given value of $y$ the corresponding value of $x$ for 5A molecular sieve is always smaller than the value for activated carbon. This also could be noted from Figures 3 - 6, because higher slopes for the isotherms at $P \rightarrow 0$ were obtained with 5A molecular sieve than with activated carbon. Adsorption isotherm curves with a steep initial slope indicate a sorbent with a high affinity for the sorbed species. This affinity is indicated by the Langmuir coefficient $B$ which determines the performance in this region. The lower the value of $B$ is the higher the value of affinity. However, a high affinity between

**Table 5.** Experimental adsorption equilibrium data for hydrogen and methane on activated carbon and 5A molecular sieve.

| System hydrogen-activated carbon | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *T*= 303K | | | *T*= 313K | | | *T*= 323K | | | *T*= 333K | |
| $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ |
| 3.31 2.78 | 0.90 0.73 | 0.37 0.30 | 3.57 2.73 | 0.82 0.68 | 0.34 0.28 | 3.72 2.37 | 0.75 0.49 | 0.31 0.20 | 3.85 3.20 | 0.68 0.58 | 0.28 0.24 |
| 1.32 0.74 | 0.38 0.22 | 0.16 0.09 | 2.26 0.72 | 0.53 0.21 | 0.22 0.09 | 1.71 1.09 | 0.37 0.22 | 0.15 0.09 | 2.55 1.23 | 0.46 0.24 | 0.19 0.10 |
| System methane-activated carbon | | | | | | | | | | | |
| | *T*= 303K | | | *T*= 313K | | | *T*= 323K | | | *T*= 333K | |
| $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ |
| 1.74 1.26 | 4.42 3.95 | 1.81 1.62 | 1.90 1.42 | 4.27 3.81 | 1.75 1.56 | 2.00 1.58 | 3.90 3.55 | 1.60 1.46 | 2.13 1.61 | 3.76 3.38 | 1.54 1.39 |
| 0.79 0.26 | 3.15 1.41 | 1.29 0.58 | 0.95 0.41 | 3.19 1.93 | 1.31 0.79 | 1.04 0.58 | 2.96 1.97 | 1.21 0.81 | 1.17 0.62 | 2.84 2.01 | 1.16 0.82 |
| System hydrogen-5A molecular sieve | | | | | | | | | | | |
| | *T*= 303K | | | *T*= 313K | | | *T*= 323K | | | *T*= 333K | |
| $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ |
| 3.38 2.62 | 0.56 0.46 | 0.46 0.38 | 3.50 2.87 | 0.53 0.44 | 0.44 0.36 | 3.63 2.37 | 0.49 0.34 | 0.40 0.28 | 3.88 3.13 | 0.47 0.39 | 0.39 0.32 |
| 1.37 0.63 | 0.26 0.13 | 0.21 0.11 | 2.13 0.88 | 0.35 0.16 | 0.29 0.13 | 1.62 1.00 | 0.24 0.16 | 0.20 0.13 | 2.50 1.12 | 0.33 0.16 | 0.27 0.13 |
| System methane-5A molecular sieve | | | | | | | | | | | |
| | *T*= 303K | | | *T*= 313K | | | *T*= 323K | | | *T*= 333K | |
| $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ | $P$ | $q$ | $q_v$ |
| 1.62 1.13 | 2.45 2.37 | 2.02 1.95 | 1.94 1.45 | 2.42 2.30 | 1.99 1.89 | 2.00 1.50 | 2.33 2.24 | 1.92 1.84 | 2.07 1.56 | 2.24 2.15 | 1.84 1.77 |
| 0.56 0.19 | 1.91 1.11 | 1.57 0.91 | 0.63 0.13 | 1.93 0.81 | 1.59 0.67 | 0.94 0.44 | 2.02 1.45 | 1.66 1.19 | 1.06 0.50 | 2.02 1.51 | 1.66 1.24 |

**Table 6.** Heat of adsorption and condensation for gases.

| Component | $\Delta H$, (kJ mole$^{-1}$) (activated carbon) | $\Delta H$, (kJ mole$^{-1}$) (5A molecular sieve) | $\Delta H_{cond}$ at BP (kJ mole$^{-1}$) |
|---|---|---|---|
| $H_2$ | 12.247 | 9.889 | 0.904 |
| $CH_4$ | 18.419 | 14.804 | 8.180 |

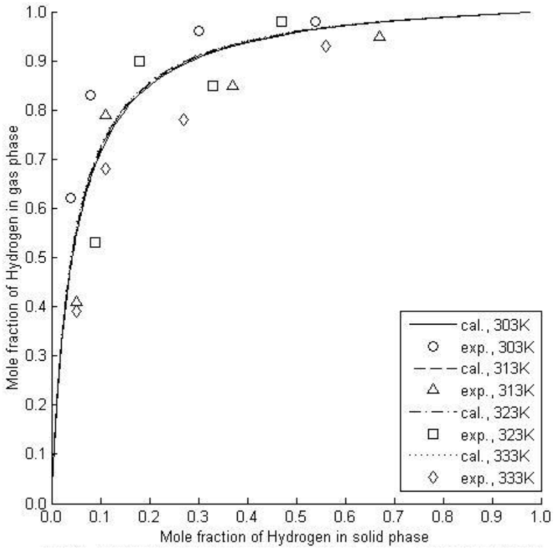

**Figure 7.** Adsorption equilibrium isotherms for the system Hydrogen-Methane-Activated Carbon correlated with extended Langmuir equation.

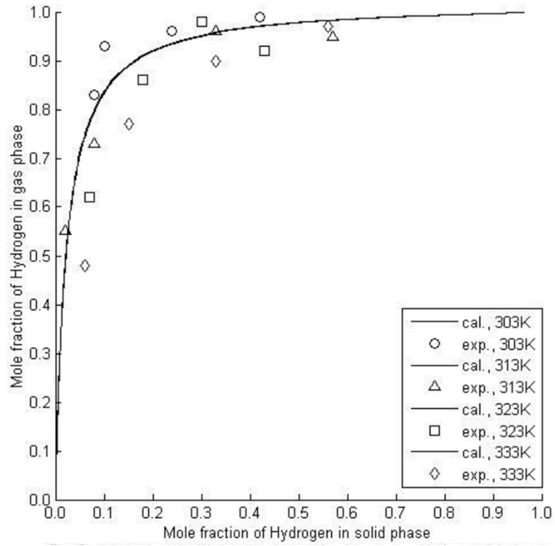

**Figure 8.** Adsorption equilibrium isotherms for the system Hydrogen-Methane-5A Molecular Sieve correlated with extended Langmuir equation.

the sorbent and sorbate is desirable and is reflected in good uptake values at low pressures.

The selectivity ratio is a useful parameter indicating the degree of preferential adsorption under a set of specific conditions, and is important for separation processes. It is defined as:

$$Selectivity = \frac{x_{CH_4}/y_{CH_4}}{x_{H_2}/y_{H_2}} \tag{15}$$

Theoretical results of the selectivity between methane and hydrogen as a function of hydrogen mole fraction in the gas phase are shown in Figure 9. The results indicate that the selectivity is approximately constant for a wide range of gas phase composition, from 10 to 80 mole percent hydrogen. This range usually covers the practical expected gas composition for the adsorption process. The results also indicate that the selectivity on 5A molecular sieve is almost greater than the selectivity on activated carbon.

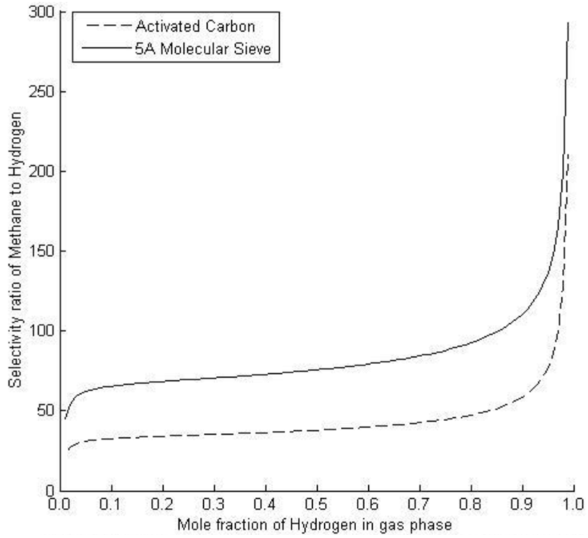

**Figure 9.** Effect of gas phase Hydrogen content on selectivity ratio of Methane to Hydrigen ar 303K.

The effects of gas phase hydrogen content on total amount adsorbed on activated carbon and 5A molecular sieve at 2 MPa and different temperatures were shown in Figures 10 and 11, respectively. It is seen that increasing the equilibrium adsorption temperature decreases the total amount adsorbed on both adsorbents. This decrease in amounts adsorbed per bulk volume for 5A molecular sieve is smaller than for activated carbon.

The effects of gas phase hydrogen content on total amount adsorbed on activated carbon and 5A molecular sieve at 303 K and different pressures were shown in Figures 12 and 13. The experimental and theoretical data points show that the equilibrium composition of adsorbed hydrogen-methane mixtures is relatively insensitive to the total pressure. Experimental equilibrium points were obtained for total pressure

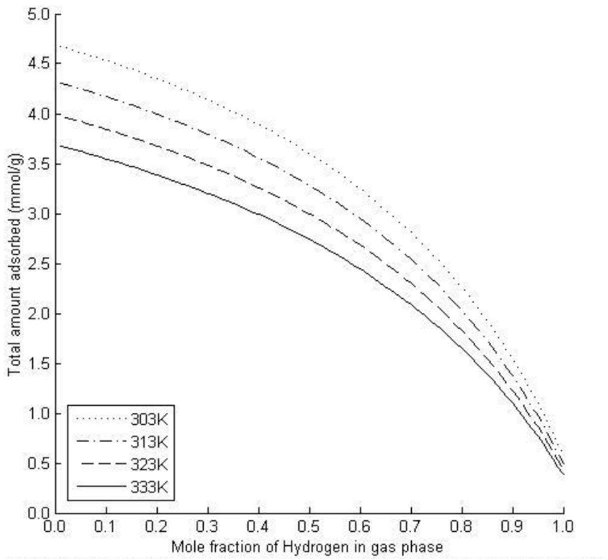

**Figure 10.** Effect of gas phase Hydrogen content on total amount adsorbed for the system Hydrogen-Methane-Activated Carbon at 2 MPa.

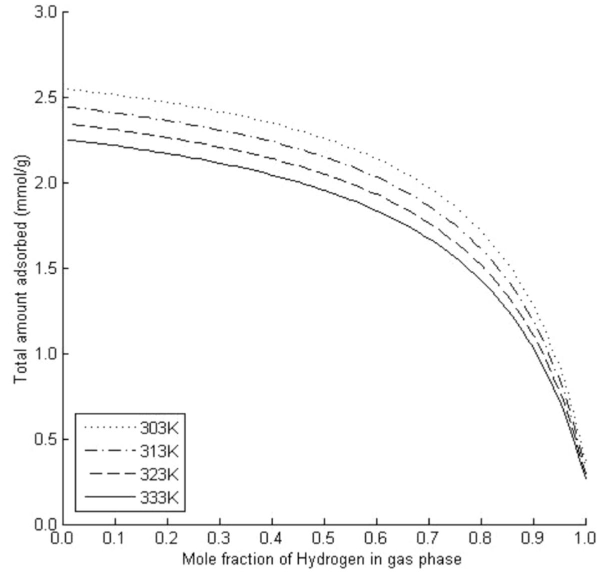

**Figure 11.** Effect of gas phase Hydrogen content on total amount adsorbed for the system Hydrogen-Methane-5molecular weight at 2 MPa.

ranging from 626 to 3623 kPa and no data point shows any tendency to deviate from this result. However, the total pressure has a very large effect on the total adsorbed quantity.

Finally, it is clearly seen from the study that both adsorbents provide suitable adsorption characteristics for the separation process under focus. However, many points were examined to select the most favorable adsorbent. It is recognized that the 5A molecular sieve has better properties than activated carbon in the following statuses: mass transfer properties, amount adsorbed per unit bulk volume, heat of adsorption, affinity, selectivity.

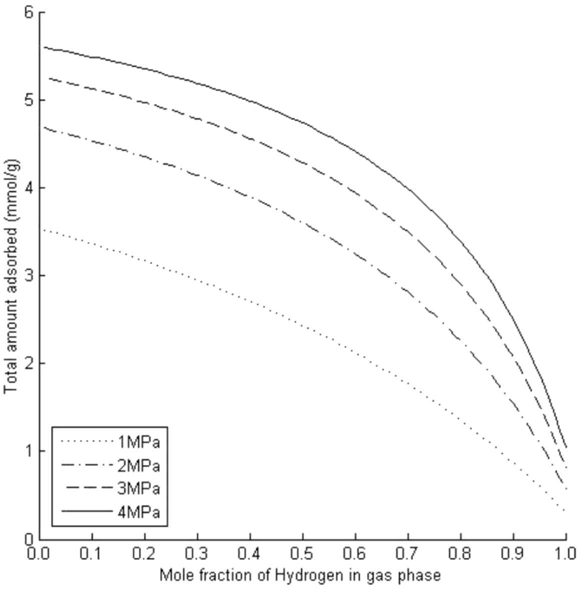

**Figure 12.** Effect of gas phase Hydrogen content on total amount adsorbed for the system Hydrogen-Methane-Activated Carbon at 303K.

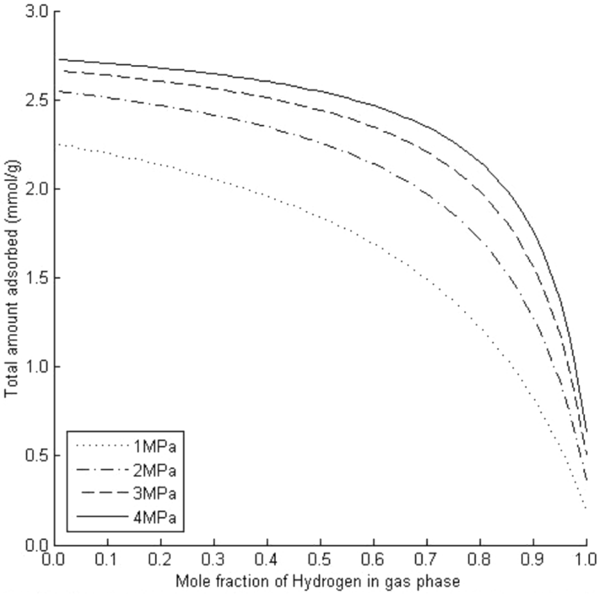

**Figure 13.** Effect of gas phase Hydrogen content on total amount adsorbed for the system Hydrogen-Methane-5A Molecular Sieve at 303 K.

Therefore, 5A molecular sieve was selected as the most efficient adsorbent for the hydrogen - methane separation by adsorption processes.

## SUMMARY AND CONCLUSIONS

Equilibrium isotherms for single component adsorption of hydrogen or methane on activated carbon or 5A molecular sieve could be correlated by the Langmuir equation. Furthermore, the adsorption of a hydrogen-methane mixture on activated carbon or 5A molecular sieve could be correlated by an Extended Langmuir isotherm equation. Increasing the temperature or decreasing the pressure decreases the total amount adsorbed on both adsorbents.

5A molecular sieve has better adsorption properties than activated carbon in the following statuses: mass transfer properties, amount adsorbed per unit bulk volume, affinity, selectivity and heat of adsorption.

## NOMENCLATURE

| Symbol | Notation | Unit |
|---|---|---|
| $a_1$,.., $a_4$ | Langmuir isotherm coefficients | - |
| $b_1$,.., $b_4$ | Freundlich isotherm coefficients | - |
| $k_F$ | Constant in Freundlich equation | $Pa^{1-nF}$ |
| $n$ | Number of moles | mole |
| $n_F$ | Parameter in Freundlich equation | - |
| $q$ | Adsorbed phase concentration based on unit mass of adsorbent | mmole $g^{-1}$ |
| $q_v$ | Adsorbed phase concentration based on unit volume of adsorbent | mmole $cm^{-3}$ |
| $x$ | Mole fraction in adsorbed phase | - |
| $y$ | Mole fraction in gas phase | - |
| $B$ | Adsorption coefficient in the Langmuir equation | $Pa^{-1}$ |
| $E$ | Average relative error | - |
| $N$ | Number of experimental points | - |
| $P$ | Pressure | Pa |
| $R$ | Ideal gas constant | J $mole^{-1}$ $K^{-1}$ |
| $T$ | Temperature | K |
| $V$ | Volume | $m^3$ |
| $W$ | Mass of adsorbent | g |
| $\theta$ | Fraction of surface coverage | - |
| $\Delta H$ | Heat of adsorption | J $mole^{-1}$ |

## REFERENCES

Ahmadpour, A., Wang, K. and Do, D., Comparison of Models on the Prediction of Binary Equilibrium Data of Activated Carbons, AIChE J., 44(3) 740-752 (1998).

Dąbrowski, A., Adsorption — from theory to practice, Adv. Coll. Inter. Sci., 93(1-3), 135-224 (2001).

Gaskin, T.K., Use of a stripping gas in flash regeneration solvent absorption systems, US Patent: 20030106334A1, Jun. 12 (2003).

Hyun, S.H. and Danner, R.P., Equilibrium adsorption of ethane, ethylene, isobutane, carbon dioxide and their binary mixtures on 13 X molecular sieve, J. Chem. Eng. Data, 27(2) 196-200 (1982).

Klaewkla, R., Arend, M. and Hoelderich, W. F., A review of mass transfer controlling the reaction rate in heterogeneous catalytic systems, Mass Transfer - Advanced Aspects, Dr. Hironori Nakajima (Ed.), ISBN: 978-953-307-636-2, InTech, Croatia (2011).

Lopes, F.V.S., Grande, C.A., Ribeiro, A.M., Loureiro, J.M., Evaggelos, O., Nikolakis, V. and Rodrigues, A.E., Adsorption of $H_2$, $CO_2$, $CH_4$, CO, $N_2$ and $H_2O$ in activated carbon and zeolite for hydrogen production, Sep. Sci. Tech., 44(5) 1045-1073 (2009).

Ma, D.M., Zhang, J.C., Bai, J.P. and Zhang, H., Thermodynamic Characteristics of Adsorption-Desorption of Methane in $3^{\#}$ Coal Seam of Sihe, Natural Resources, 5, 782 (2014).

Mohammed, R.R., Separation of multi-components gas mixtures by adsorption, Ph.D. thesis, University of Technology (1996).

Monemtabary, S., Niasar, M.S., Jahanshahi, M. and Ghoreyshi, A.A., Equilibrium and thermodynamic studies of methane adsorption on multi-walled carbon nanotube, Iranica Journal of Energy & Environment, 4(1) 17-24 (2013).

Othman, M.R., Mukhtar, H. and Ahmad, A.L., Gas permeation characteristics across nano-porous inorganic membranes, I.I.U.M. Eng. J., 5(2) 17-33 (2004).

Pistikopoulos, E.N., Georgiadis, M.C. and Dua, V., Dynamic process modeling, Vol. 7, Wiley - VCH verlag GmbH & Co., Germany (2011).

Shindo R. and Nagai K., Gas Separation Membranes in Encyclopedia of Polymeric Nano-materials, Springer Berlin Heidelberg, Berlin (2013).

Suzuki M., Adsorption engineering, Kodansha, Tokyo (1990).

Teiseh E. and Capareda S., Purification of Hydrogen from a Thermo-chemical Process using a Single-Column Pressure Swing Adsorption System with Compound Adsorbent, ASABE Ann. Inter. Meet., Paper Number: 1009782, Pittsburgh, Pennsylvania (2010).

Wakasugi, Y., Ozawa, S. and Ogino, Y., Physical adsorption of gases at high pressure: V. An extension of a generalized adsorption equation to systems with polar adsorbents, Journal of Colloid and Interface Science, 79(2) 399-409 (1981).

Wu, J., Zhou, L., Sun, Y., Su, W. and Zhou, Y., Measurement and prediction of adsorption equilibrium for a $H_2$/ $N_2$/ $CH_4$/ $CO_2$ mixture, AIChE J., 53(5) 1178-1191 (2007).

Yang, R.T., Gas separation by adsorption processes, Butterworths, Stoneham, U.S.A. (1987).

Yavary, M., Ale Ebrahim, H. and Falamaki, C., Competitive adsorption equilibrium isotherms of CO, $CO_2$, $CH_4$ and $H_2$ on activated carbon and zeolite 5A for hydrogen purification, J. Chem. Eng. Data, 61(10) 3420-3427 (2016).