

Sorptive Storage of Natural Gas on Molecular Sieves: Dynamic Investigation

S. Al-Asheh, and K. Al-Emadi

Abstract—In recent years, there have been attempts to store natural gas in adsorptive form. This is called adsorptive natural gas, or ANG. The problem with this technology is the low sorption capacity. The purpose is to achieve compressed natural gas (CNG) capacity of 230 V/V. Further research is required to achieve such target. Several research studies have been performed with this target; through either the modification or development of new sorbents or the optimization of the operation sorption process itself. In this work, storage of methane on molecular sieves 5A and 13X was studied on dry basis, and on wet basis to certain extent. The temperature and the pressure dynamics were investigated. The results indicated that regardless of the charge pressure, the time for the peak temperature during the methane charge process is always the same. This can be used as a characteristic of the adsorbent. The total achieved deliveries using molecular sieves were much lower than that of activated carbons; 53.0 V/V for the case of 13X molecular sieves and 43 V/V for the case of 5A molecular sieves, both at 2°C and 4 MPa (580 psi). Investigation of charge pressure dynamic using wet molecular sieves at 2°C and a mass ratio of 0.5, revealed slowness of the process and unexpected behavior.

Keywords—Methane, Molecular sieves, Adsorption, Delivery, Storage.

I. INTRODUCTION

NATURAL gas is much cheaper than conventional petroleum-based gasoline and diesel fuel. Thus, since last three decades, the interest in natural gas (NG) as a vehicular fuel has grown considerably. In addition, worldwide people started thinking of using other sources of energy and this led to the development of new technologies to enable the use of other fuels to meet their transportation energy demand. Among the possible fuel alternatives, NG is one of the most promising. In addition to those economical reasons, NG is an attractive fuel for vehicles because it is a relatively clean burning fuel compared with gasoline. With air quality issues gaining prominence around the world, this characteristic of NG is very important. Natural gas vehicles have the potential to lower polluting emissions, especially in urban areas, where air quality has become a major public health concern.

One form of natural gas fuel is the compressed natural gas (CNG). In this case, natural gas is stored as a compressed supercritical fluid at room temperature and at maximum pressure of about 20–25 MPa. A maximum density of about 230 times greater than at STP can be attained with CNG, which is usually designated as 230 V/V. This implies that CNG at 20 MPa and 25°C has a maximum volumetric energy density of about 8.8 MJ/l (25% of that of gasoline). However, the use of CNG has some disadvantages. The CNG storage tanks must be pressure vessels and are thus constrained in their geometry (they are typically cylindrical), and are also rather heavy. Moreover, attainment of a pressure of 20.7 MPa (3000 psi) requires costly multi-stage compression [1]. Although CNG vehicles have already been commercialized [2], the effort to improve the onboard storage method has never been stopped.

Natural gas can also be stored as an adsorbed phase in porous materials and is referred to as ANG. Adsorbed natural gas is supposed to decrease the storage pressure and, therefore, to decrease the costs in both investment and operation. In this case, storage of NG in the adsorbent materials occurred at relatively low pressure (500–580 psi) and at room temperature. This results in another possibility for making NG vehicles competitive with other types of vehicles. With regards to effectiveness of this process, two values are normally reported: the value corresponding to the maximum theoretical delivery at 508 psi and 25°C for activated carbons, which is 213 v/v [3] and the value corresponding to a delivery of 120 v/v, which has been exceeded by several adsorbents [1]-[3]. To move from 120 V/V to the theoretical value, new adsorbents with improved properties have to be developed.

For evaluating the performance of an adsorbent for NG storage system for vehicles, the parameter known as 'delivery' is commonly used in the literature. This parameter is defined as the volume of gas delivered per volume of the storage container and is denoted by V/V. Specifically, delivery is the amount of gas that is released from the adsorbent when the pressure is reduced to atmospheric. Of course, the use of heat or vacuum can improve the amount of gas delivered and hence, the term V/V. In the early 1990s, the US Department of Energy (USDOE) set a target figure of 150 V/V deliverable for an operational ANG vehicle system working at a pressure of 3.5 MPa (508 psi) and 25°C [2].

In literature, it can be seen that a lot of work has been, and is being, carried out mainly on two classes of microporous solids: zeolites and activated carbons [3]-[6]. Moreover, novel adsorbents, such as organic gels, have been explored for the adsorption of methane [5]. It has been shown [4],[5],[7] that

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zeolites have relatively high packing densities (compared to activated carbons) but have lower micropore volumes. In addition, zeolites are extremely hydrophilic and can lose their adsorption capacity for methane with time due to preferential moisture adsorption. On the other hand, it has been shown that activated carbons are very good adsorbents, presenting the highest ANG energy densities, and thus the highest storage capacities [2], [3], [5], [8].

The ANG technology has never been commercialized due to its technical drawbacks. A study of methane adsorption on wet activated carbon suggested a new approach to store natural gas: charging natural gas into the wet activated carbon. All drawbacks of the traditional ANG can be overcome in this new approach. First, about 63% more methane was stored per unit mass of carbon. Next, the bulk density of the wet activated carbon can be easily increased and, thus, making pellets [9] is no longer needed. The heavier components of natural gas are easier to form hydrates than methane; therefore, the pre-adsorption bed [8] is no longer required. The thermal effect of fast charging/discharging is decreased to one tenth of ANG [10]; therefore, it actually does not affect the storage capacity. Furthermore, more gas will be released on discharging because the adsorption isotherm of the wet carbon is much lower than that of dry carbon at low pressures. Different types of activated carbon were tested with the wet

storage method [10] aiming to maximize the storage capacity. Zhou et al. [10] evaluated the dependence of the storage capacity on the pore size distribution of activated carbons.

The use of wet molecular sieves for methane storage will be evaluated in this work. The primary objective is to describe a new technology for producing effective ANG operation. Specific objectives include: construction of the apparatus for the ANG operation, use of different types of molecular sieves for natural gas adsorption, comparison between wet and dry forms of molecular sieves for the ANG sorption process, studying the ANG sorption process at different pressures and obtain the equilibrium isotherms, and investigation of the charge/discharge dynamics.

II. MATERIAL AND METHODS

A. Materials

Two types of molecular sieves were used in this study; these include 5A and 13X. The properties of these two materials are shown in Table I. The dry and wet forms were investigated. High purity methane (99.95%) was used as a natural gas model. Paraffin and glycol were used for the heating and cooling processes, respectively.

TABLE I
PROPERTIES AND CHARACTERISTICS OF MOLECULAR SIEVES 5A AND 13X*

Type	Form	Bead or particle size	Pore diameter (Å)	Bulk density (lb/ft ³)	Eq'm. H ₂ O capacity (theory)	pH (5% slurry)	Regeneration Temperature (°C)	Max. ΔH_{ads} BTU/lb H ₂ O
5A	bead	4-8 mesh	4.3	44	21.7	10.5	200-315	1800
13X	bead	4-8 mesh	8	43	29.5	10.3	200-315	1800

* Adapted from Aldrich, Technical Information Bulletin, Internet [11]

B. Experimental Apparatus

Adsorption isotherms were collected by volumetric method. Tests for charging/discharging processes onto/from the dry and wet molecular sieves were carried out using the apparatus shown in Fig. 1. It consists of methane cylinder connected by copper tube to the sorbent container. The container was packed by the molecular sieves. The sorbent container is a stainless steel cylinder, which is 70.48 mm (ID); 77.10 mm (OD); 300 mm (length) with an effective volume of 1170 cm³. About 715 g of molecular sieves was required to pack the bed. The digital pressure device was used to measure the pressure of the bed. Three temperature probes (Chromel – alumel, K – type) were inserted along three positions of the bed, namely at the top, middle and bottom of the bed. The temperatures were recorded using temperature display.

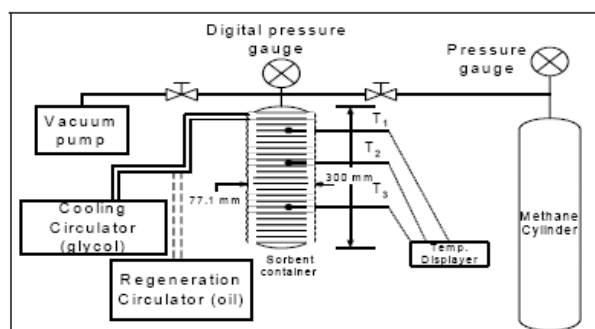


Fig. 1 Experimental set up for methane storage on molecular sieves

C. Bed Generation

Before charging process, i.e. adsorption of methane, the molecular sieves bed was regenerated. This was accomplished using paraffin oil circulation path which was circulated around the bed under vacuum. The temperature of the oil was increased gradually to 195°C and the sorbent bed was vacuumed, using the vacuum pump (Fig. 1) or about 7 hours, to make sure that the bed is completely evacuated. In some cases, the oil circulation path was replaced by a heater blower.

During the regeneration step, the gauge pressure was almost below zero. After this period, the regeneration circulator and the vacuum pump were disconnected in order to start the charging process.

D. Charging of Methane

The oil path circulator was replaced by a cooling path circulator. Glycol was used as a cooling agent that passed through the coil and allowed to circulate around the bed. The temperature of the cooling path was adjusted at the required set point. The glycol was allowed to circulate around the bed for about 5 hours to ensure that the temperature of the bed is the same as that of the circulator. This was confirmed using the temperature probes and temperature displayer. Methane was then allowed to feed into the container until certain pressure was achieved. At this moment, the valve at the feed gas was closed and equilibrium was allowed to attain. During this period, it was noticed, as expected, that the pressure of the bed was reduced, which is due to the adsorption process. The dynamics of the process was followed. The equilibrium pressure was recorded and the difference between this pressure and the initial pressure, i.e. charging pressure, was used to estimate the amount of methane being adsorbed using RSK equation of state (Soave-Redlich-Kwong). The temperatures along the bed during the sorption process were recorded in order to include it in the dynamics investigation. The process was repeated using different charging pressures in order to obtain the required isotherms. It was repeated until there was unnoticeable reduction in the charging pressure.

E. Discharge Test

The set up for the discharge test is shown in Fig. 2. Pressure regulator was used to maintain the discharge flow at certain flowrate. A flowmeter was used to measure the flowrate. After the bed being saturated or reached the target pressure, the gas was discharged by venting using a ventilation system. During gas discharge, the pressure was recorded and the venting process continued until a zero pressure gauge inside the bed was reached. Also during the discharge process, the pressure regulator was adjusted in order to provide a constant gas flowrate of almost 1.2 L/min. After this, another test was carried out following molecular sieves regeneration by heating under vacuum, as previously mentioned.

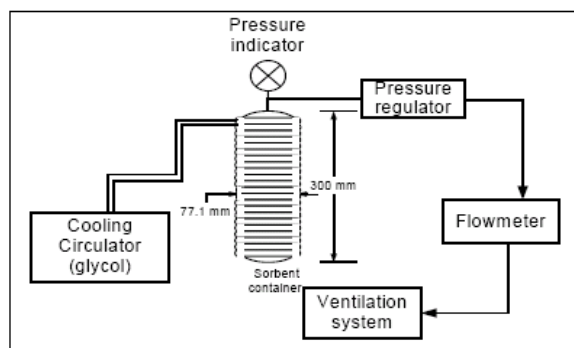


Fig. 2 Discharge set up for methane storage

In the case of wet molecular sieve, the amount of water was weighted and charged into the bed using a funnel after the regeneration stage. The funnel was made of glass which has a sign, or graduation, to indicate the beginning of water addition; it was connected using a pipe to the inlet valve. An extra amount of water was inserted up to the graduation and then the desired amount of water was inserted. After that, the water level was allowed to enter till it reached the graduation by opening the inlet valve. Upon reaching the graduation on the funnel, the valve was closed to prevent the entrance of air.

III. RESULTS AND DISCUSSION

A. Charge Dynamics

The investigation of the temperature and pressure dynamics is an important area of study. This is because heat and mass transfer limitations have a significant effect on the ANG storage process. However, the mass transfer limitation is considerably more limited than heat transfer in beds with fine particles size compared with granular particles [12]. The adsorbent used in this study is molecular sieves monolith, so the effect of heat transfer will be investigated in details. The methane charge dynamics using molecular sieves 5A was investigated at 25°C. The results are shown in Figs. 3A-G at different charging pressures, respectively, and different locations along the bed. It should be emphasized that, in all cases, the initial temperature was maintained at 25°C before the charging process and then variations appeared on this temperature through the bed due to the charging and sorption process. All curves exhibited maxima indicating the exothermic nature of the adsorption process. This is consistence with the data reported in literature for a similar study [13]. The temperature values recorded by the two probes located at the lower section of the bed were close to each other, indicating the high thermal conductivity of the adsorbent. However, the temperature recorded by the probe near the gas inlet was lower than the other probes. Similar phenomenon was observed by Goetz et al. [14]; they explained such trend due to the inlet gas that provides a cooling effect which locally minimizes the temperature rise.

When plotting all dynamics curves presented in Figs. 3 A-G, it was observed that regardless of the charge pressure the maximum temperatures are reached at approximately 7 minutes. This value can be used as a characteristic of this adsorption process and as an indicator of its thermal conductivity [13]. Temperature dynamics using molecular sieves 5A at other initial temperatures have also been investigated (data not shown) up to certain extent and similar behaviors were observed.

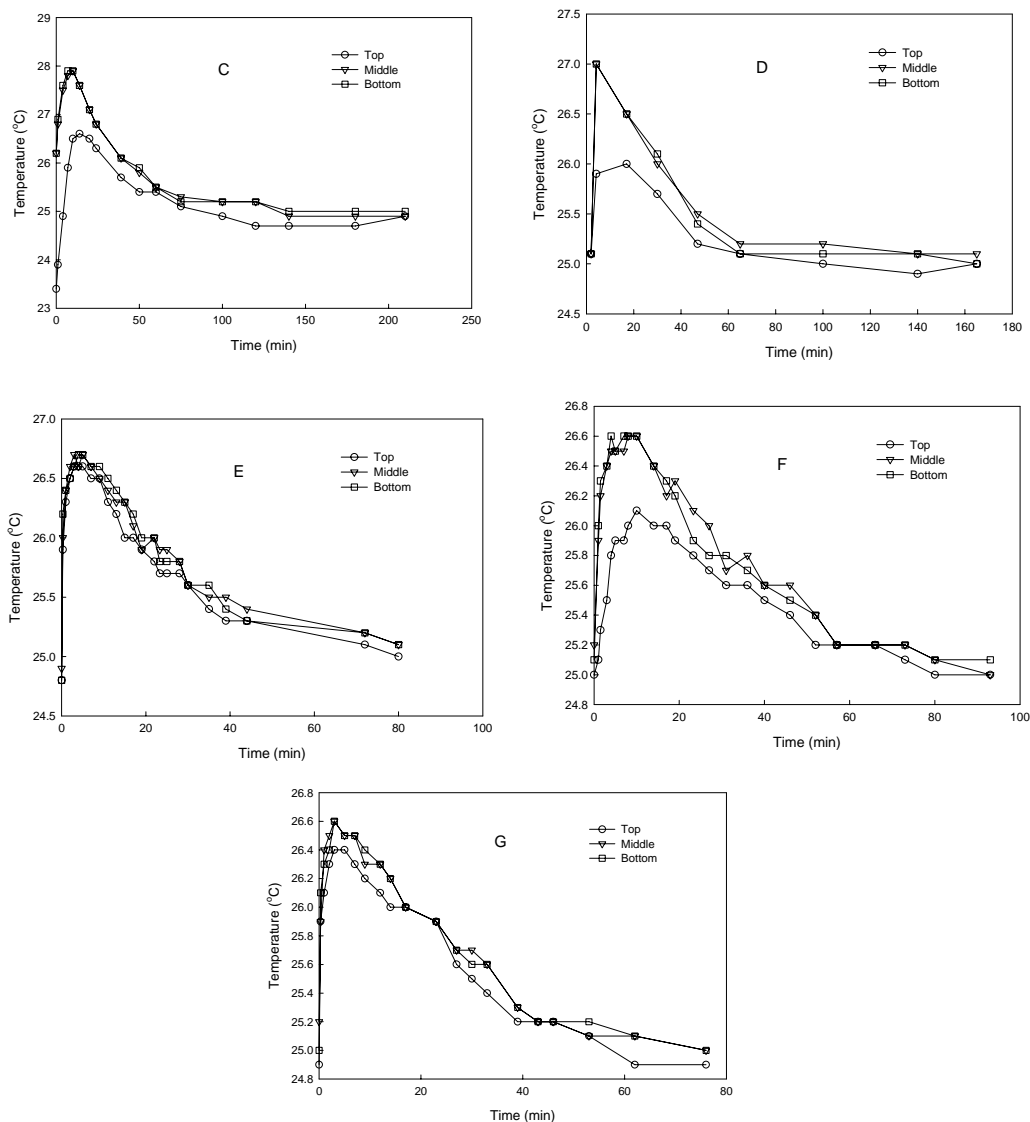


Fig. 3 Temperature dynamics for storage of methane on MS 5A at initial temperature of 25°C and different charge pressures of (A) 97, (B) 150, (C) 270, (D) 396, (E) 502, (F) 631, and (G) 744 psig

Molecular sieves 13X was investigated at 2°C only, i.e. the initial temperature was maintained at 2°C before the charging process. The temperature dynamics was investigated using one probe only located at the middle of the bed. The temperature dynamics at different charging pressures are shown in Fig. 4. The trends are similar to that of molecular sieves 5A. However, the time at which a maximum occurred was 8.4 minutes, which is longer than that for the molecular sieves 5A (7minutes). This could be attributed to the large pore-size of the MS 13X, i.e. low density. In other word, in this case the thermal conductivity of the gas becomes less than that for the solid.

The charge pressure dynamics for storage of methane on molecular sieves 5A were investigated at the temperatures of 2°C, 25°C and 50°C and different initial charge pressures. The results are shown in Figs. 5A-C, at temperatures of 2°C, 25°C and 50°C, respectively. The pressure dynamics at different temperatures were similar to each other in terms of the rate of adsorption (or depletion). This is attributed to the linear isotherm (will be presented later) behavior of this sorption process; i.e. high sorption capacity of molecular sieves 5A.

The charge pressure dynamics for the case of using MS 13X were also investigated at 2°C and different charge pressures. The results are shown in Fig. 6. In this case, pressure dynamics are a little different than that in the case for MS 5A. Since, in this case, the rate of adsorption (or

depletion) decreases as the pressure increases. This could be attributed to the non-linear isotherm behavior for molecular sieves 13X, as will be illustrated later; i.e. lower sorption capacity.

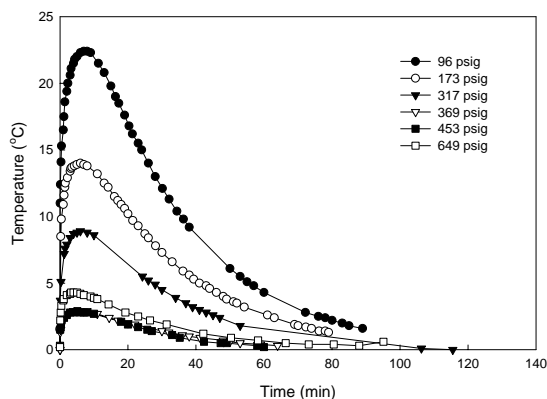


Fig. 4 Temperature dynamics for storage of methane on MS 13X at initial temperature of 2°C and different charge pressures

B. Discharge Dynamics

When releasing methane from the storage system, the adsorbent will be cooled down since desorption is an endothermic process and a considerable amount of methane will be accordingly retained in the system at total depletion pressure. For vehicular applications, performance of the ANG storage should be receiving more concerns since the discharge amount is directly demanded by the output power in need [12]. According to Ridha et al. [12], the discharge flow rate of 1-5 L/min corresponds to the demand rate for a 4 cylinder car traveling at low speed. Thus, a discharge flowrate of 1.1855 L/min was used for the discharge investigation. Since desorption is an endothermic process, the steady state delivery capacity was considered, which is the most important capacity for vehicular application [12]. This capacity is defined as the one which supplies a constant rate of methane to the engine. Once this capacity starts to decrease in supply, then the unsteady state interval ended with the instant delivery capacity. This is achieved at the depletion pressure 14.7 psi. However, when the bed absorbs more heat and reaches thermal equilibrium with surrounding, i.e. isothermal condition, the cumulative amount of gas delivered at that particular stage is the total delivery capacity [12].

The discharge temperature dynamics was investigated using MS 5A at 25°C. The results, Fig. 7, agree with the reported data in literature [15]. The temperature decreases smoothly, while discharging, indicating the endothermic nature of the desorption process. The discharge pressure dynamics for the molecular sieves 5A are shown in the Figs. 8 at 50°C and 2°C, respectively. The discharge pressure dynamics for 13X was also investigated; the results are also shown in Fig. 8. The trends are expected; the pressure decreases smoothly, for all cases, and turns to the atmospheric value, i.e. 0.0 psig. It is also noticed that the pressure decreases linearly with time at the beginning of the discharge process, but then at a slower rate due to the low driving force in the bed.

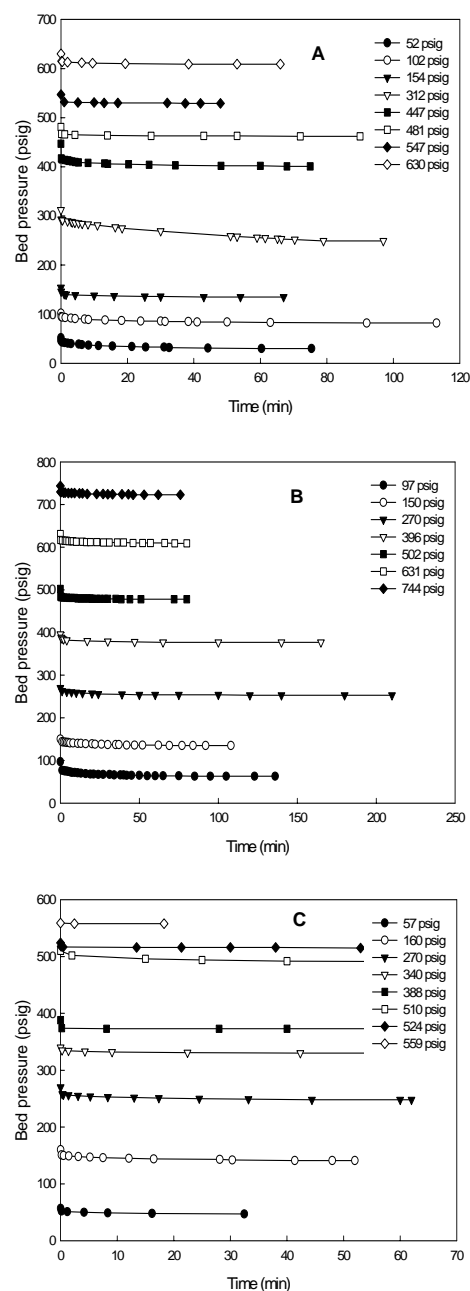


Fig. 5 Pressure dynamics for storage of methane on MS 5A at 2°C (A), 25°C (B) and 50°C (C) and different initial charge pressures

C. Steady State Deliveries

The steady state delivery capacities for the molecular sieves 5A at 2°C and 50°C and for the molecular sieves 13X at 2°C are shown in the Fig. 9. According to these results, at 2°C the steady state delivery was 28.6 L, while at 50°C it was 26 L; 24.3 and 22.5 minutes were required to reach these deliveries, respectively. For molecular sieves 13X, at 2°C the steady state delivery was 34.4 L, which was reached in 29 min. For the molecular sieves 5A the cumulative methane delivered was higher at 2°C than that at 50°C. This is attributed to the higher

amount of methane stored at 2°C than that at 50°C. For the molecular sieves 13X at 2°C the steady state delivery capacity was higher than that for the 5A at the same temperature. This is attributed to the larger size of the pores for the 13X which maximizes the deliverability at the ambient pressure [1].

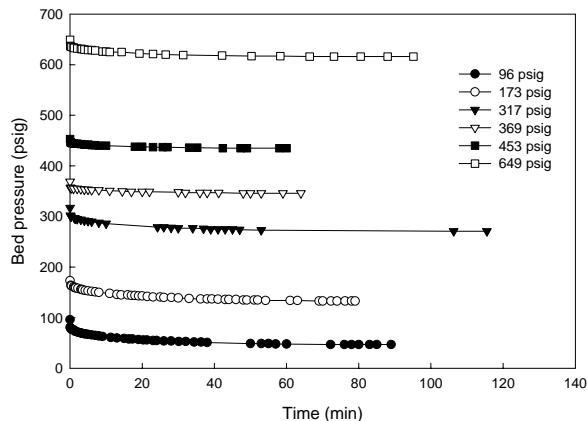


Fig. 6 Pressure dynamics for storage of methane on MS 13X at 2°C at different

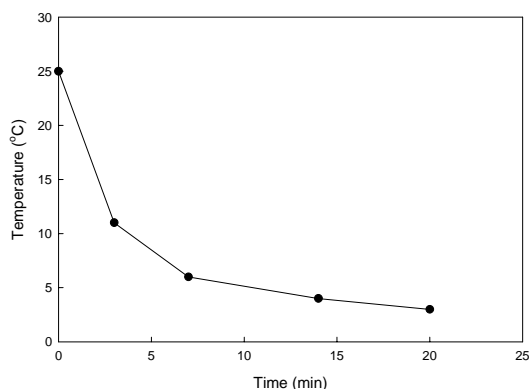


Fig. 7 Discharge temperature dynamics during release of methane from MS 5A bed at 2°C

D. Equilibrium Isotherms

The equilibrium isotherms for the molecular sieves 5A at 2°C, 25°C and 50°C are shown in Fig. 10A. As expected, a decrease in temperature resulted in higher adsorption capacity [14]. The isotherms reveal linear behavior. This is because the molecular sieves 5A has narrow micropore size distribution and the flat region is achieved at higher pressures [14].

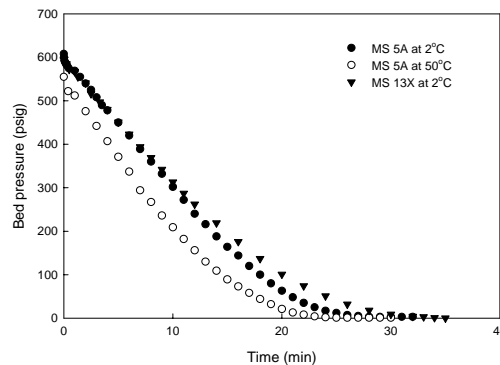


Fig. 8 Discharge pressure dynamics for release of methane from MS 5A bed at 2°C

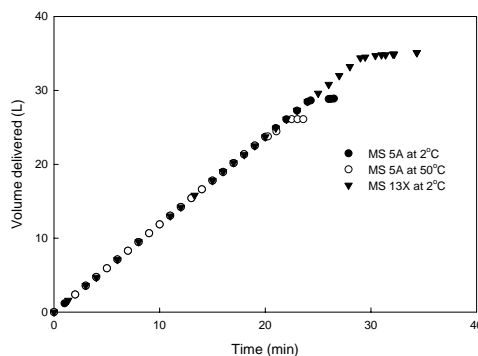


Fig. 9 Steady state delivery of methane from MS 5A bed at 50°C and 2°C and from MS 13X bed at 2°C

The Equilibrium isotherm for molecular sieves 13X at 2°C is shown in Fig. 10B. Platitude behavior is noted for this case with non-linear trend. This is attributed to the large size of the pores compared to the size of the molecular sieves 5A [1]. The amount adsorbed at 4 MPa (580 psi) is 0.017 g methane/ g adsorbent.

E. Bed Capacity

As previously mentioned, the target of the ANG storage technology is to obtain the same amount stored by the compressed natural gas technology (CNG) at 25% of the pressure required for the CNG; this corresponds to 4 MPa (580 psi). The uptakes data for MS 5A were expressed in V/V ratio and these are shown in Fig. 11A. Table II summarizes the total and the delivery capacities, as well as the total amount adsorbed. It is also seen that methane delivery decreases with the increases in temperature.

Unfortunately, the methane uptake by molecular sieves 5A was not reported in literature, to our best knowledge. However, the values displayed in Table II are much lower than those reported in literature for activated carbon. For example, Biloe et al. [6] reported volumetric sorption capacity of adsorbent composite blocks made of activated carbon in the range of 110-125 V/V. Total methane storage capacity reaches 164 V/V of activated pellets without binder [9]. Volumetric methane adsorption capacities of some of granular carbons produced by physical activation from a bituminous coal are

about 70 V/V [16]. These values were all reported at 298 K and 3.5 MPa (508 psi).

TABLE II
AMOUNTS OF METHANE STORED ON MS 5A AT 4 MPa AND DIFFERENT TEMPERATURES

T (°C)	Total uptake (V/V)	Delivery uptake (V/V)	Methane adsorbed (mg/g)
2	48.0	43.2	15.82
25	38.3	34.47	8.1
50	33.0	29.7	5.8

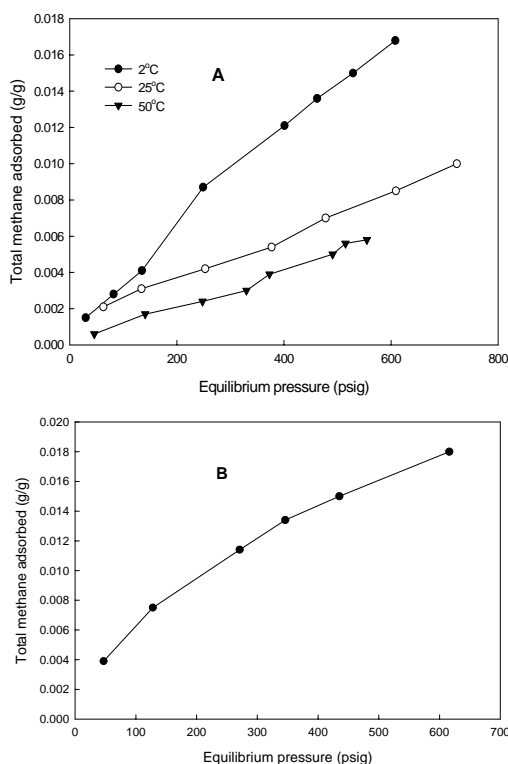


Fig. 10 Equilibrium isotherms for sorption of methane on MS 5A at different temperatures (A) and on MS 13X at 2°C (B)

The total methane adsorption capacity of MS 13X (Fig. 10B and Table III) is higher than that for using molecular sieves 5A at the same temperature, i.e. 2°C. The results are very close to that found in literature [12]. The value reported in literature is 57.8 V/V and the one obtained in this work is 52.9 V/V. The difference between these results could be due to the different nature of molecular sieves; in the literature it was in powder form while in this work, it is in monolith form. According to [9], the micropores in the powder form are more available than that in the monolith form. Hence, the amount adsorbed by the powder form is higher than that in the monolith form.

TABLE III
AMOUNTS OF METHANE STORED ON MS 13X AT 4 MPa AND 2°C

T (°C)	Total uptake (V/V)	Delivery uptake (V/V)	Methane adsorbed (mg/g)
2	47.6	52.9	17.0

F. Storage of Methane on Wet Media

Another technology for storing natural gas is by hydrate formation. At 2°C, hydrate is formed in the pressure range of 3.5 to 4.2 MPa (609 psi), depending of the adsorbent [15]. The hydrate was formed around the expected pressure using molecular sieves 5A with water to adsorbent ratio of 0.5. However, the charge dynamics exhibited a strange behavior. The formation of hydrate is a slow process; according to the results of Perrin et al. [15] for storage on activated carbon, it required about 1.5 months in order to attain equilibrium. Thus, due to the shortage of time the experiments were not completed.

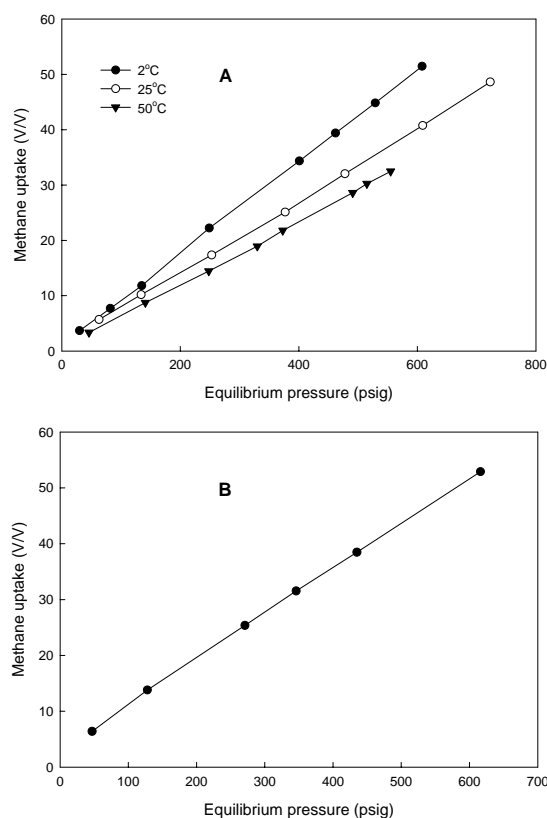


Fig. 11 Total methane capacity (V/V) using MS 5A at different temperatures (A) and on MS 13X at 2°C (B)

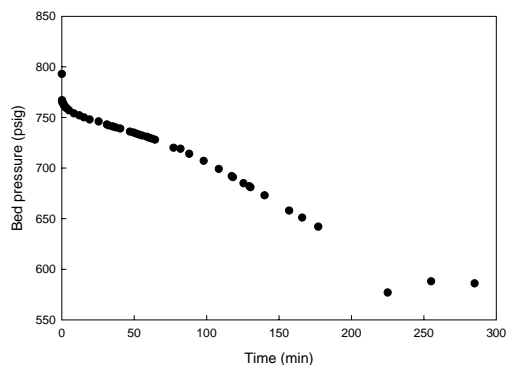


Fig. 12 Charge pressure dynamics at 2°C and charge pressure of 793 psig using wet molecular sieves 5A with water to adsorbent ratio of 0.5

The behavior of charge pressure dynamics was unexpected. An exponential curve was expected; however a strange curve was obtained using MS 5A as shown in Fig. 12. This requires further investigations. With regards to the discharge dynamics, the stored methane was released immediately when pressure began to reduce. A similar behavior is reported by Ridha et al. [12] when they studied the dynamic delivery of natural gas storage at room temperature.

The uptake of methane in terms of V/V ratio using wet molecular sieves 5A is shown in Fig. 13. At 2°C, wetted adsorbent exhibits stepwise uptake, which is consistent with the results of Perrin et al. [15]. The methane uptake increases slowly with the pressure and then suddenly sharply increases around the hydrate formation pressure of 4.1 MPa, 595 psi [12]. The first part of the curves is attributed to the classical physi-sorption of methane within the smallest pores of the adsorbent. In deed, the amounts of methane stored in the lower part are much higher for the dry adsorbent [12]. However, the amounts of methane stored increases rapidly, indicating the hydrate formation. Although the experiment was not completed because of the shortage of time, a promising sign was noticed at the hydrate formation pressure, which really requires further investigations.

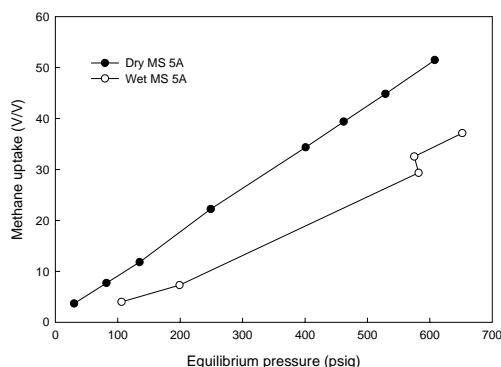


Fig. 13 Storage of methane on wet and dry molecular sieves 5A at 2°C

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