

Experimental analysis of the efficiency on charge/discharge cycles in natural gas storage by adsorption

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ABSTRACT

The use of vessels filled with activated carbon to store and transport natural gas (NG) at moderate pressures (about 3.5 MPa) and ambient temperature (about 298 K) has been studied as a potential alternative to compressed natural gas at high pressures (ca. 20 MPa). The present study provides an experimental investigation of charge and discharge cycles of natural gas in a prototype storage vessel filled with activated carbon and analyses the effect of the gas composition on the adsorption capacity. The adsorption properties were evaluated by measuring isotherms for each component of NG in a magnetic suspension balance. The selectivities of the main constituents of natural gas in relation to methane were determined and the influence of the pressure on the selectivity was also observed. Although NG is composed mainly of methane (ca. 90% vol.), our experimental results indicate that the preferential adsorption of the heavier hydrocarbons and CO₂ should be properly taken into account for the evaluation of the behavior of adsorbed natural gas systems along several charge and discharge cycles.

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1. Introduction

Natural gas (NG) has been considered an important alternative for the expansion of the world's energy supply. It is a non-renewable natural resource still largely available; it is cheap and has a relatively clean combustion when compared to other fossil fuels such as gasoline and diesel. However, its applications as fuel are limited under ambient temperature conditions, mainly due to its low energy density [1,2]. Therefore, the major problem of increasing NG utilization is the high transportation costs due to the difficulty of achieving high energy densities in appropriate containers.

The most common way to store NG is by compression, but the use of high pressures (ca. 20 MPa) is seen as a disadvantage of this technique since it requires special vessels with restricted geometry and weight, which leads to high costs. On the other hand, if porous media would be used to store natural gas by adsorption, the charge pressure in the reservoir could be considerably lower (about 3.5–4.0 MPa), meaning lower costs with vessel construction and compression and also higher safety [3,4].

Activated carbon has been considered to be the most adequate material to store natural gas by adsorption [5], due to its high surface area and micropore volume, high chemical affinity for organic substances, low cost and high availability.

Current studies on adsorbed natural gas (ANG) are guided by targets set by energy companies and governmental sectors. The most commonly found on literature is the target of 180 (v/v) set by the United States Department of Energy (DOE), as the stored gas volume that must be delivered from an ANG system for it to be considered economically feasible [6,7].

Several factors can affect the capacity and gas deliverability. Properties, such as the adsorption affinity, the packing density of the bed, the adsorbent textural characteristics and the gas composition play an important role on the storage system performance [8–10]. In order to maximize the stored volume, high packing density and adsorption affinity are desirable. Enhanced heat exchange through the vessel walls is also essential for improved storage and delivery capacity, since adsorption is an exothermic phenomenon [11,12].

Additionally, there is an important issue concerning the influence of the composition of NG on the performance of successive charge and discharge cycles. Several studies reported in the literature have been carried out considering natural gas as pure methane [1,13–15]. This approach simplifies methodologies and calculations, but it does not fully account for the effects involved in NG storage process. NG is a mixture of hydrocarbons and small amounts of other gases, which influence the efficiency of an ANG system. Unfortunately, there are few experimental studies [7,8,16] quantifying and analyzing performance evolution of ANG storage vessels in long-term operation. Simulation and experimental data in literature report efficiency decrease, due to the accumulation of the heavier NG hydrocarbons

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Nomenclature

M	molar mass of the natural gas charged (g/mol)	T_0	temperature in standard conditions (293 K)
m_{ads}	mass of adsorbed NG on the AC bed (g)	V_{charge}	stored volume (cm ³)
m_{charge}	stored mass of NG (g)	$y_{\text{ads},i}$	mass fraction of component i in the adsorbed phase
m_{gas}	mass of compressed NG (non-adsorbed) in the bed void volume (g)	$y_{\text{charge},i}$	mass fraction of component i that is charged
P_0	pressure in standard conditions (0.1 MPa)	$y_{\text{gas},i}$	mass fraction of component i in the gas phase
Q_1	stored mass in the first cycle (g)	Greek letters	
Q_n	stored mass in the n th cycle (g)	$\alpha_{\text{C}1\text{C}1}$	selectivity of component i in relation to methane (C1)
R	ideal gas constant (8.314 MPa cm ³ mol ⁻¹ K ⁻¹)	$\eta(\%)$	efficiency of the ANG system at the n th cycle

and CO₂ in the activated carbon [7,8,15,17]. In a cyclic long-term use, the heavier components are gradually accumulated in the pores leaving fewer sites to adsorb methane, the main constituent of NG, which is not so strongly adsorbed.

Another aspect to be considered is that the storage of NG for transport purposes is not necessarily related to an immediate use. Therefore, in many cases, one can assume that there is enough time for the adsorption equilibrium to be reached. In some studies of adsorptive NG storage for vehicular applications [7,8], the thermal equilibrium (temperatures inside and outside the vessel are the same) is the set point for the charge step and no further time is given for the adsorption equilibrium to be achieved. In this case, the NG heavier components, with slower adsorption kinetics in comparison with methane, would not be adsorbed as much as if they were in equilibrium.

The present study aims to simulate a storage system, in which the time difference between a charge step and the gas delivery qualitatively corresponds to vessel transportation, by carrying out experiments over long time periods. The influence of the different NG components on the system performance along several charge and discharge cycles was also studied.

2. Materials and methods

2.1. Experimental device

The prototype system used to perform natural gas charge and discharge cycles is shown in Fig. 1. A cylindrical stainless steel vessel of about 30 dm³ (19.7 cm diameter and 96 cm length) was filled with 9.32 kg of a granular activated carbon sample, WV1050 (MeadWestvaco, USA). The charge and discharge of gas to and from the prototype were performed using a concentric cylinder with 2.54 cm diameter and 40 holes (3.0 mm each) distributed along all its extension, allowing radial flow through the adsorbent bed, in an attempt to minimize thermal effects [11]. Heating of the system (during regeneration of the adsorbent bed) was accomplished using a heating tape that encircled the whole vessel connected to a temperature controller. Carbon textural properties were obtained by measuring adsorption isotherms of nitrogen at 77 K using an Autosorb-1 MP apparatus (Quantachrome, USA).

The prototype vessel was equipped with two pressure sensors (K1 Ashcroft, USA), axially distributed, and three temperature sensors (PT 100) were placed in different radial positions. The amount of gas that enters and leaves the system was measured using an electronic balance (Toledo model 2090, Brazil) with precision of 5 g. The gas phase composition at equilibrium was analyzed by gas chromatography (Varian model CP4900, USA).

2.2. Single components from natural gas adsorption isotherms

The adsorption isotherms for the main NG components (methane, ethane, propane, nitrogen and carbon dioxide) were obtained

gravimetrically with the aid of a magnetic suspension balance (Rubotherm, Germany).

The activated carbon was regenerated at 373 K and vacuum until no mass variation in the system was observed. After that, the temperature (298 K) was set and the amount adsorbed of each gas was evaluated in different pressure ranges, depending on the gas.

A detailed description of the procedures to determine the adsorption isotherms can be found elsewhere [18,19].

2.3. System characterization and preparation for the cycles

The internal volume of the empty vessel (V_p) was determined by gradually charging it with nitrogen up to 3.5 MPa. Thermal equilibrium was verified at the end of each pressurization step. The amount of charged nitrogen on each step was weighted and the gas density was estimated by the Bender's equation of state for pure fluids as described by Herbst and Harting [20]. The value of V_p was obtained from the slope of the plot of charged mass versus nitrogen density.

Before starting the natural gas charge and discharge cycles, the activated carbon bed was regenerated *in situ* at 393 K under vacuum (1.3×10^{-8} MPa), using an Edwards vacuum pump connected to the charge/discharge outlet of the vessel, until no mass variation in the system could be observed. The mass of regenerated activated carbon (m_{AC}) was calculated by the difference between the cylinder mass before this procedure (non regenerated bed), the mass of the empty cylinder and the mass loss during the regeneration. The packing density of the bed (ρ_b) was represented by the ratio between the mass of regenerated adsorbent and the prototype volume.

After the regeneration process, the bed void volume (V_v) was determined by the same procedure applied to evaluate V_p , but using Helium (99.995% purity), which is known to be practically not adsorbed in the given conditions, up to 4.0 MPa. Helium density was evaluated by the Virial equation of state [21].

2.4. Selectivity and cycles

The experimental procedure to determine selectivity was carried out only at the first charge step at room temperature (298 K) and loadings corresponding to pressures varying from vacuum (1.3×10^{-8} MPa) up to 3.5 MPa. After each loading step, the system was allowed to reach equilibrium (about 24 h). The total stored mass was directly measured by the balance (mass increase) and the concentration of each component was calculated by a chromatographic analysis of the gas phase in equilibrium.

Assuming that no mass is adsorbed at the beginning of the first charge experiment, the adsorbed excess amount of each NG component was calculated according to Eqs. (1) and (2). Then the adsorption selectivity was evaluated by using Eq. (3).

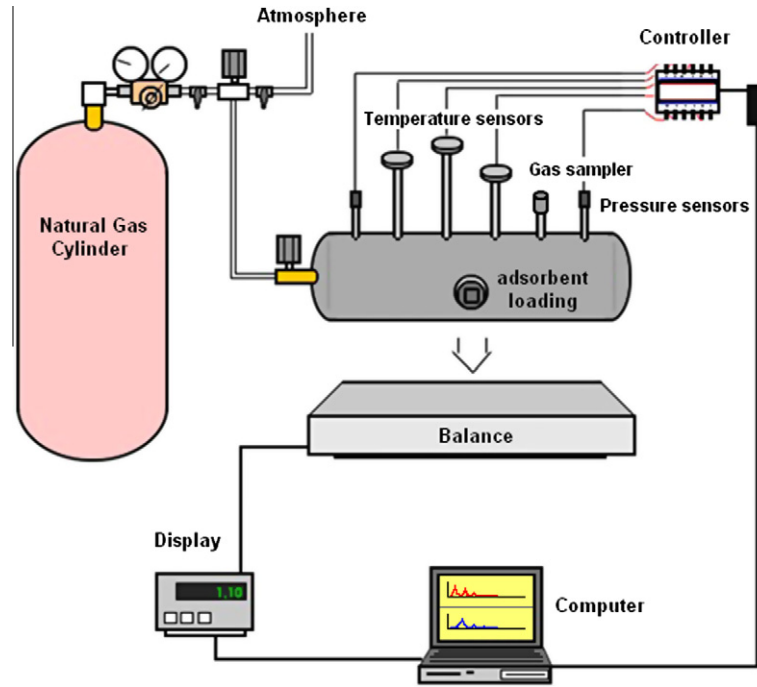


Fig. 1. Experimental device used for charge and discharge cycles.

Table 1

Composition of the natural gas used in the experiments.

Component	Molar fraction (%)
Methane	90.68
Ethane	6.72
Propane	0.36
Carbon dioxide	1.41
Nitrogen	1.03

$$m_{\text{charge}} = m_{\text{ads}} + m_{\text{gas}} \quad (1)$$

$$y_{\text{charge},Ci} \cdot m_{\text{charge}} = y_{\text{ads},Ci} \cdot m_{\text{ads}} + y_{\text{gas},Ci} \cdot m_{\text{gas}} \quad (2)$$

$$\alpha_{CiC1} = \frac{\left(\frac{y_{\text{ads},Ci}}{y_{\text{ads},C1}} \right)}{\left(\frac{y_{\text{gas},Ci}}{y_{\text{gas},C1}} \right)} \quad (3)$$

After the evaluation of the selectivity on the first charge, the experimental cycles were carried on by successively pressurizing the vessel up to 3.5 MPa and outgassing it down to atmospheric pressure (0.1 MPa). Around 24 h were allowed for the adsorption equilibrium to be achieved following each charge and discharge step, before natural gas composition analysis was performed by gas chromatography.

The efficiency of the ANG system was evaluated according to Eq. (4).

$$\eta_{(\%)} = \frac{Q_n}{Q_1} \times 100 \quad (4)$$

The specific volume of NG stored in standard conditions (293 K and 0.1 MPa) was evaluated according to Eq. (5).

$$V_{\text{charge}} = \frac{R \cdot T_0}{M \cdot P_0} \cdot m_{\text{charge}} \quad (5)$$

As the natural gas source is the same for all cycles, it is assumed that the NG composition is kept constant and consequently its molar mass. The chemical composition of the natural gas used in this study is presented in Table 1.

3. Results and discussions

3.1. Adsorbent particle and bed

The textural characteristics of the activated carbon sample used in the experiments are summarized in Table 2. Its high surface area and micropore volume are suitable for gas NG storage [9,10].

The calculated mass of regenerated adsorbent (AC) was 9.32 kg. The total internal volume of the vessel was 27.691 dm³ and the bed void volume was 21.262 dm³, which leads to an estimated bed porosity of 0.768.

The reason for such high bed porosity may be found on the adsorbent packing procedure. In order to ease the vessel manufacture, the opening for the adsorbent sample was built in the axial middle-point of the covering shell, as shown in Fig. 1. Despite its easy handling, this setup does not allow an adequate filling and thus generates a relatively high void volume.

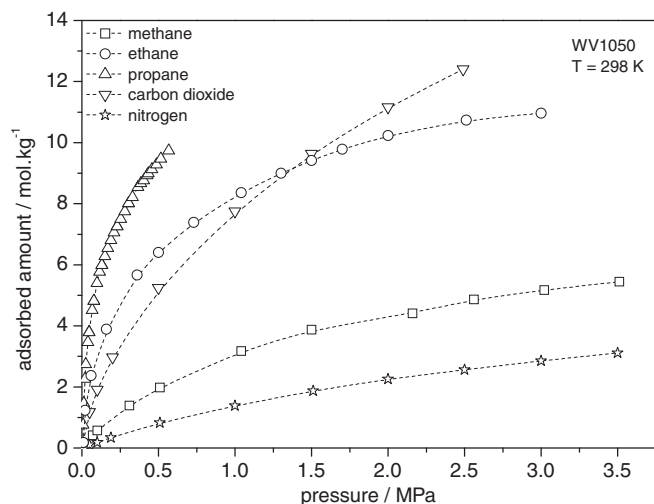
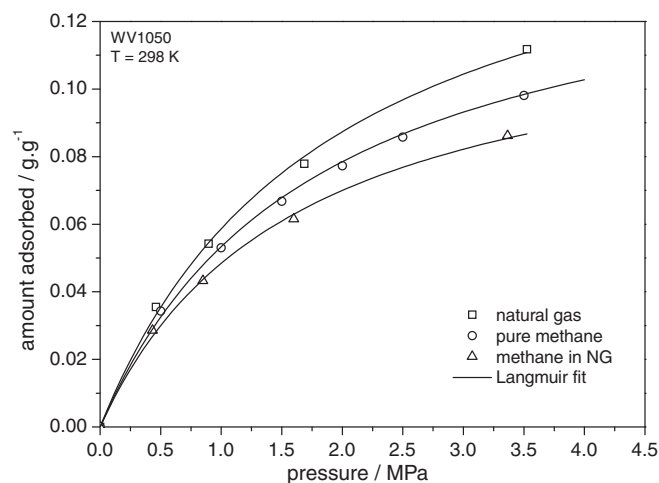
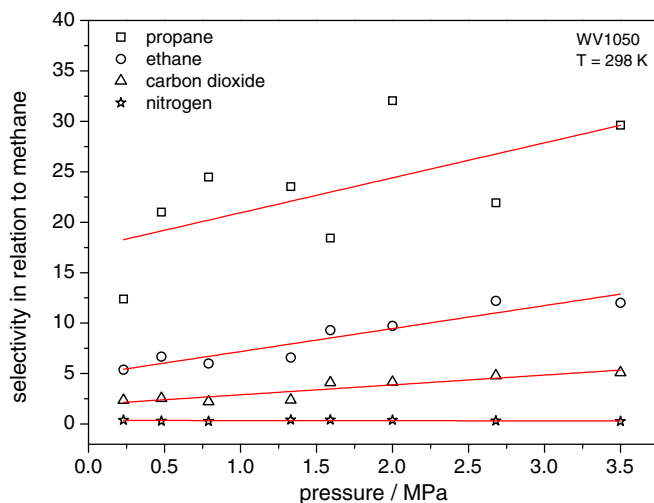
The packing density, obtained from the regenerated bed, was then 0.337 g/cm³, which is however a common value for granular activated carbons [1,22,23]. It is an important parameter because it has a direct impact on the storage capacity per unit volume. A good packing density should minimize the voids, increasing the adsorptive capacity of the system.

3.2. Adsorption isotherms of natural gas components

The adsorption isotherms for the main components of natural gas (pure gases) on the carbon sample WV1050 are presented in Fig. 2. For the hydrocarbons, the adsorbed amount tends to increase with the molar mass, as the saturation pressure is decreased. Carbonaceous adsorbents are usually much more selective for higher alkanes and carbon dioxide over methane. Even though the higher alkanes are normally available at lower concentrations (see Table 1), their higher affinity towards the material makes their desorption more difficult, causing gradual accumulation in the porous medium, reducing the efficiency of storage systems as they are cycled with charge and discharge steps [24–26].

Table 2Textural characteristics of the adsorbent, obtained from adsorption isotherms of N₂ at 77 K.

Sample	BET surface area (m ² /g)	Micropore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Average pore width (Å)
WV1050	1615	0.76	1.04	25.5

**Fig. 2.** Pure component isotherms of the main NG components in activated carbon WV1050 (Mead Westvaco, USA) at 298 K.**Fig. 4.** Adsorption isotherms of pure methane, natural gas and methane present in NG at 298 K. Adsorbent: activated carbon WV1050 (Mead Westvaco, USA).**Fig. 3.** Selectivity (α) for C₂H₆, C₃H₈, CO₂ and N₂ in relation to CH₄, at 298 K. Straight lines only indicate trends of the experimental points.

3.3. Analysis of the adsorption selectivity

The selectivity is a useful parameter which provides an insight on the competition of the different species in a mixture for the adsorption sites of a given material. As previously described, the evaluation of this parameter was carried out on the first charge step, with the regenerated adsorbent bed, at successive pressure steps up to 3.5 MPa. The selectivity for ethane, propane, carbon dioxide and nitrogen in relation to methane was calculated using Eq. (3) and the respective values are plotted in Fig. 3.

As expected, the activated carbon showed the highest selectivity for propane, followed by ethane, and carbon dioxide. This observation could be also directly related to the isotherms plotted in Fig. 2. Although carbon dioxide can be more adsorbed than eth-

ane at pressures higher than 1.4 MPa, on a molar basis, its partial pressures in selectivity experiments were no higher than 0.25 MPa.

It is important to note that the isotherms were measured for pure gases, while the selectivity was evaluated for the natural gas mixture, in which situation there shall be considerable competition for the adsorption sites.

The affinity between the adsorbent material and the gas expressed by the isotherms gives an approximate idea of the probable behavior of the mixture components contacting the solid surface at the same time. However we should also take into account the influence that the concentration of each species may have on this competition, by analyzing Eq. (3). If the partial pressure of carbon dioxide were larger than that in the selectivity experiments, perhaps CO₂ would show higher selectivity in relation to ethane, which would be the expected behavior, judging from the pure component isotherms to pressures above 1.4 MPa.

Nitrogen has a distinct adsorption behavior as compared to methane, on a molar basis. Methane is either more adsorbed or in a higher concentration, which causes the selectivity for nitrogen to be less than unity.

An additional analysis of the influence of the composition on the adsorption performance is represented in Fig. 4. Adsorption isotherms of pure methane, methane in natural gas and natural gas itself were plotted for the same temperature and fitted by the Langmuir model. The two last set of data points were obtained from the same stepwise pressurization carried out for the selectivity evaluation, performed in the prototype vessel with natural gas, with the aid of mass balances and gas chromatographic analyses. It can be verified that the adsorbed amount of NG is the upper limit and that methane in NG cannot be more adsorbed than pure methane due to the composition and co-adsorption effects.

3.4. Charge/discharge cycles

The investigation of the influence of the gas composition on the adsorbed amount was carried out along 30 cycles of charge and discharge on the prototype vessel.

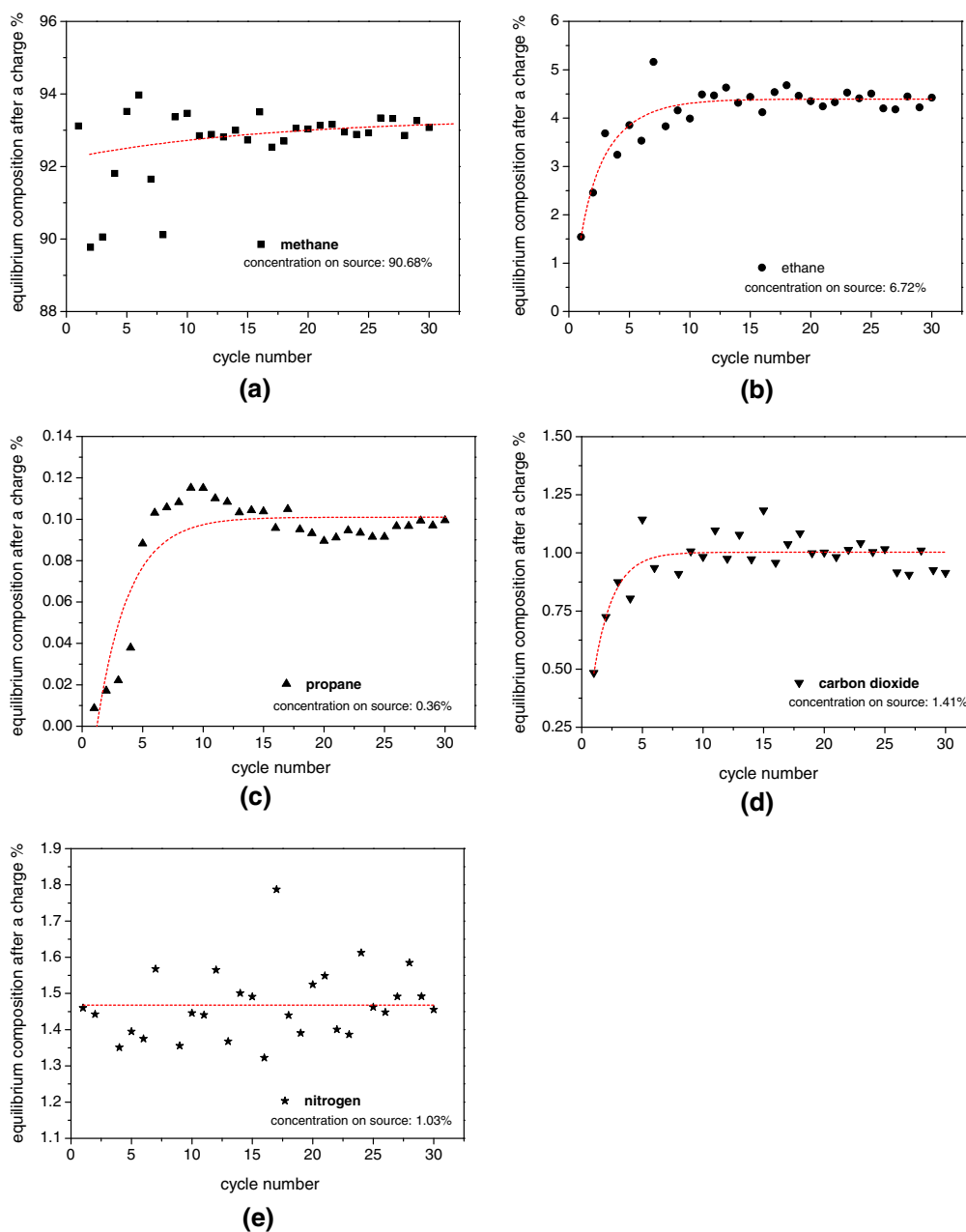


Fig. 5. Composition of the gas phase along the cycles for CH_4 (a), C_2H_6 (b), C_3H_8 (c), CO_2 (d) and N_2 (e) at 3.5 MPa and 298 K. Dashed lines only indicate trends of the experimental points.

As previously mentioned, most of the studies on natural gas storage aims at the use of natural gas on vehicles, in which case only the thermal equilibrium is usually reached, without allowing enough time for the adsorption equilibrium to be established. Since the NG heavier components have slower adsorption kinetics in comparison to methane, it may be assumed that the accumulation effect of those heavier components tends to occur more slowly in that case. Therefore, for adsorbed natural gas on vehicles, the storage system takes more cycles to reach an apparent steady-state condition.

In the first cycles, the gas phase concentration in equilibrium after the charge is poorer on heavy alkanes and carbon dioxide. But during discharge, the desorption of the lighter components – with better kinetics – is favored, leaving the heavier components behind. After a certain number of cycles, when the adsorbent bed gets saturated, the gas phase composition tends to be the same

as in the natural gas originally charged (source). This is illustrated in Fig. 5, with the plot of the concentration of each NG component along the cycles after equilibrium is reached at each charge step.

The concentration increase for propane along the cycles is more easily noticed probably due to its highest selectivity. Its steady-state composition is around 10 times higher than the composition after the first charge step (Fig. 5a). Similar selectivity behaviors could be observed for ethane and carbon dioxide compositions (Fig. 5b and d, respectively). Their steady-state compositions are around three and two times higher than the first step composition, respectively. It was observed that the selectivity values of the NG components in the system (see Fig. 3) follow the same trend (ratio between the final steady-state composition and the first step composition) for the concentration along the charge/discharge cycles, which is quite obvious from the preferential adsorption for each component in relation to methane observed in the pure component isotherms.

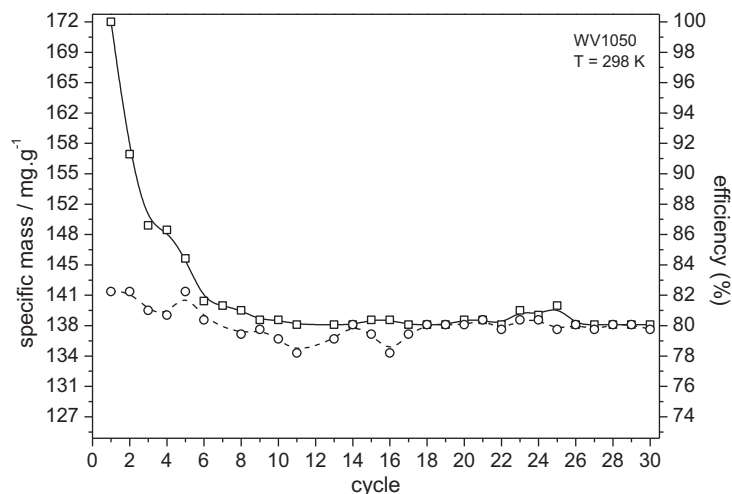


Fig. 6. Specific stored mass (\square ; 3.5 MPa and 298 K) and delivered mass (\circ ; 0.1 MPa and 298 K) (read on the left axis) and respective efficiencies of storage and delivery (read on the right axis) of the ANG system along the cycles.

The nitrogen fraction is almost not affected, presenting a very slight decrease, since the other components are more adsorbed at the beginning.

The whole system seems to reach steady-state conditions after the ninth cycle, when the adsorbent achieves apparent saturation. The consequences of this phenomenon can be verified in Fig. 6, which shows the storage capacity of natural gas and storage efficiency along successive charge and discharge cycles.

In the first cycle, the stored mass is high, due to the high retention of gas molecules in the empty pores of the adsorbent, since the system was previously regenerated. However, the stored mass decreases significantly in the following cycles and, after the ninth cycle, the system reaches an apparent steady-state behavior. This number depends on the amount of heavy components and the adsorbent characteristics, as well as on the cycling period. The heavier components, which are more strongly adsorbed, may move the lighter ones from the adsorbed phase to the gaseous phase, where there is no competition between species [17]. Thus the lighter components are continuously replaced by the heavier ones in the adsorbed phase. Nevertheless the heavier components gradually reach the steady-state condition and so the rate of deactivation of the adsorbent bed decreases over the cycles. At the ninth cycle, the storage efficiency falls down to 80%. This reduction is closely linked to the progressive saturation of the different gases in the carbon bed. After the system reaches the steady-state condition, the natural gas composition inside the vessel, at the end of each charge step, changes little during the cycling operation. This fact indicates that the accumulation of heavier components has no further significant influence on the system performance.

However, despite the significant reduction in stored mass observed in the early cycles, the delivered mass does not show a similar behavior after the same number of cycles (drop in delivery is only ca. 2% between the first cycle and the steady-state condition, see Fig. 6). This is obviously because on the first cycle the heavier components are immediately retained and will be for the most part kept adsorbed throughout the remaining cycles. At the subsequent cycles, the heavier components will slowly further concentrate in the adsorbed phase, reaching steady-state conditions after ca. 10 cycles.

To prevent the problem of the accumulation of the heavier components in a carbon adsorbent bed, Cook et al. [27] proposed the utilization of a device which consists of a guard bed placed at the entry of the cylinder of ANG storage. This guard bed would avoid

the accumulation of the heavier alkanes in the ANG system at the charge step and allow those components to return to the natural gas stream during the discharge step. During the charge of the cylinder, the gas would necessarily pass through that device before being stored, and so the heavier components would be retained in this protection bed. Cook et al. [27] reported that the guard bed is able to meet its goal, avoiding the accumulation of the heavier components in the ANG system (their experiments showed no loss of capacity over the cycles).

Converting the experimental data of stored mass into stored gas volume in the STP (293 K and 0.1 MPa) according to Eq. (5), we were able to plot Fig. 7. Both stored volume and delivered gas in the steady-state condition was about 63 v/v. However, the stored volume is directly related to the adsorbent capacity and packing density. Higher capacities and densities of the adsorbent bed may increase the efficiency to values closer to the target established by the DOE.

The economical feasibility of the ANG technology will depend mainly on the choice of a good adsorbent. However, the price of the adsorbent (and also the costs related to the aging of this material) and the costs to deploy the ANG technology should still be

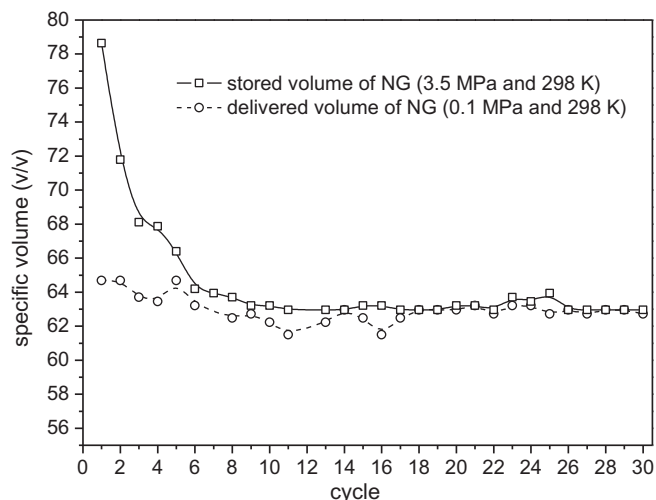


Fig. 7. Stored volume (\square) and delivered volume (\circ) per vessel volume as a function of the number of cycles.

evaluated against the costs of storage and transport of the GNC and GNL technology, for the same amount of gas.

4. Conclusions

Charge and discharge cycles of natural gas were performed on a prototype vessel filled with activated carbon. The experiments showed the effect of gas composition on the amount of stored gas and on the efficiency of the storage system over the cycles. The selectivity of the carbon sample for the main components of natural gas in regards to methane tends to increase with the pressure, except for nitrogen, which is less adsorbed than methane. Preferential adsorption of the heavier components and carbon dioxide was also observed and the contribution of this fact to the partial deactivation of the adsorbent bed was evaluated.

The attainment of steady-state conditions is directly dependent on the cycle steps (charge and discharge). If cycle steps (adsorption/desorption) are allowed to last for as long as it takes to come to thermal equilibrium, then the steady-state conditions are reached in ca. 10 cycles with stored and delivered masses reduced to 80% and to 2% of their original value, respectively.

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