Adsorbed Natural Gas Tank feeded with Liquid Natural Gas

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Abstract. This paper present the idea of a natural gas reservoir, which uses technology of gas storage by adsorption on activated carbon. Such reservoir can be feeded with Liquid Natural Gas. The framework of article includes theoretical principals of gas-solid physical adsorption, and explains most important concepts associated with it. Moreover, concept of such tank and working regime is presented. Selected subject is very promising in the field of natural gas storage, although this is still a niche issue. Lack of universal models of gases physical adsorption made it very difficult to predict the runs of processes occurring in the proposed reservoir, which is why this project was based on models confirmed during in the earlier studies.

1 Natural Gas as an alternative fuel

Natural gas NG (natural gas) is the most favorable alternative to oil among liquid fuels [9]. Many advantages of this fuel causes that market connected with it is growing rapidly. Natural gas is a fuel with a very clean combustion without the production of compounds of sulfur, lead, benzene or particulates. Emission of carbon dioxide is reduced by more than 20% compared to standard gasoline combustion with emissions of carbon monoxide can be reduced by up to 85%. The products of combustion of methane, the main constituent of NG are only carbon monoxide and water vapor. Compressed natural gas can successfully run the modern spark engines, and because of its higher octane values it is possible to use higher compression values, and consequently, improving the efficiency of these engines. Contrary to hydrogen it is the fuel of high availability, commonly found with deposits of crude oil and coal. Technological development in the near future will allow effectively exploit unconventional deposits of gas such as shale gas, tight gas, methane mine, deposits of methane hydrates or NG production of biogas, landfill gas and sewage [5].

Table 1. Comparison of the density of the energy contained in various types of fuels.

Fuel type	Gasoline	Diesel	Oil	Propane (LPG)	Butane (LPG)	Natural Gas	Methane	Hydrogen
Cal. value, MJ/mn3	32100	35800	38500	88.4	111.0	31.7–39.2	33.9	10.3
Phys. state	Liquid	Liquid	Liquid	Gas	Gas	Gas	Gas	Gas

Despite the many advantages of natural gas, it has the disadvantage that highly complicate its use and it is its low energy density per unit volume at normal conditions. Table 1 [2] shows the approximate energy content expressed per liter of fuel in normal conditions, these values can vary slightly depending on the source, it is caused the possibility of differences in the chemical compositions.

As shown in the statement of the energy density of natural gas is 3 orders lower than in liquid motor fuel, which means that natural gas storage in warehouses with conditions similar to those normally does not make economic sense. While the LPG fuel have a calorific value only several times higher than in the case of natural gas, its widespread usage is the result of different chemical composition. LPG fuel is a mixture of propane and butane, so it can be condensate at pressures slightly above the atmospheric ones (2.2 to 4 atm depending on the composition), but it is stored in tanks under pressure of at least 6 atmospheres for a total certainty that the mix is stored as a liquid. Fuel phase change associated with large changes in the density and accompanied by a sharp increase in energy density per unit volume, it is assumed that the useful calorific value of LPG is already 25300–27700 MJ / m3 [1].

In the case of natural gas to increase the energy density per unit volume it is possible to use one of three storage technologies. The first way is to use the compressibility of gases, natural gas is compressed and stored under very high pressure, up to 250 atm, which entails the need to use powerful compressor systems and the fact that the tanks in order to withstand such high pressures have to be very massive. This technology is abbreviated as CNG – Compressed Natural Gas. Another method is the technology of LNG - Liquefied Natural Gas, which is much more difficult than in the case of LPG, due to the low boiling point of the main component in natural gas – methane of approx. 111 K. Although this is a very common method, especially in maritime or long-distance transport. A serious disadvantage of this technology is the loss of exergy trapped in a large temperature difference between the LNG and the surroundings, in most cases re-gasification takes place without the participation of exergy utilization systems.

This problem was undertaken in a number of scientific papers, but the proposed solutions leaves area searching for more efficient methods. The last process, currently least developed, is the use of gas adsorption on solid surfaces. Detailed explanation of the phenomenon is in further part of work, but here already it is worth mentioning that this phenomenon greatly reduces the pressure in the reservoir with respect to CNG technology. Taking advantage of the fact that the process of gas adsorption ANG (adsorbed natural gas) occurs more effectively at low temperatures, it is possible to use exergy contained in a liquefied LNG in order to improve the conditions for adsorption of gas in the vessel construction much lighter than would have occurred using technology compressed natural gas CNG. It has been proven by calculation that the coupling of such a system with the LNG system can significantly increase the exergy efficiency of LNG regasification facilities [10,11,12].

2 Adsorbed Natural Gas Technology

Adsorbing of Natural Gas is a technology using the porous structures of activated carbon as a gas storage. A major advantage of this method is lower pressure than in the CNG, which allows the use of cheaper and lighter tanks. Due to the lower working pressure it is said about the possibility of executing reservoirs shape other than cylindrical – in many applications, it is crucial and can increase the quantity of a stored gas while reducing the external dimensions of the tanks. Lower pressures prevailing inside reflect also in the long life of the installation and lower prices not only of containers, but also the instrumentation. Currently it is possible to find commercial solutions, operating around ambient temperature.

2.1 Principles of adsorption

Adsorption is the result of uncompensated molecular forces present on phase boundaries of the condensed body. Cohesive interactions occurring between the molecules within the body are offset by the same effects particles in round, impacts molecules located on the boundary phases are not thereby saturated. Therefore, a solid phase boundaries generated unbalanced forces which the operation can be considered as directed perpendicular to the surface of the body. When the surface of the solid is in contact with a gas or liquid, the particles of the substance (the adsorbate) in the gas phase or liquid are attracted to the surface of the body (adsorbent) to balance the residual strength. The result is a greater concentration of gas or liquid in close proximity to the surface of a solid than the rest of volume.

Adsorption involves two types of forces: the relatively weak physical forces (polarization, dispersion, short-range repulsive interaction) as well as stronger chemical forces (the binding valence). Depending on the type of impacts occurring adsorption divided into: chemical adsorption and physical adsorption. Physisorption is non-specific, present in any system adsorbate-adsorbent forming multilayer systems, does not require activation energy, which translates into a high adsorption rate, also due to the nature of the forces in charge this adsorption process is reversible. Chemisorption is a specific phenomenon, occurs between selected pairs of adsorbate-adsorbent, its required some activation energy, and appearing creates a monolayer of molecules of adsorbate at the adsorbent surface, which have a more permanent character. Natural Gas adsorption on activated carbon is determined by physisorption.

2.2 Heat of adsorption, adsorption isotherms and capillary condensation.

Adsorption is an exothermic process, and proceeds with the separation of certain amount of heat. This heat is called the heat of adsorption and is an important function of the thermodynamic used to characterize the surface of a solid. The value of heat generation is significant, because its knowing is important for practical and theoretical solutions. Analogously to the adsorption process, during the desorption certain amount of heat is absorbed from the environment. This amount of heat determines the heat of desorption. Values of this heats are very important for realization of the loading-unloading cycles because generated heat can block the whole process.

There exists a large number models of physical adsorption. R. Ch. Bansal [3] lists even 9 basic models, which are the foundation for creating new ones. The first physical model describing the adsorption process leading to the formation of a monolayer, gave Irving Langmuir. He assumed that on the surface of the homogeneous adsorbent exists determined number of identical adsorption centers, which can adsorb only one molecule of the adsorbate and the probability of adsorption increases with the numbers of the free surface and the gas pressure and the results obtained by this method are lower than those observed experimentally, but the Langmuir isotherm is the most fundamental correlation.

Adsorption in the micropores, which is much stronger than in the materials with similar chemical structure but a different geometric models describe Dubnin-Radushkevich and Dubnin-Astachov. In these models they have been permanently connected to the size and distribution of micropores in the material. Due to the high complexity of the adsorption issues there is no universal gas adsorption model, which describes this phenomenon in a wider range of conditions or on different adsorbent. Therefore in the performance of the calculations should be chosen model for with conformity to the experimental results on a specific pair of adsorbent-adsorbate and similar conditions to the assumed.

Very important phenomena for adsorption realization is also capillary condensation, which explains fact that the condensation on the curved layers takes place at definitely lower

pressures than the saturation pressure of the adsorbate in the given temperature. In fact the adsorbent has a certain radius distribution of capillaries, with the result that condensation occurs over a range of pressures. This entails the occurrence of hysteresis. In practice, the presence of the hysteresis loop is undesirable due to the lack of repeatability of the process, problems in controlling the adsorption process and the difficulties of penetration the bed by the gas phase adsorbate. Founded operating conditions of the proposed reservoir ANG should prevent the occurrence of capillary condensation, or reduce its occurrence to a smallest possible volume.

3 Development of the Tank construction

Considered tank works in a strictly defined operating cycle. Before the loading, and after the unloading, tank would contain natural gas adsorbed under the ambient temperature and in the pressure around 1 bar. During the loading process, tank will be charged with LNG which will evaporate at the heat exchanger, with simultaneous cooling the volume of the adsorbent bed. Due to the strong dependence of the physisorption with the temperature, by cooling storage capacity of the bed increases. Natural Gas will adsorb on the activated carbon and after some time, the temperature of the bed will match to the ambient and pressure will increase to the adsorption equilibrium. Then it will be possible to unload the tank, with reducing of the pressure inside the tank.

3.1 Bed selection

The adsorption of gases occurs on a greater or lesser extent, at the surface of each solid body. The size of this phenomenon depends on many factors, such as temperature, pressure, chemical composition or the nature of the interaction between gas molecules and the solid, but it is also directly proportional to the surface area on which the phases are in contact. Therefore, the aim is that the materials which adsorbs fluids is to have a high surface area per unit volume [6]. For the purpose of adsorption the natural gas the most proven and common choice is activated carbons in the form of dust, fibers or pellets. This is caused by the huge specific surface area (500-2600 m2 / g) [4], majority participation of micropores over the meso- and macropores and relatively low cost of production.
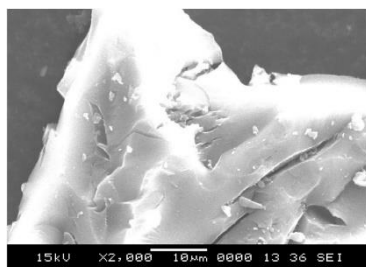

Fig. 2. Image of activated carbon Maxsorb III dust particles, made with an electron microscope [7].

For the needs of this paper commercial activated carbon Maxsorb III was chosen for the adsorbent (Fig. 4.1.). It is one of the best adsorbent materials available on the market, it has excellent thermo-physical properties which are shown on Table 2 [12,14]. The great advantage is also relatively good availability of test results on adsorption of methane on Maxsorb III in wide temperature conditions.

Table 2. Maxsorb III properties.

BET surface area, m2/kg	3.14*106
Total pores volume, m3/kg	20.1*10-4
Micropores volume, m3/kg	1.79*10-4
Average pore diameter, nm	2.008
Skeletal density, kg/m3	2200
Bulk density, kg/m3	156
Thermal conductivity, W/(mK)	0.71

3.2 Design assumptions

In the proposed tank assumes the presence of spiral HX to cool the bed and receive heat of ads. during charging, and to receive heat of desorption to allow emptying. Provided in the construction capability to receive medium flowing through the exchanger, without introd. it to the bed provides add.l opportunity to soak the bed objective to regenerate it.

Due to brittleness of carbon steels in low temp. it is suggested to use austenitic steels for LNG operated constructions. Therefore, material was chosen as a stainless steel X5CrNi18-10 / 1.4301 (AISI 304) with parameters described in the table below. This steel can be used for construction of the tank and the internal heat exchanger.

3.3 Concept of the ANG Tank.

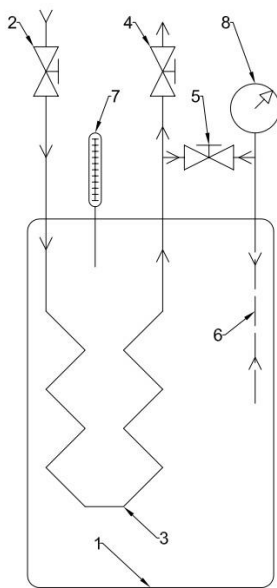Concept of the ANG Tank is presented in a Fig. 3

Fig. 3. Concept of the ANG Tank. 1-steel tank; 2,4-check valve; 3-heat exchanger; 5- shut-off valve; 6- perforated distribution pipe; 7- temperature transducer; 8- pressure gauge with pressure transmitter.

4 Work regime of the tank

4.1 Maximum capacity of the bed

Adsorption of methane on a bed of Maxsorb III has been tested and published in the form of scientific articles. "Improved Isoterm Data for Adsorption of Methane on Activated Carbons," Wai Song Loh et al. [13] describes the results of measurements of adsorption in the temperature range 288-348 K and a pressure of 50-2200 kPa, so underneath supercritical region, and "Experimental Adsorption Isotherm of Methan onto activated carbon at Sub- and Supercritical Temperatures" Kazi Afzalur Rahman et al. [7] in the temperature range 120-220 K and pressures well below dew point pressure for a given temperature. In both articles the results of measurements were compared to the Tóth and Dubnin-Astakhov adsorption models, proving the convergence of these models with actual measurements. Isotherms models are described by the formulas 4.1. and 4.2., and coefficients used in the calculation are given in Table 3.

$$\text{Tóth isotherm-}\quad \frac{C}{C_0} = \frac{k_0 \times \exp\left(\frac{h_{st}}{RT}\right) \times P}{\left(1 + \left(k_0 \times \exp\left(\frac{h_{st}}{RT}\right) \times P\right)^t\right)^{\frac{1}{t}}} \qquad 4.1$$

$$\text{DA isotherm-}\quad \frac{C}{W_0/v_a} = \exp\left\{-\left[\frac{RT}{E}\ln\left(\frac{P_{sat}}{P}\right)\right]^n\right\} \qquad 4.2$$

Table 3. The experimental coefficients determined for the calculation of adsorption isotherms [7, 14].

	Temperature range	120 – 220 K	288 - 348 K
Tóth	$C_0; \frac{kg}{kg}$	1,503	0,439
	$\frac{h_{st}}{R}; K$	1674	1610
	$k_0; \frac{1}{Pa}$	$3,65 \times 10^{-9}$	$1,97 \times 10^{-9}$
	$t; -$	0,,274	0,780
DA	$W_0; \frac{m^3}{kg}$	$2,454 \times 10^{-3}$	$1,618 \times 10^{-3}$
	$E, \frac{kJ}{kg}$	287,26	327,77
	$n; -$	0,945	1,33

Fig. 4 Presents Tóth isotherms for selected temperatures, calculated with experimental data from Tab 3
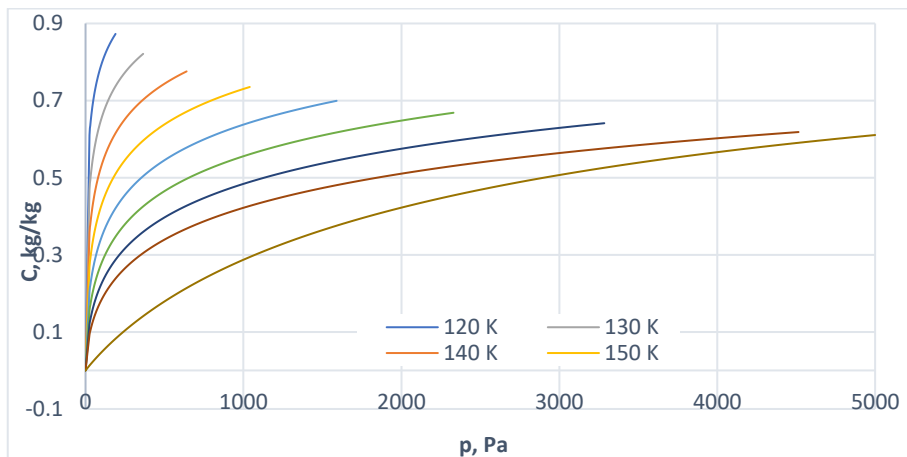
Fig. 4. Calculated isotherms of methane at Maxsorb III for selected temperatures.

To determine the supply conditions of the bed can be used balance of the mass and energy. Assuming zero losses of mass and energy, and ignoring changes in the internal heat of the exchanger, tank and other elements.The mass balance of the deposit is represented by the formula 4.3

$$m_{in}=m_2-m_1\text{-mass of liquid methane introduced into the exchanger} \qquad 4.3$$

where: m_1-mass of methane in the tank before loading $m_1=m_{ads,1}+m_{gas,1}$;
m_2-mass of methane after loading; $m_2=m_{ads,2}+m_{gas,2}$

and: $m_{ads}=C(T,p)\times m_{ac}$, $m_{gas}=\dfrac{V_{por}-(m_{ads}\times v_{ads})}{v_{gas}(T,p)}$; $v_{ads}=v_b(T_b,p)\times \exp\left(\dfrac{T-T_b(p)}{T}\right)$ [8]

The energy balance is shown in the formula 4.4.

$$\Delta E_{in}=\Delta U_{ac}+H_{ads}+\Delta E_{1-2} \qquad 4.4$$

where:

$$\Delta E_{in}=m_{in}\left[h_l(T_1,p_l)-h_g(T,p)\right]; \ \Delta U_{ac}=m_{ac}\times c_{ac}\times(T_0-T); \ \Delta E_{1-2}=m_{ad,1}\times\left(\dfrac{c_{p,ad2}+c_{p,ad1}}{2}\right)\times(T_0-T)$$

For the purpose of determining the maximal capacity of the bed C, calculations of balances for methane subcritical conditions were carried out, the results of these calculations (with the accuracy of determination of conditions up to 1kPa and 1K). Results shows that the maximal mass of the LNG which can be adsorbed by 10 l bed, is 0,78kg. Such amount of LNG will cool down the bed to the 186 K, and it will adsorb in the tank at the pressure of 1530 kPa. Capacity of the bed is equal 0,5 kg of NG per 1 kg of activated carbon. All of the calculated parameters are presented in table 4.

Table 4. Parameters of the adsorption mass-energy balance.

T,	P,	C,	v_{ad},	$c_{p,ad}$;	h_{st},	H_{ads},	ΔU_{ac},	ΔE_{1-}	ΔH_{in},	m_{ad},	m_{gas},	m_{in},
K	kPa	kg/kg	m3/kg	kW/kgK	kJ/kg	kJ	kJ	2, kJ	kJ	kg	kg	kg
186	1530	0,500	0,0047	10,8	436,0	326,3	113,1	23,8	463,3	0,780	0	0,730

Such amount of NG in the tank coresponds to the pressure equal 2900 kPa after warming up the bed to the ambient temperature (288 K).

5 Summary

In the paper mass-energy equilibrium points were determined, i.e. pressure and adsorption temperature values, which can be achieved by introducing a given mass of LNG, without the need to collect natural gas after regasification in the form of cold natural gas. Maximal amount of stored Natural Gas in 10 l tank is equal to 0.78 kg and it gives possibility for recovering 0.75 kg of NG from the warm tank.

In further work on the ANG technology, it should carry out a series of measurements on a prototype test stand, based on which it can be possible to designate the adsorption isotherms for adsorbent MaxSorb III in the broader scope of conditions. It would also carry out studies adsorption of boil-off gas for other, cheaper adsorbents. This knowledge could be used to create a vessel for optimum performance, in which, apart from technological factors, also economical will be taken into account.

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