

METHOD AND SYSTEM FOR STORING NATURAL GAS

5 FIELD OF INVENTION

The present invention relates to a method and system for storing natural gas.

10 BACKGROUND

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Natural gas (NG) is considered as an alternative fuel in e.g. the transportation technology. It provides better combustion and minimizes exhaust pollutants. Moreover, its lower price and copious availability makes it more attractive as a vehicular fuel. NG comprises more than 80 % of methane gas, which has a heating value per unit mass
15 (50.1 MJ/kg, LHV) higher than the other hydrocarbon fuels (e.g. butane, diesel fuel, gasoline, etc.).

In recent years, adsorbed natural gas storage systems have been mooted as an alternative to the compressed natural gas for energy storage and transportation
20 purposes. In adsorptive storage systems, the natural gas molecules are captured in the micro pores of a solid adsorbent; adsorbate molecules are more stabilized on the solid adsorbent surface than in the bulk phase. Hence adsorptive storage of natural gas has the promise of being more efficient than "pure" compression storage.

25 One system for adsorbing and storing gaseous hydrocarbon fuel in automotive vehicles have been proposed in for example Patent No. 20020023539. That system implements a separation of the fuel into high and low carbon number components, which adds to the complexity of the system. Furthermore, the low carbon number component is pressurized to about 20 MPa (about 200 bar) for storage, which still requires substantive
30 compression overhead adding to the cost of storage.

A need therefore exists to provide a method and system for storing NG in an adsorbent storage device that seek to address at least one of the above problems.

SUMMARY

According to a first aspect of the present invention there is provided a method for storing NG in an adsorbent storage device, the method comprising the steps of providing the NG in a liquid phase to a first heat exchanger; gasifying the NG using the first heat exchanger; and feeding the NG in the gaseous phase into the adsorbent storage device, wherein the NG is gasified using the first heat exchanger such that the NG in the gaseous phase is fed into the adsorbent storage device at a cryogenic temperature for cooling of an adsorbent material of the adsorbent storage device.

Gasifying the NG using the first heat exchanger may comprise cooling a liquid for heat exchange to gasify the NG.

The method may further comprise using the cooled liquid for further processes.

The NG may be gasified using the first heat exchanger such that the NG in the gaseous phase is fed into the adsorbent storage device at a cryogenic temperature for cooling of an adsorbent material of the adsorbent storage device.

The method may further comprise regulating a pressure of the NG in the gaseous phase for feeding into the adsorbent storage device.

The NG may be fed into the adsorbent storage device at a near atmospheric pressure.

The NG may be stored in the adsorbent storage device at a pressure in the range of 30 - 40 bar.

Feeding the NG in the gaseous state into the adsorbent storage device may comprise cooling an adsorbent material of the adsorbent storage device.

The cooling of the adsorbent material of the adsorbent storage device may use a second heat exchanger.

The second heat exchanger may be incorporated into the adsorbent storage device.

The method may further comprise discharging the NG from the adsorbent storage device using a pressure swing method.

Discharging the NG from the adsorbent storage device may further comprise heating an adsorbent material of the adsorbent storage device.

The heating of the adsorbent material of the adsorbent storage device may use the second heat exchanger.

According to a second aspect of the present invention there is provided a system for storing NG, the system comprising a first heat exchanger for gasifying the NG; an adsorbent storage device; means for providing the NG in a liquid phase to the first heat exchanger; and means for feeding the NG in the gaseous phase from the first heat exchanger into the adsorbent storage device at a cryogenic temperature for cooling of an adsorbent material of the adsorbent storage device.

The system may further comprise means for regulating a pressure of the NG in the gaseous phase for feeding into the adsorbent storage device.

The system may store the NG in the adsorbent storage device at a pressure in the range of 30 – 40 bar.

The system may further comprise means for discharging the NG from the adsorbent storage device using a pressure swing method.

The system may further comprise a second heat exchanger for cooling or heating of an adsorbent material of the adsorbent storage device.

The second heat exchanger may be incorporated into the adsorbent storage device.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will be better understood and readily apparent to one of ordinary skill in the art from the following written description, by way of example only, and in conjunction with the drawings, in which:

Figure 1 is a diagram showing the advanced system in natural gas adsorptive device according to an example embodiment.

Figure 2 is a diagram showing the scanning electron micrograph (SEM) photo of the activated carbon at (a) 2000 magnifications, and (b) 200000 magnifications.

Figure 3 is a diagram showing a relationship between the methane uptake capacities with pressures at cryogenic temperature (120 to 220 K).

Figure 4 is a diagram showing a relationship between the methane uptake capacities with pressures at near ambient temperature (278 to 338 K).

Figure 5 is a diagram showing a comparison of natural gas volume storage capacity in an embodiment of the present invention with conventional compressed gas.

Figure 6 is a diagram showing the process path of the advanced natural gas filling system at cryogenic temperature of an example embodiment.

Figure 7 is a diagram showing the simulated results of the natural gas discharging rate at different valve coefficient value for a 10 liters ANG cylinder, according to an example embodiment.

Figure 8 shows a flow chart illustrating a method for storing NG in an adsorbent storage device according to an example embodiment.

DETAILED DESCRIPTION

Fig.1 depicts one embodiment of the invention and provides a schematic view of an ANG storage device 11 cum district cooling system consisting of a double-walled tank of liquefied natural gas (LNG) 1, two heat exchangers 4 and 12, and the ANG storage device 11 which is fully packed with solid adsorbent 14. According to the example embodiment, the process involves the phase change of the liquefied natural gas at approximately -162°C to vapor state at temperature above -150°C . The said liquid phase NG, is allowed to pass through cryogenic connections 2 into the heat exchanger 4, where the phase change takes place. Water at ambient condition with typical temperatures e.g. between 30 and 35°C enters the heat exchanger 4 from inlet 5; utilizes the cold energy from the LNG to produce chilled water with temperature ranging from 18 to 27°C and leaves the heat exchanger 4 at exit 3. The chilled water produced can be used for various purposes such as building cooling etc.

The natural gas vapor at cryogenic temperature of about -150°C after the re-gasification of the LNG in the heat exchange 4 is charged into the adsorptive storage device at near atmospheric pressures of approximately 1 to 1.5 bar using an electronic-controlled pressure regulator 7 through tubing 6.

The regulator 7 is connected to a quick connector 8 at the charging port of the ANG storage device 11. The NG vapor after re-gasification is regulated to suitable charging pressure which is normally at near atmospheric pressure for charging. The charging process continues until the ANG storage device 11 is fully charged at predefined pressures. The ANG storage device 11 is then closed and left to warm up to ambient temperatures, usually in the range of 10 to 40°C where the gas or system pressure is at its design pressure, preferably 40 bar. In this way, the charging process requires no additional cooling during adsorption because the NG at cryogenic temperature will cool the solid adsorbent 14 during the adsorption process.

During discharging, the NG vapor leaves the ANG storage device 11 from outlet 9. The desorption process is carried out using a pressure swing method at which the NG vapor desorbs from the solid adsorbent 14 surface when the pressure in the ANG storage device 11 drops. A flow regulator (not shown) can be used to achieve the desired

discharging rate. No additional heating is necessary in a preferred embodiment so that the ANG storage device 11 is preferably highly portable and its implementation convenient.

- 5 The charging rate of the NG vapor may be increased by cooling the adsorbent beds during the adsorption phase while the discharging rate can be increased by heating the adsorbent bed during the desorbing phase.

10 More particularly, in the example embodiment, cold water, in the case of improving charging rate, or warm water, in the case of improving discharging rate, can be dispensed through heat exchanger 12 incorporated with the ANG storage device 11. The cold or warm water enters the heat exchanger 12 from inlet 13 and exits at outlet 10. The cold or warm water of desired temperature used for this purpose may be supplied and maintained using a re-circulation system at the user boundary.

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Preferably, commercially available thin-walled carbon steel may be used for the proposed ANG storage device 11 for design pressure of up to 40 bar.

20 In accordance with different embodiments of the invention, the proposed portable storage device can be a gas bottle, cylinder, vessel or media thereof.

25 Preferably, the NG vapor emanating directly from a double-wall tank 1 of LNG via a heat exchanger 4 after re-gasification is regulated to near atmospheric pressure of approximately 14 to 20 psig (≈ 0.956 to 1.38 bar), from which the NG is charged into the ANG storage device 11. No additional compression power is required to compress the NG to its storage pressures, typically between 30 to 40 bar as is required using conventional methods.

30 In a preferred, but non-limiting, embodiment, a stainless steel sintered filter may be installed at the charging and discharging port of the ANG storage device 11 to prevent the solid adsorbent from escape into the reticulate.

The ANG storage device 11 is packed with solid adsorbent to operate as an adsorptive storage device in which natural gas is stored at low pressures, i.e. 30 to 40 bar. Among

the practical solid adsorbents used in industries, pitch-based activated carbon is one of the most promising adsorbent for natural gas uptake. This is because of, i) its bi-peak pore size distribution provides a good access of adsorbate molecules to the interior pores, and ii) its good thermal conductivity allows for improved thermal management of the adsorptive gas storage device.

Natural gas (NG) will be stored in the pores of the activated carbon and in spaces around the carbon particles. The adsorbent molecules will form an inter-molecular force with the NG molecules and capture the gaseous molecules onto the pores surface. This leads to a higher storage density than the compressed gas at same pressures. Thus, it follows that the pores volume of the solid adsorbent are preferably as large as possible to maximize gas storage. On the other hand, the space surround the solid adsorbent is preferably minimized since the gas in this space is expected to have its normal density.

The solid adsorbent used can be any porous material having high specific pore surface area. In a preferred, but non-limiting embodiment, porous pitch-based activated carbon (AC) powder having a pore surface area of more than $3000 \text{ m}^2\text{g}^{-1}$, a pore volume in the order of $20 \times 10^{-7} \text{ m}^3\text{g}^{-1}$, and an average pore diameter of $20 \text{ \AA}$ is used. Experimentally, the storage capacity is found to be approximately 4 times higher than that of conventional compressed gases at near ambient temperature and at a pressure of 40 bar. The performance of the ANG storage device 11 in example embodiments is presented in terms of volume storage capacity, defined here as m^3 of gaseous fuel to the storage bed volume, V/V .

Preferably, the AC packed in the ANG storage device 11 has a suitable packing density to control transport resistance between the AC and NG molecules so as to streamline optimum charging of NG to, and discharging the NG from, the ANG storage device 11.

Preferably, the AC packed in the ANG storage device 11 is maintained with a minimal gap to the wall of the ANG storage device 11 to enhance the adsorption and desorption process in both radial and longitudinal directions.

Fig.2 (a) and 2 (b) show scanning electron micrographs (SEM) of activated carbon, which may be used with ANG storage device 11 in an embodiment, with thermophysical

properties of pore surface area greater than $3000 \text{ m}^2\text{g}^{-1}$, pore volume of $20 \times 10^{-7} \text{ m}^3\text{g}^{-1}$, and average pore diameter of $20 \text{ \AA}$. The surface structure is observed to be flake-like layers with porous voids entrenched in between. During adsorption, the adsorbate molecules could be deposited onto the vacant sites of pores by the action of van der Waals and electrostatic forces.

Returning to Fig. 1, according to embodiments of the invention, the NG is first charged into the ANG storage device 11 at cryogenic temperatures of about 120 to 130 K. The NG is allowed to emanate directly via the heat exchanger 4 from the double-wall tank 1 of LNG. No cooling sources for the solid adsorbent are advantageously instituted in a preferred embodiment even though the exothermic process of adsorption generates heat. Instead, the NG vapor at the cryogenic state is used to cool the solid adsorbent to preferably provide higher storage capacity.

An adsorption process refers to the vapor uptake with heat generation within the solid adsorbent, i.e. an exothermic process. For vapor adsorption at cryogenic temperature in example embodiments, additional cooling of the adsorbent is preferably effected by the adsorbate/vapor itself.

In embodiments of the invention, desorption of NG from the ANG storage device 11 is performed by natural degassing of the NG from the solid adsorbent using the pressure saving heatlock.

In some embodiments, the desorption process is enhanced by supplying an external heat source such as warm water from an automobile engine through a heat exchanger in the ANG storage device.

In a preferred, but non-limiting embodiment, the ANG storage device 11 comprises a finned-tube heat exchanger with the adsorbent material placed in the interstitial spaces between the finned tubes. Preferably, commercially available thick-walled copper alloy finned-tube can be used for the proposed heat exchanger inside the ANG storage device 11 for design pressure of up to 40 bar.

The NG vapor emanating directly via the heat exchanger 4 from the double-wall tank of LNG after re-gasification is regulated to near atmospheric pressure (14 to 20 psig), from which the NG is charged into the ANG storage device 11. No additional compression power may be required in some embodiments compared to conventional storage method at which the NG is compressed to respective storage pressures, i.e. 30 to 40 bar.

According to embodiments of the invention, the initial temperature and pressure of the NG after re-gasification is controlled so that the ANG storage device 11 can be tailored for the final ambient temperature and pressures.

Fig.3 shows experimental isotherm data of methane gas uptake using pitch-based activated carbon as adsorbent for embodiments of the present invention. The isotherm data are graphically plotted on a pressure-concentration-temperature ($P-q-T$) scale with a temperature range of 120 to 220 K and pressures up to 13 bar. From Fig.3, the maximum uptake capacity is observed at the lowest temperature, i.e. 120 K for all pressures even at near atmospheric pressure. Uptake capacity decreases as the temperature of solid adsorbent increases. Further, from data obtained at 120K and 140K, it can be seen that uptake capacity increases sharply with increasing system pressure when the solid adsorbent temperature is below the critical temperature (190.3K). As temperature approaches the critical temperature (at 160K and 190K) and exceeds it (at 200K and 220K), monotonic increment was observed with increase in pressure. Fig.3 can provide guidance in setting the initial temperature and pressure for charging according to embodiments of the present invention.

Fig.4 shows additional experimental isotherm data of methane gas uptake using pitch-based activated carbon as adsorbent for embodiments of the present invention. The isotherm data are graphically plotted on a pressure-concentration-temperature ($P-q-T$) scale with a temperature range of 278 to 338 K and pressures up to 25 bar. From Fig.4, the maximum uptake capacity is observed at the lowest temperature, i.e. 278 K and uptake capacity decreases with increase in solid adsorbent temperature. Also, the uptake capacity curves obtained in Fig.4 display similar trend with those shown in Fig.3; whereby the uptake capacity increases monotonically with pressure for adsorbent temperatures above the critical temperature. Fig.4 can serve as reference to the final

adsorptive storage temperature and pressure according to embodiments of the present invention.

Fig.5 summarizes the estimated volume storage capacity, defined as m^3 of gaseous fuel to the storage bed volume derived using data in Fig.3 and Fig.4. It can be seen that packing density, defined as mass (kg) of solid adsorbent to storage bed volume (m^3), is important in estimating volume storage capacity. As seen in Fig.5, the adsorptive storage capacity is $144 \text{ V}\cdot\text{V}^{-1}$ and $114 \text{ V}\cdot\text{V}^{-1}$ for packing density of $380 \text{ kg}\cdot\text{m}^{-3}$ and $300 \text{ kg}\cdot\text{m}^{-3}$, respectively; approximately 3 to 4 times higher than that of conventional compressed gas which typically has a value of $40 \text{ V}\cdot\text{V}^{-1}$ at the same conditions, i.e. at ambient temperature (25°C) and 40 bar pressure. Therefore, the method according to embodiments of the present invention can advantageously increase volume storage capacity at lower pressures compared to conventional methods relating to compressed gas.

In an example embodiment of the invention, a chart such as shown in Fig.6 showing the process path at which the natural gas is filled or charged at near critical temperatures and near atmospheric pressures may be used to determine the initial temperature and pressure. The empty circles in Fig.6 show the experimental uptake capacity at respective pressures and isotherms. On the other hand, the solid lines show the predicted uptake capacity using the adsorption model, i.e. Tóth equation.

The process path for embodiments of the adsorptive storage system is shown by the dashed arrow lines. Prior to the charging of the NG vapor to the adsorptive storage device, one decides on the final storage pressure. For example, in Fig.6, the final storage pressure is set at 40 bar and 25°C . In order to predict the initial charging pressure and temperature, first, a vertical line is drawn parallel to the y-axis, which will intersect with the isotherm curve (25°C) at point A. The horizontal lines e.g. 600, 602 will intersect with the respective isotherm curves e.g. 604, 606. Hence, the initial charging pressures and temperatures can be determined as the intersection points for the respective isotherms curves.

As one example, the NG is charged into the adsorptive storage device with an initial charging pressure at near atmospheric pressure, i.e. 1 bar for vapor temperature at -93

°C (intersection point B). When the NG is fully charged into the ANG storage device, the device is closed and is allowed to warm up to ambient temperature of 25 °C. According to the representations in Fig.6, the final gas or system pressure will be at the design pressure of 40 bar, thus, eliminating the need for compressive means such as a compressor while allowing charging to take place at 1 bar and attain the final pressure of 40 bar as designed vis-à-vis conventional charging methods which require charging to be carried out at 40 bar.

In different embodiments, the charging process may be conducted at higher than atmospheric pressure with the aid of minimal compression power.

For example, to attain the final gas or system pressure of 40 bar (design pressure) at ambient temperature of 25 °C, an initial charging pressure at 2.5 bar is used for vapor temperature at -73°C (intersection point C). Therefore, certain compressive means may be used to prepare the vapor to a pressure of 2.5 bar for charging.

Fig.7 summarizes stimulation results for a 10 liters ANG vessel according to an example embodiment containing NG vapor at the pressure range of 30 bar to near atmospheric pressure subjected to different discharging rates, i.e. different valve coefficient values (Cv). The solid adsorbent is packed in interstitial spaces of a fin- tubed heat exchanger inside the ANG vessel. Heat is supplied to the heat exchanger from a heat source during discharging. The range of valve coefficient values used is from 0.1 to 0.5, with a smaller value corresponding to a lower flow rate, i.e. higher friction in the valve. From Fig.7, it is seen that the discharging rate increases with increasing valve coefficient value. Thus, from the simulation results, it is found that discharging of natural gas can preferably be readily regulated by adjusting the valve in example embodiments, instead of using complicated means.

Figure 8 shows a flow chart 800 illustrating a method for storing NG in an adsorbent storage device according to an example embodiment. At step 802, the NG in a liquid phase is provided to a first heat exchanger. At step 804, the NG is gasified using the first heat exchanger. At step 806, the NG in the gaseous phase is fed into the adsorbent storage device.

It will be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

CLAIMS

1. A method for storing NG in an adsorbent storage device, the method comprising the steps of:

- 5 providing the NG in a liquid phase to a first heat exchanger;
gasifying the NG using the first heat exchanger; and
feeding the NG in the gaseous phase into the adsorbent storage device,
wherein the NG is gasified using the first heat exchanger such that the NG in the
gaseous phase is fed into the adsorbent storage device at a cryogenic temperature for
10 cooling of an adsorbent material of the adsorbent storage device.

2. The method as claimed in claim 1, wherein gasifying the NG using the first heat exchanger comprises cooling a liquid for heat exchange to gasify the NG.

- 15 3. The method as claimed in claim 2, further comprising using the cooled liquid for further processes.

4. The method as claimed in any one of the preceding claims, further comprising regulating a pressure of the NG in the gaseous phase for feeding into the
20 adsorbent storage device.

5. The method as claimed in claim 4, wherein the NG is fed into the adsorbent storage device at a near atmospheric pressure.

- 25 6. The method as claimed in any one of the preceding claims, wherein the NG is stored in the adsorbent storage device at a pressure in the range of 30 bar to 40 bar.

7. The method as claimed in any one of the preceding claims, wherein feeding the NG in the gaseous state into the adsorbent storage device comprises cooling an adsorbent material of the adsorbent storage device.

5 8. The method as claimed in claim 7, wherein the cooling of the adsorbent material of the adsorbent storage device uses a second heat exchanger.

9. The method as claimed in claim 8, wherein the second heat exchanger is incorporated into the adsorbent storage device.

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10. The method as claimed in any one of the preceding claims, further comprising discharging the NG from the adsorbent storage device using a pressure swing method.

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11. The method as claimed in claim 10, wherein discharging the NG from the adsorbent storage device further comprises heating an adsorbent material of the adsorbent storage device.

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12. The method as claimed in claim 11, wherein the heating of the adsorbent material of the adsorbent storage device uses the second heat exchanger.

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13. A system for storing NG, the system comprising:
a first heat exchanger for gasifying the NG;
an adsorbent storage device;
means for providing the NG in a liquid phase to the first heat exchanger; and
means for feeding the NG in the gaseous phase from the first heat exchanger into the adsorbent storage device at a cryogenic temperature for cooling of an adsorbent material of the adsorbent storage device.

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14. The system as claimed in claim 13, further comprising means for regulating a pressure of the NG in the gaseous phase for feeding into the adsorbent storage device.

15. The system as claimed in claim 13 or 14, wherein the NG is stored in the adsorbent storage device at a pressure in the range of 30 bar to 40 bar

5 16. The system as claimed in any one of claims 13 to 15, further comprising means for discharging the NG from the adsorbent storage device using a pressure swing method.

10 17. The system as claimed in any one of claims 13 to 16, further comprising a second heat exchanger for cooling or heating of an adsorbent material of the adsorbent storage device.

18. The system as claimed in claim 17, wherein the second heat exchanger is incorporated into the adsorbent storage device.