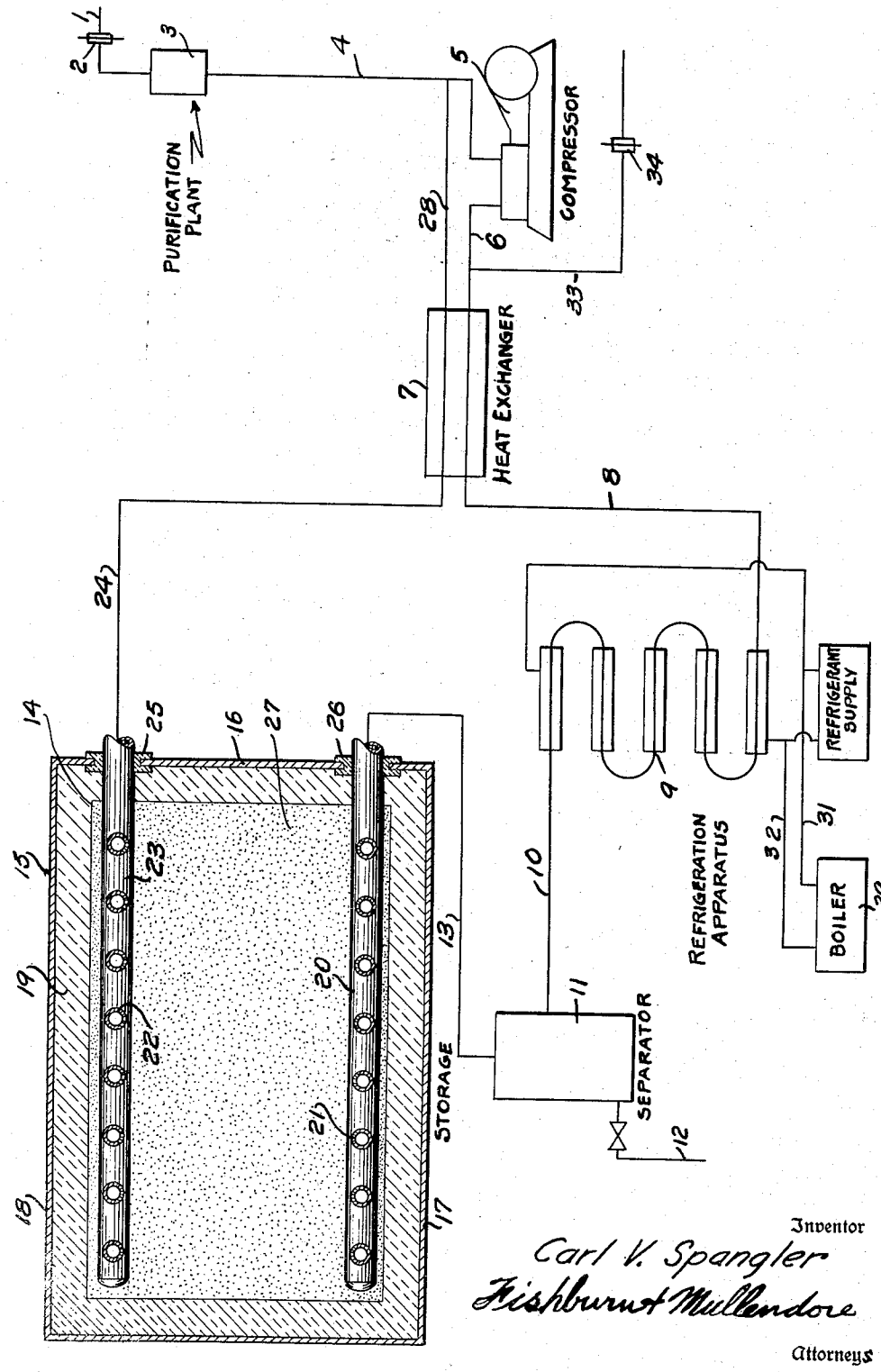
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METHOD OF STORING GASES

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METHOD OF STORING GASES

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1

This invention relates to a method of storing or stock piling of gases, for example, hydrocarbon gases such as propane, methane or natural gas such as the commercial pipe line gas which is now distributed on almost a nation-wide basis; the principal object being the provision of a practical, safe and economical storage of such gas through adsorption by a solid adsorbent material at relatively low pressures and at a temperature conveniently above liquefaction temperature of methane.

It is also an object of the invention to provide for release of the adsorbed gas when the gas is desired for use or to augment the flow volume in a pipe line at times of high demand.

In accomplishing these and other objects of the invention hereinafter described, I have provided an improved method and apparatus which is diagrammatically illustrated in the accompanying drawing wherein:

1 designates a pipe line leading from a supply of natural gas, for example, a commercial high pressure gas transportion system by which natural gas is conveyed from a field of production to a market which may be many miles from the source of supply. Profitable operation of such systems depend upon substantially full pipe line flow. Consequently, during times of low demand for the gas, adequate storage must be provided for the surplus gas which is made available for augmenting the pipe line flow during times of high market demand. This storage gas may be taken at the start of the transportation system and at various points along the length of the line where it is convenient to remove and store the gas. It is therefore to be understood that the pipe line 1 merely connects a source for the gas to be stored in accordance with the present invention. It is also to be understood that such gas is substantially methane although pipe line gas in addition to normal impurities may contain carbon dioxide, nitrogen, traces of the rare gases such as helium, argon, etc., limited amounts of vapor or gas of the heavier hydrocarbons such as ethane, propane, butanes, pentanes, etc. which are not removed from it completely in commercial practice. Essentially, however, the major flow is methane and therefore in the present description the terms methane and natural gas are used synonomously.

I have discovered that methane can be adsorbed as an adsorbate on adsorbent materials at temperatures near its liquefaction temperature in sufficient amounts to make such storage system commercially practical.

2

In carrying out the invention the gas to be stored is brought from the line 1 into the storage system through an orifice meter indicated at 2 and passed through a purification plant 3 in which all traces of vapor phase moisture is removed from the gas together with any possible carbon dioxide, hydrogen sulfide, or other acid gases which may be mixed in the main gas supply as impurities.

After purification the gas passes through a pipe 4 to a compressor 5 by which the gas is conducted through a pipe 6 to a heat exchanger 7 in which the gas is prechilled prior to discharge through a pipe 8 to a refrigerating apparatus 9. The refrigeration apparatus may be of any suitable type and utilize various methods of refrigeration depending upon the individual situation. The temperature of the gas as it leaves the refrigeration system will be just above the liquefaction temperature of the methane at the operating pressure. I have determined that a practical operating temperature range is from substantially —160° C. to substantially —147° C. The refrigerated gas is then conducted through a pipe 10 to a separator 11 wherein those materials which have been liquefied or solidified are separated together with any liquid methane that may have formed in the refrigeration process. The liquid so removed will be taken out through a pipe 12 to a separate outside storage system (not shown) and will not enter into any processing embodying the present invention. The vapor phase methane that is left in the system is chilled almost to liquefaction temperature and is conducted through a pipe 13 to the adsorbent container 14 wherein the methane cools the adsorbent bed and by continuous re-circulation eventually becomes an integral part of the solid adsorbent material by adsorption thereon.

The storage constitutes a vessel 15 of ample capacity to contain the required amount of material to adsorb the volume of gas to be stored. The vessel may be of any suitable shape, for example, it may comprise a circular side wall 16, a bottom 17 and a top 18 constructed with substantially tight joints to prevent direct leakage into and out of the vessel. The vessel is completely insulated preferably by lining all the interior surfaces with an insulating material 19 sufficient to maintain the desired low temperature of the methane. With this method of insulation, the walls of the vessel are protected from becoming friable and structurally unsafe at the extremely low temperatures involved. Therefore, special expensive alloys and construction are not re-

quired as in cases where the metal is in direct contact with low temperatures. In fact, such tanks as now used for large oil or gas storage might be used with modifications for handling the materials herein involved. It is important, however, that the thickness and nature of the insulating material be selected as the best available for the duty. Suitable insulating materials are readily obtained which have adequate strength, thermal capacities and general physical and chemical qualifications for the duty described. It is also desirable to select an insulation that is resistant to abrasion by the adsorbing material. Such materials need only protection from the weather, which function is supplied by the container.

The gas from the separator is discharged into the vessel through a duct distribution system which in the illustrated instance comprises a header 20 which connects the inlet pipe with a plurality of distribution ducts 21 having perforations through which the gas is distributed substantially uniformly over the horizontal cross sectional area of the vessel.

A similar collection system of perforate ducts 22 is located under the roof insulation and connected by a header 23 with a discharge pipe 24. The header systems are formed of a suitable material to withstand the temperatures involved. Since the header systems are cooled by the gas passing therethrough, insulating seals 25 and 26 are required where the pipes pass through the walls of the vessel.

Filling the space within the vessel is a body of solid adsorbent material 27. The adsorbent material is allowed to rest directly on the insulating material on the bottom of the vessel and to fill out against the sides. In turn the insulation across the top of the vessel and above the adsorbent material rests directly on the bed of adsorbent. In order to take advantage of possible physical characteristics of either insulation or adsorbent material, structural props or supports might be supplied if needed to take or distribute some of the stress.

In case an insulating material is used requiring some support for the adsorbent, a thin sheet metal sheathing may be used to protect the insulation from abrasion by the solid adsorbent as a protection against physical damage during filling, construction or maintenance operations. Such sheathing would not be installed as a pressure vessel but is perforated to allow free passage of gas into the insulation so that the sheathing would not collapse under differential pressure during operation.

The adsorbent 27 may comprise one or a mixture of two or more of the well-known adsorbent materials such as an adsorbent clay, attapulgite, fuller's earth, activated carbons and charcoals, bauxites, aluminas, calcium sulfate, silica or alumina gels, etc. These materials are all solids and may be prepared for use in a variety of ways.

In operation, the adsorbent material is cooled by the methane gas entering the storage vessel and the methane is adapted to be adsorbed in progressively increasing amount by recycling the gas. Unadsorbed gas is discharged from the storage vessel through the discharge system and is returned to the heat exchanger 7 through the pipe 28 for heat exchange with the incoming gas to precool the incoming gas. The unadsorbed gas after passing through the heat exchanger is discharged through a pipe 29 which connects with the pipe 5 on the suction side of the compressor.

The unadsorbed gas is thus mixed with the incoming gas and is recirculated through the system. Passage of the unadsorbed gas through the adsorbent bed reduces the temperature of the adsorbent 27 by removal of sensible heat from the adsorbent bed and removal of latent heat of adsorption, the heat being carried away by the gas which is drawn off for recirculation through the refrigeration system. Progressively, the adsorbent material will gradually be chilled down to a temperature approaching the inlet methane temperature. The lower the temperature of the adsorbent bed the more methane it will adsorb up to its indicated maximum capacity.

When it becomes necessary and desirable to use the gas in storage, a warm methane or natural gas is circulated by the compressor 5 through the heat exchanger 7 and through the refrigeration apparatus 9 which is now used as a heater to increase the temperature of the circulated gas. The refrigeration apparatus is converted to a heating system by circulating therethrough in heat exchange relation with the gas, heat from a source of supply indicated at 29 which might be a steam boiler plant, the steam being circulated through the pipe connections 31 and 32 with the refrigerating coil. The heated gas is then passed through or around the separator column 11 (which now has no function) and into and through the adsorbent storage bed through the distribution duct 21. On passing through the adsorbent bed the comparatively warm gas adds heat to it, raising the temperature thereof, adding sensible heat to the adsorbent, and furnishing the latent heat of desorption for the methane adsorbate, thus effecting its release as a free vapor or gas. The desorbed gas thus freed is led out through the heat exchanger 7 and compressor 5 for release through an orifice meter 34 and delivery pipe 33 for repressuring the gas supply in a pipe line or for use as desired.

In addition to storage of methane, the invention involves separation of methane and/or other hydrocarbons in natural gas, from nitrogen which, as above stated, occurs in the natural gas in variable amounts from certain natural gas field sources. The nitrogen not being combustible and having no heat value decreases the B. t. u. value of the natural gas mixture on a volume basis. Therefore, nitrogen is usually and justly regarded as an undesirable dilutent or impurity. To avoid the expense of handling the nitrogen through a pipe line transmission and distribution system, the nitrogen should be removed.

I have found that nitrogen and methane as a natural gas mixture can be separated by means of the adsorbent bed when the gas mixture is passed through the bed of solid adsorbent with both the mixture and the adsorbent bed at temperatures just above the liquefaction temperature of methane at the contact pressure. Under these temperature conditions, the methane is adsorbed on the adsorbent as an adsorbate, but the nitrogen is adsorbed to a lesser extent as shown in Example 4 hereinafter included and the unadsorbed nitrogen passes through the adsorbent bed as a free gas. The nitrogen so released can then be disposed of as required under the operating conditions, if it has no further value.

After processing a methane-nitrogen natural gas mixture as described, the adsorbent eventually becomes saturated with the methane adsorbate, and no longer removes methane from the gas mixture under circulation.

The valuable methane adsorbate can be recovered from the adsorbent when needed by circulating gas through the adsorbent bed at a temperature higher than the separation or adsorbing temperature in the same manner as previously described.

Attention is directed to the fact that it is possible and practical to desorb at a changed pressure than the adsorption pressure, thus altering the equilibrium to desorb at a more favorable temperature, however, under normal operating conditions desorption would be accomplished at adsorption pressure.

If the container of the adsorbent should rupture and the adsorbent spill out on the ground it will not flow as a liquid nor will the gas escape rapidly as a free gas. The adsorbent will merely accumulate in a pile as a solid at the location where it is spilled. On exposure to atmospheric temperatures, the methane will escape slowly as a gas from the pile of solid material. This is because the latent heat of desorption required to release the gas from the adsorbent as vapor must be obtained from the atmosphere or other source. This effect or flow of heat is retarded since the comparatively low temperature of the solid material causes the atmospheric moisture to condense thereon as frost or ice, thus insulating the material from further increase of temperature or heat input from atmosphere which slows down escape or vaporization of the gas.

The results are given by the following examples:

Example 1

Results on the adsorption of the adsorbate methane, on the adsorbent attapulgite (activated at 316° C., 30/60 mesh):

Temperature in degrees Centigrade	Capacity of adsorbent for adsorbate methane, CH_4, at 800 mm. Hg pressure
+25° C.	16.5 ml./gram.
−160° C.	340 ml./gram.

Example 2

Results on the adsorption of the adsorbate methane on the adsorbent carbon (commercial sample, 20/60 mesh):

Temperature in degrees Centigrade	Capacity of adsorbent for adsorbate methane, CH_4, at 800 mm. Hg pressure
+25° C.	17.7 ml./gram.
−159° C.	335 ml./gram.

Example 3

Results on the adsorption of the adsorbate methane, on the adsorbent bauxite (activated 1100° F. 20/60 mesh):

Temperature in degrees Centigrade	Capacity of adsorbent for adsorbate methane, CH_4, at 800 mm. Hg pressure
+25° C.	12.0 ml./gram.
−158° C.	145 ml./gram.

Example 4

Comparison of results on the adsorption of methane CH_4 and nitrogen N_2, on the adsorbent attapulgite (activated at 316° C. 30/60 mesh):

Temperature in degrees Centigrade	Capacity of adsorbent for adsorbate at 800 mm. Hg pressure
Methane, +25° C.	16.5 ml./gram.
Methane, −160° C.	340 ml./gram.
Nitrogen, +25° C.	17.4 ml./gram.
Nitrogen, −155° C.	21.1 ml./gram.

It is to be emphasized that the drawing is schematic and has been made as simple as possible for illustrative purposes and it is obvious that various bypasses, automatic controls, valves, etc. are used to obtain the most advantageous heat balance and design consistent with economics, engineering, local gas pressures and temperatures and other attendant local gas pressures and temperatures. Such additions, however, will not change the principles of the invention as herein described.

From the foregoing it is obvious that I have provided a practical, safe and economical method of storing methane or natural gas through adsorption by a solid adsorbent material at relatively low pressures and temperature conveniently above the liquefaction temperature of methane. It is also obvious that the adsorbed gas is readily released for use when it is desired to augment the flow volume in a pipe line at times of high demand for gas.

While I have specifically illustrated and described the adaptation of my invention to the storage and stock piling of natural gas, it is obvious that other gases may be stored in like manner by maintaining temperature suitable for holding the gas as an adsorbate in an adsorbent material.

What I claim and desire to secure by Letters Patent is:

1. The method of storing a high pressure natural gas on a solid adsorbent material and releasing the gas from storage when needed including cooling the gas to a temperature above the liquefaction temperature of the gas, bringing the cooled gas into contact with a solid adsorbent material to effect adsorption of the gas on said material, maintaining the adsorbent material at a temperature for holding the adsorbed gas as an adsorbate in said material, heating the natural gas when storage gas is needed, passing the heated natural gas to the place of adsorption to release the adsorbed gas, and mixing the released gas with the heated natural gas.

2. The method of storing a high pressure natural gas on a solid adsorbent material including cooling the gas to a temperature above the liquefaction temperature of the gas, bringing the cooled gas into contact with a solid adsorbent material to effect adsorption of the gas on said material, recirculating unadsorbed gas to the place of cooling, and returning the unadsorbed gas to the place of adsorption to maintain adsorbent at a temperature for holding the adsorbed gas as an adsorbate in said material.

3. The method of storing a high pressure natural gas on a solid adsorbent material including cooling the gas to a temperature above the liquefaction temperature of the gas, bringing the cooled gas into contact with a solid adsorbent material to effect adsorption of the gas on said material, removing unadsorbed gas from the place of adsorption, bringing the unadsorbed gas into heat exchange relation with incoming warm gas,

mixing said removed gas with the incoming gas, cooling said mixture and passing the cooled mixture into contact with the adsorbent material to effect adsorption of additional gas, and maintaining temperature of the adsorbent material at the place of adsorption to hold the adsorbed gas as an adsorbate in said material.

4. The method of separating and storing a gas component of a mixed gas stream on a solid adsorbent material including cooling said gas stream to a temperature above the liquefaction temperature of said component gas to be separated and stored, bringing the gas stream into contact with a solid adsorbent material to effect adsorption of said component gas on said material, removing unadsorbed gas from the place of adsorption, bringing the unadsorbed gas into heat exchange relation with the incoming gas stream, mixing the unadsorbed gas with the incoming gas stream, cooling said mixture and passing the cooled mixture into contact with the adsorbent material to effect additional adsorption of said component, and maintaining temperature of the adsorbent material to hold the adsorbed component gas as an adsorbate in said material.

5. The method of separating and storing the methane content of natural gas on a solid adsorbent material including cooling the natural gas to a temperature just above the liquefaction temperature of the methane content of the gas at storage pressure, bringing the natural gas into contact with a solid adsorbent material to effect adsorption of the methane on said material, removing unadsorbed gas from the place of adsorption, bringing the unadsorbed gas into heat exchange relation with incoming warm natural gas, mixing the unadsorbed gas with the incoming natural gas, cooling said mixture and passing the cooled mixture into contact with the

adsorbent material to effect adsorption of additional methane, and maintaining temperature of the adsorbent material to hold the adsorbed methane as an adsorbate in said material at storage pressure.

6. The method of storing natural gas on a solid adsorbent material and releasing the natural gas from storage when needed for use including cooling the gas to a temperature just above the liquefaction temperature of the gas, bringing the gas into contact with a solid adsorbent material to effect adsorption of the gas on said material, recirculating unadsorbed gas to the place of cooling, returning the unadsorbed gas to the place of adsorption to maintain adsorbent at a temperature for holding the adsorbed gas as an adsorbate in said material while in storage, and heating the adsorbent material to release the adsorbed gas when the gas is needed for use.

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