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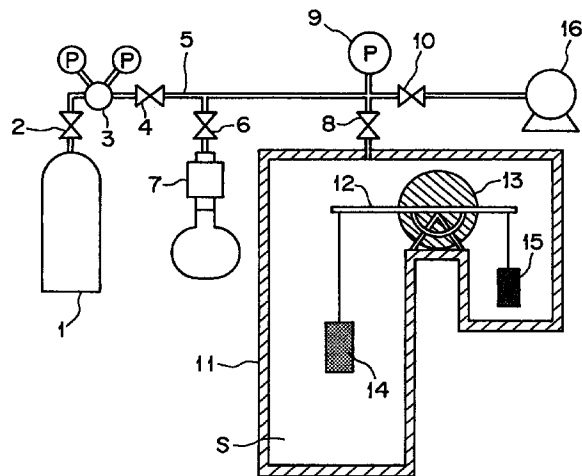
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(54) Method for utilization of material comprising a hydrate-like product of gases and tank therefor

(57) The invention relates to a method of and a tank for utilizing a material comprising a porous material (14, 20, 27), a host compound, such as water, and one or more lower hydrocarbons serving as guest compound wherein a novel and beneficial hydrate-like matter of the lower hydrocarbons are formed inside the fine pores of the porous material (14, 20, 27). The invention is applicable to a method of supplying city gas, a method of controlling a feed of city gas, a city gas tank for supplying city gas or controlling a feed of city gas, a portable and replaceable fuel gas tank, a fuel gas tank for automobile, and the like by utilizing the formation action of the material containing the hydrate-like matter of lower hydrocarbons inside the fine pores of the porous material (14, 20, 27) and the separation and release action of the lower hydrocarbons from the material.

FIG. 1



Description

This intention relates to a method for utilization of a material comprising a novel and useful hydrate-like matter of gases and a tank therefor. Particularly, the invention relates to a method for utilizing a material of the type which comprises a porous material, a host compound, such as water, and one or more guest compounds made of lower hydrocarbons so that the material contains a hydrate-like matter of the lower hydrocarbons inside the fine pores of the porous material and a tank therefor. Further, the invention relates to a method for utilization of a high-density methane hydrate formed inside the fine pores of a porous material, and to a tank therefor.

More particularly, the invention relates various methods indicated under (1) to (7) below and tanks therefor wherein the action of forming a material comprising the hydrate-like matter of a lower hydrocarbon inside the fine pores of the porous material, and the action of separating and releasing the lower hydrocarbon from the formed material are utilized.

(1) The invention relates to a method of supplying city gas, a method of controlling the feed of city gas, and a city gas tank therefor.

(2) The invention relates to a method of normally or in emergency supplying fuel gas, such as city gas, petroleum gas or the like, to individual consumers, and also to fuel gas tank therefor.

(3) The invention relates to a method of normally or emergently supplying fuel gas, such as city gas, petroleum gas or the like, to gas turbines or gas engines for driving electric generators assembled in cogeneration systems, and also to a fuel gas tank therefor.

(4) The invention relates to a portable and replaceable fuel gas tank wherein various types of gases, such as methane, ethane, ethylene, propane, butane and the like lower hydrocarbons, natural gas, and city gas, can be adsorbed to and filled in porous materials simply in large amounts, and can be released as required.

(5) The invention relates to a fuel gas tank for automobiles capable of causing a large amount of a fuel gas for automobiles, particularly methane or a fuel gas (natural gas or the like) composed mainly of methane, to be adsorbed to the porous material, and also to a fuel gas stand for automobiles in which the gas tank is arranged.

(6) The intention relates to a method of transporting natural gas from its exploitation base to an acceptance base by land or sea, a method of transporting a large amount of natural gas from the acceptance base to delivery base tanks by land, and a method of transporting natural gas in an energy-saving and economical manner without resorting to conventional LNG ship or LNG tank truck.

(7) The invention also related to a method of transporting a large amount of petroleum gas generated in oil wells or petrochemical complexes, and also to a method of transporting the petroleum gas in an energy-saving and economical manner without resorting to conventional LNG ship or LNG tank truck.

In recent years attention has been drawn, as an energy source or starting material for various syntheses, to methane, ethane, propane, butane and the like lower hydrocarbons or mixtures thereof, natural gas (NG) or petroleum gas (PG). However, these are gaseous in nature, so that close attention should be paid thereto with respect to their handling. Gas in a gaseous state has a very large volume and a low specific gravity. Consequently, methods of increasing a density of gas have been adopted in order to improve storage and transportation efficiencies, for example, in storing and transporting gas by compression.

Such methods include (1) a method of compressing gas under high pressure (high pressure compression method), and (2) a method of cooling and liquefying gas as seen in the case of liquid nitrogen, liquid oxygen, or liquefied natural gas (LNG) or liquefied petroleum gas (LPG) (liquefaction-by-cooling method).

However, the high pressure compression method referred to under (1) above not only requires means of compressing gas under high pressure, but also a high pressure gas cylinder as a storage container. Sufficient pressure-resistant strength is required of containers, so that the method has a drawback that the weight of a container becomes very large in comparison with the weight of gas to be stored. In Japan, for example, in case of a gas pressure exceeding 10.68 atm (equivalent to 10 kg/cm² by gauge pressure), materials, facilities, pipings and the like meeting specifications specified under the regulations for the control of high pressure gas are required, causing the method to become costly as a result.

In the method referred to under (2) above, gas needs to be compressed, and cooled for liquefaction thereof, not only resulting in high cost, but also requiring separate and special facilities to keep the liquefied gas cooled. Furthermore, similar to the method (1) as above, this method is subject to regulatory constraints. Under the circumstances, viable application of this method is limited to high-valued gas, such as helium, or LNG or LPG in which economies of scale can be realized.

Besides, the methods referred to under (3) to (6) below have also been proposed including (3) a method wherein gas is adsorbed to the surfaces of a solid adsorbent such as silica gel, active carbon or the like (JP-A- 49-104213, and JP-A- 6-55067), (4) a method using a storage alloy of hydrogen or the like, or a method using combinations of a hydrogen storage alloy and an adsorbent (JP-A-4-131598), (5) a method utilizing chemical reaction occurring on the surface

of a solid substance accompanied by decomposition of methane (JP-A- 59-197699), and (6) a method wherein hydrocarbon gas containing methane or ethane as a main constituent is brought into contact with water in the presence of aliphatic amine, thereby utilizing the gas hydrate ((JP-A- 54-135708).

5 In the method (3) above wherein gas is stored through physical adsorption to the solid surfaces, a phenomenon of equilibrium with pressure is utilized. As a result, its adsorption speed is slow, and appreciable pressurization of gas is required to obtain a sufficient amount of adsorption. According to this method, gas can be stored at a pressure lower than that for the above-mentioned method using a high pressure cylinder. Still, a pressure at 10.68 atm (equivalent to 10 kg/cm² by gauge pressure) is normally required.

10 In the method (4) above, if gas to be stored is, for example, hydrogen, its storing material has to be, for example, palladium or its alloy. Thus, a suitable storage material is limited to specific materials on the basis of nearly one-to-one relation with the gas to be stored, and further, a cost of the method becomes higher since the storage material is of a specific type and expensive. In addition, meticulous care needs to be exercised in handling of the storage material because of a tendency of embrittlement thereof when used repeatedly.

15 Similar to the case of the method (4), the method referred to under (5) above has a problem that a kind of gas to be stored is limited, and a material required for storage is of a special type and expensive. Then, in the case of the method (6), it is of a gas-liquid contact type, and therefore, its effect is largely dependent on a gas-liquid contact efficiency, with the attendant problem that an amount of gas actually stored is substantially lower than an amount anticipated on a theoretical basis.

20 Among various types of gases, city gas is prepared in a city gas-making plant using LNG or the like as starting material, for example, and is supplied to individual users via gas supply pipes. In this case, the amount of city gas being supplied to individual consumers varies seasonally or daily. To this end, scrupulous care should be paid in order to conform the capabilities of the city gas-making plant and the supply pipes to the varying amount of the gas being supplied so that a maximum demand of city gas can be met.

25 However, where LNG is used as main starting material of city gas, storage facilities of LNG in the city gas preparation plant should be ones whose capacity meets a peak demand in winter, and a cost therefor becomes immense. In the case of city gas supply pipes, high pressure-resistant piping is, for example, necessary for meeting a maximum demand, and a cost thereof becomes high.

30 Where the supply of city gas to individual consumers is temporarily stopped at the time of accidents such as earthquake or by piping work of gas in a short period, any special gas supplying method has never been used conventionally. To cope with this situation, simple portable gas heaters or oil heaters have to be inconveniently employed.

35 From the environmental and energy-saving standpoint, electricity-generating facilities; in which gas turbines or gas engines are employed by use of gas fuel therefore, are utilized in cogeneration systems provided with the function of recovering waste heat from combustion exhaust. The cogeneration system has been adopted in production plants, buildings such as for offices, hospitals and the like, and waste heat of combustion exhaust gas can be effectively utilized along with generated electric power.

40 A gas fuel, such as city gas, is normally used as fuel for normal operation of a generator in the cogeneration system. At the time of suspending the supply of city gas in an emergency such as by earthquake, the fuel is changed over to a liquid fuel such as heavy oil, kerosine or the like, thereby ensuring the operation at that time. The use of a liquid fuel not only requires a separate tank for the liquid fuel and separate facilities including a piping and a burner for exclusive use, but also results in a factor of increasing a cost. Further, the use of liquid fuel causes an operation control system and its handling to be complicated. The duration time of the electric generation is usually as short as around two hours although depending on the capacity of a fuel storage tank. When the stop of city gas supply continues over a long time, the liquid fuel has to be often supplemented.

45 A gas fan-forced heater for heating a room is advantageous in that it is able to heat quickly, lightweight and portable, and is now in the mainstream of gas heating. However, a gas fuel has to be fed to the gas fan-forced heater, a separate pipe is essential. Accordingly, such a heater cannot be used in a room which is free of any pipe or stopcock. This is true of gas heaters. On the other hand, oil fan-forced heaters and oil heaters have a problem on the feed of oil fuel in liquid form and also on an offensive odor thereof.

50 The gas fuel mainly composed of methane, such as natural gas, city gas or the like, is clean and generates only a small amount of carbon dioxide, and attention has been drawn to automobiles making use of these gas fuels as power source. However, the fuel gas is filled in a tank according to a high pressure compression method, in which it is required to pressurize the fuel gas in the tank, thus needing a high pressure container. Moreover, where a high pressure container is mounted in automobiles, not only the pressure resistance, but also strength sufficient to withstand tossing and impact occurring during the running of an automobile is required of the container, resulting in a very great weight thereof.

55 In case where a large amount of natural gas or petroleum gas is transported to a distant place, especially, to an area where pipelines are not arranged fully, the transport efficiency becomes poor if it is in gaseous form. Conventionally, the gas is liquefied according to a liquefying-by-cooling method and transported in the form of LNG or LPG. For

instance, for the transport of natural gas the gas is exploited from an oil well at an exploitation base, liquefied by use of liquefaction facilities and stored in the form of LNG. This LNG is conveyed to an acceptance base by means of LNG ship equipped with a special construction capable of pressurization and cold storage of LNG. The acceptance base is provided with a pier for LNG exclusive use which permits a giant ship to come alongside and which has shipping and discharging facilities, followed by transfer of LNG to an acceptance tank provided with an overland pressurizing and heat-insulating function where it is stored.

The transport of LNG from the acceptance tank to inland areas, where LNG is employed as city gas, is such that LNG is transmitted from the acceptance tank via pipelines or LNG tank lorries to LNG tanks of city gas-making plants, and supplied to individual consumers through the respective pipeline networks.

The LNG tank lorry used is one which is provided with a pressurizing and heat-insulating function and is exclusively used for LNG. The tank lorry is charged with LNG at the acceptance base, and the LNG is transported to a satellite base along the route described in the public peace regulations.

However, the liquefaction and transport of natural gas involves an extremely large energy consumption necessary for compressing and cooling the gas for liquefaction, and needs an additional energy for transport and heat insulating during the storage, presenting the problem that the energy consumption is very great as a whole. In addition, the handling and storage of liquefied gas needs facilities and apparatuses required in conformity with the security regulations, resulting in a great burden with respect to facility investment and operation costs.

Many problems conventionally involved in the handlings, i.e. a storing method, a transporting method, a supplying method and a method controlling its feed, of lower hydrocarbons such as methane, ethane, ethylene, propane, butane and the like, natural gas and city gas each mainly composed of methane, or other gases such as petroleum gas, have been discussed hereinabove.

It is known that a lower hydrocarbon, e.g. methane, forms a clathrate compound with water, that is, a methane hydrate, under high pressure at low temperature. The methane hydrate consists of water and methane which do not react with each other under ordinary conditions, and the formation thereof requires, for example, a high pressure of not less than around 80 MPa at a temperature of 303 K. In view of its structure, the methane clathrate is a very unstable substance and has to be handled while avoiding its decomposition, thus being very troublesome.

We have found unexpectedly in the light of the above-mentioned prior art knowledge or technology pertaining to methane hydrate and the like that when a porous material, such as active carbon or ceramics, is caused to exist in addition to a host compound such as water and a guest compound, i.e. a lower hydrocarbon such as methane, ethane, propane, butane or the like, there can be obtained a hydrate-like matter containing a large amount of the lower hydrocarbon in the fine pores of the porous material. Further, it has also been found that the hydrate-like matter is structurally stable and is readily decomposed and removed by application of heat or the like to release a lower hydrocarbon in gaseous form.

Furthermore, we have found that when a porous material, such as active carbon or ceramics, is caused to exist along with water and methane, there can be obtained a high-density methane hydrate containing a large amount of methane in the fine pores of the porous material, and the methane hydrate is structurally stable and is readily decomposed and separated by application of heat or the like to release methane gas.

According to the invention, a porous material, a compound serving as host, such as water, and a lower hydrocarbon are brought in contact with one another under mild conditions at or close to ordinary temperature under or close to ordinary pressure, thereby forming a hydrate-like matter composed of the porous material, the host compound, such as water, and the lower hydrocarbon. In the formation, a large volume of the lower hydrocarbon equivalent, for example, to not less than 180 times (converted to the standard state basis) an unit volume of the porous material can be taken therein within a very short time. In this way, the formation of the material containing a hydrate-like product of the lower hydrocarbon in the fine pores of the porous material does not need any separate, special cooling device or any special pressurizing facilities.

As having set out before, known methane hydrate is a substance which is structurally very unstable, and has to be handled while avoiding its decomposition. In view of the above fact, the hydrate-like matter of the lower hydrocarbon obtained in the present invention is beyond expectation. Further, it has also been unexpected at all that the hydrate-like matter of the lower hydrocarbon is formed under mild conditions at or close to ordinary temperature and under or close to ordinary pressure according to the invention on comparison with the fact that a conventional manner of forming methane hydrate needs high pressure.

In the practice of the invention, the various problems involved in the handlings, i.e. the manners of storage, transport, supply and feed control, of gases such as lower hydrocarbons including methane, ethane, ethylene, propane, butane and the like, mixtures thereof, natural gas and city gas mainly composed of methane, and petroleum gas, can be solved at a stroke by utilizing the action of forming a material containing a hydrate-like matter of a lower hydrocarbon inside the fine pores of a porous material in the presence of a host compound, the action of separating the lower hydrocarbon from the formed material, and the action of releasing the lower hydrocarbon.

It will be noted that in USP 5, 473, 904, a method of forming a clathrate hydrate is described wherein while water

is cooled to a temperature lower than that of a gas-water-hydrate equilibrium curve, and a gas such as methane, ethane or the like is supercooled, the hydrate-forming gas and water are combined to form the clathrate-hydrate. However, in this technique, no porous material is caused to exist as in the present invention, making mere mention of an improvement in prior-art method of forming hydrate.

5

(1) The invention provides a method of supplying city gas, characterized by comprising arranging city gas tanks at city gas-making plants or city gas supplying bases, or on the way of city gas feed pipes wherein, in each city gas, a porous material is accommodated, and is caused to be adsorbed with the city gas in the presence of a compound serving as host.

10

(2) The invention provides a method of controlling a feed of city gas, characterized by comprising arranging city gas tanks at city gas-making plants or city gas supplying bases or on the way of city gas feed pipes, wherein in each city gas tank, a porous material is accommodated, and is caused to be adsorbed with the city gas in the presence of a compound serving as host, and controlling a feed of city gas.

15

(3) The invention provides a city gas tank for supplying city gas or controlling a feed of city gas, characterized by accommodating a porous material in a container, and causing a city gas to be adsorbed to the porous material in the presence of a compound serving as host.

20

(4) The invention provides a method of supplying a fuel gas for individual consumers, characterized by comprising providing a fuel gas tank between a flowmeter and emergency shut-off switch and a check valve via a branch pipe in a fuel gas pipe for individual consumer wherein a porous material is placed in the fuel gas tank which has been caused to be adsorbed with a fuel gas containing one or more lower hydrocarbon selected from methane, ethane, ethylene, propane and butane in presence of a compound serving as host of the fuel gas beforehand, connecting the fuel gas tank to the branch pipe via a pressure control valve, and releasing and supplying the fuel gas from the tank normally or in emergency.

25

(5) The invention provides a method of normally supplying a fuel gas to a gas turbine or gas engine for generator in a cogeneration system, characterized by comprising placing a porous material in a fuel gas tank, causing a fuel gas comprising one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in presence of a compound serving as host to be adsorbed to the porous material, and normally supplying the thus adsorbed fuel gas to a gas turbine or gas engine for generator in a cogeneration system.

30

(6) The invention provides a method of supplying a fuel gas to a gas turbine or gas engine for generator in a cogeneration system in an emergency, characterized by comprising placing a porous material in a fuel gas tank, causing a fuel gas comprising one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in presence of a compound serving as host to be adsorbed to the porous material, and supplying the thus adsorbed fuel gas to a gas turbine or gas engine for generator in a cogeneration system in case of emergency.

35

(7) The invention provides a portable, replaceable fuel gas tank, characterized by placing a porous material in a container, and causing a fuel gas consisting essentially of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in presence of a compound serving as host to be adsorbed to the porous material.

40

(8) The invention provides a fuel gas tank for automobiles, characterized by placing a porous material in a container, and causing a fuel gas consisting essentially of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in presence of a compound serving as host to be adsorbed to the porous material.

45

(9) The invention provides a fuel gas stand for automobiles, characterized by arranging a fuel gas tank for automobiles wherein a porous material is placed in the fuel gas tank, and causing a fuel gas consisting essentially of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane to be adsorbed to the porous material in the presence of a compound serving as host.

50

(10) The invention provides a gas stand for automobiles, characterized by comprising a storage tank of a fuel gas consisting essentially of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane to be adsorbed to the porous material in the presence of a compound serving as host, a pipe connected thereto, and a mechanism for feeding a compound serving as host for the fuel gas.

(11) The invention provides a method of transporting a large amount of natural gas or petroleum gas, characterized by comprising placing a porous material in a container, causing a large amount of natural gas or petroleum gas to be adsorbed to the porous material, and transporting the container through automobile, railway or ship.

55

The drawings show the principle and preferred embodiments of the invention and should not be construed as limiting the invention.

Fig. 1 is a schematic view showing an experimental or making apparatus used in Examples 1 to 3;

Fig. 2 is a graph showing variation with time in the amount of methane adsorbed to 1 g of ACF in the presence of

water in comparison with the variation when methane was brought straight in contact with ACF without presence of water (at a temperature of 303 K under a pressure of 0.2 atm);

Fig. 3 is a graph showing variation under different pressures in the amount of methane adsorbed to 1 g of ACF, comparing the case conducted in the presence of water with the case of methane being brought straight in contact with ACF (at a temperature of 303 K under 0 to 2000 kPa);

Fig. 4 is a graph showing variation under different pressures in the amount of methane adsorbed to 1 g of ACF, comparing the case conducted in the presence of water with the case of methane being brought straight in contact with the active carbon (at a temperature of 303 K under 0 to 40 kPa);

Fig. 5 is a schematic view showing an apparatus of making a material of the invention;

Figs. 6(a) and 6(b) are, respectively, sectional views showing a tank of supplying city gas and city gas tank of controlling the feed of city gas according to embodiments of the invention;

Figs. 7(a) to 7(e) are, respectively, sectional views showing different types of tanks of supplying city gas and city gas tank of controlling the feed of city gas according to further embodiments of the invention;

Fig. 8 is a sectional view showing a modification of the tank of Fig. 7(e);

Fig. 9 is a sectional view showing another modification of the tank of Fig. 7(e);

Fig. 10 is a schematic view showing an arrangement of city gas tanks installed in or along with a city gas-making plant or a satellite base (supply base) or placed on the way of a city gas supply main line or branch lines;

Fig. 11 is a schematic view showing a city gas tank arranged in or along with a city gas supply main line or branch line;

Fig. 12 is a view showing normal or emergent supply of city gas against individual consumers;

Fig. 13 is a view showing normal or emergent supply of a fuel gas, such as city gas, to a gas turbine or gas engine for driving generators assembled in a cogeneration system such as of production plants, office buildings, hospitals and the like;

Fig. 14 is a schematic view showing a conventional gas fan-forced heater utilizing the Bunsen combustion of city gas; and

Fig. 15 is a schematic view showing an example of connecting a portable, replaceable fuel gas tank to a fuel gas supply pipe of a gas fan-forced heater as shown in Fig. 14.

We have found that, where a lower hydrocarbon is, for example, methane, a material comprising a hydrate-like matter of the lower hydrocarbon is obtained inside the fine pores of a porous material wherein the compositional ratio between methane and water in the hydrate-like matter ranges 0.5 to 1.5: 1. We have also found that a high-density methane hydrate having a compositional ratio between methane and water of 0.5 to 1.5:1 and formed in the fine pores of the porous material is obtained. Similar results are obtained when using lower hydrocarbons other than methane.

The porous materials are not critical provided that they are porous materials having fine pores and have a large specific surface area. Solid materials having microfine holes are used. Preferably, porous materials having microfine holes with a pore size of several nanometers to several tens nanometers and a specific surface area of 100 m²/g or above are used.

Examples of the porous materials include active carbon, ceramics, activated clay, and the like. These active carbon, ceramics, activated clay and the like are inexpensive and readily available. The invention is quite advantageous in this regard.

Active carbon includes ones having various characteristics and shapes. Active carbon suitable for the present invention includes, aside from ordinary active carbon, active carbon fibers, porous carbon and the like. For instance, porous carbon having, for example, a specific surface area of 2280 m²/g, a pore capacity of 1.48 ml/g, and an average pore size of 1.3 nm is commercially sold. The pore size distribution and the specific surface area can be readily confirmed by measuring an amount of nitrogen adsorbed at the liquid nitrogen temperature and an adsorption isotherm. As the active carbon material has a very large specific surface area, a very large number of molecules can be adsorbed on the surfaces inside the fine pores.

The molecules of a lower hydrocarbon adsorbed on the active carbon are considered to react in a state where most of the molecules are exposed to the surface at the inside of the fine pores. The active carbon may be used in powder form, granular form, and various required forms molded to an extent of not impeding the porosity. Active carbon fibers are not limited to fibrous form, but may be in powder form, granular form, or various required forms molded to an extent not impeding the porosity thereof.

(1) Ordinary carbon, (2) active carbon fibers, and (3) porous carbon may be sometimes dealt with separately depending on the origin of starting material, the manner of preparation, the external appearance and the like. All of them are individually made of carbonaceous substances and have a small pore size, a large pore capacity and a large specific surface area. Since these properties are utilized in the present invention, the term "active carbon" used herein includes, aside from (1) ordinary active carbon, (2) active carbon fibers and (3) porous carbon.

So far as the porous materials do not react with a compound serving as host or dissolved in the host compound, they can be used irrespective of the type of material, the manner of preparation and the shape. The shape of the fine pores and the pore size distribution should preferably be uniform, but may be non-uniform.

5 The lower hydrocarbons used for this purpose in the invention include methane, ethane, ethylene, propane, butane and mixed gases of two or more of these gases. The gas may contain a minor amount of other components. Examples of the mixed gas include natural gas, city gas, petroleum gas, and the like. These gases are compounds serving as guest in the hydrate-like matter of a lower hydrocarbon or high-density methane hydrate of the invention. Water, which is the other constituent component of the lower hydrocarbon hydrate-like matter or high-density methane hydrate, is a compound serving as host when such lower hydrocarbon hydrate-like matter or high-density methane hydrate is formed. Likewise, carbon dioxide can form a hydrate-like matter inside the fine pores of the porous material.

10 Examples of a compound serving as host include, aside from water, alcohols such as methyl alcohol, ethyl alcohol and the like, organic acids such as formic acid, acetic acid and the like, quinones such as benzoquinone, hydroquinone and the like, and urea. Of these, water or alcohols are preferably used. It will be noted that hydroquinone is able to form a hydrate-like matter of a rare gas serving as guest inside the fine pores of the porous material.

15 The case where water is used as host compound and a lower hydrocarbon as guest compound is mainly described hereinafter, which is true of the cases where other host compounds are used and where other guest compounds are used.

20 According to the invention, a porous material, water, and a lower hydrocarbon are brought in contact with one another under mild conditions at or close to ordinary temperature and under or close to ordinary pressure to form a hydrate-like matter of the lower hydrocarbon inside the fine pores of the porous material. The hydrate-like matter is formed in a short time, and a large amount of the lower hydrocarbon equivalent, for example, to not less than 180 times (converted to the standard state basis) an unit volume of the porous material can be taken in or occluded. The temperature conditions are in the range of -40°C to 50°C, preferably -30°C to 40°C, more preferably 0°C to 40°C, and most preferably 3°C to 40°C. The pressure conditions are preferably in the range of 0.1 atm to 35 atm including atmospheric pressure. In view of the results of various experiments based on the invention, the formation is probably possible from 25 0.1 atm, however, from the standpoint of pressure-reducing means and a material for reaction container, a pressure of 0.5 atm or above is preferred. The upper limit of pressure is not limited, and it is preferred from the viewpoint of legal regulations and security to use around 35 atm or below.

30 The fine pores of active carbon is sufficiently small in diameter ranging from, for example, several nanometers to several tens of nanometers, and as a result, the molecules adsorbed to the surfaces of the fine pores behave as if they were under high pressure conditions. Such behavior represents a phenomenon known as a quasi-high pressure effect. Phase transition, reaction, and the like which occur normally only under high pressure can occasionally happen under moderate conditions of lower pressure and lower temperature by use of a porous material having fine pores. The formation of the hydrate-like matter of a lower hydrocarbon according to the invention is presumably attributable to such a phenomenon as described above although the cause thereof is not known in detail.

35 On the other hand, water is a compound which is able to take a certain structure via hydrogen bond when several molecules thereof cluster. When water serving as host coexists with gas molecules (referred to as "guest molecules") each having dimensions in a certain range, a clathrate compound is formed, causing gas molecules to be crystallized in a very close proximity to each other and stabilized. This is a phenomenon wherein the host substance coexisting with gas molecules serving as guest under certain pressure and temperature conditions forms jointly with the gas molecules, through hydrogen bond, specific cubic structures, for example, cage-like structures in which the guest molecules are surrounded by the host molecules, and such a clathrate is normally formed under conditions of low temperature and high pressure.

40 On the contrary, the invention enables a large amount of a lower hydrocarbon to be occluded rapidly without need of high pressure, for example, under reduced or non-pressurizing conditions, through combination of a high absorbing capacity of the porous material, the above-mentioned quasi-high pressure effect inside the fine pores, and the characteristic of the lower hydrocarbon capable of forming clathrates, thereby forming the hydrate-like matter of the lower hydrocarbon inside the fine pores of the porous material.

45 Furthermore, with respect to the lower hydrocarbon occluding capacity obtained according to the method of the invention, a ratio of the number of guest molecules to that of host molecules far exceeds that obtained for any clathrates known thus far (a compositional ratio between methane and water in conventionally known methane hydrate is 1:5.75, and thus, the content of water is preponderantly large). Such a phenomenon as described above cannot be explained by any known theory pertaining to the formation of clathrates alone. It appears that some synergistic effects due to the combination of the porous material and clathrates, i.e. an effective and excellent lower hydrocarbon occlusion action according to some new and beneficial theory, has occurred.

50 The embodiments of the method of forming a material containing a hydrate-like matter of a lower hydrocarbon inside the fine pores of a porous material according to the invention include, for example: (1) the porous material is placed in a reaction container first, and then water is fed into the container wherein it is adsorbed to the porous material,

followed by further feed of a lower hydrocarbon thereinto; (2) the porous material to which water has already been adsorbed is placed in a reaction container, and then lower hydrocarbon gas is fed into the container; (3) the porous material is placed in a reaction container, into which water and lower hydrocarbon gas are introduced at the same time; and (4) the procedures mentioned above under (1) to (3) are used in combination.

In the embodiments referred to under (1) to (4) above, water may be fed and adsorbed to the porous material by spraying or impregnation. Alternatively, water may be fed in steam form. Among them, it is preferred to feed water as steam. In the embodiment under (3), steam and lower hydrocarbon gas are introduced at the same time. In this case, care should be paid in order not to cause any inconvenience such as of condensation of the vapor by controlling the flow rate or temperature of the lower hydrocarbon gas or by appropriately designing an inner diameter of a pipe thereof.

In any of the embodiments (1) to (4), the hydrate-like matter may be formed under reduced pressure or normal pressure, so that any high pressure container is not necessary for use as the reaction container. Of course, a high pressure container may be used. According to the method of the invention, the hydrate-like matter can be prepared under a pressure exceeding, for example 10.68 atm (\approx 1082 kPa or 10 kg/cm² by gauge pressure). In the case, a high pressure container which is resistant to such a high pressure is employed.

These embodiments (1) to (4) are also applicable to the case where the material comprising the hydrate-like matter of a lower hydrocarbon is formed inside the fine pores of the porous material in the presence of water, and the lower hydrocarbon is desorbed or separated from the formed material and released from a container.

Where heating is applied to for the desorption and release, for example, of methane, a temperature of about 60°C enables methane to be desorbed substantially completely. The same applies to the other lower hydrocarbons. Appropriate means such as of electric heating, heating mediums including hot water, steam, etc., may be used as heat source. Heat may be applied to via known heat exchanging means such as various types of heat exchangers.

By the application of heat, not only the lower hydrocarbon is desorbed, but also water is desorbed. Part of the desorbed water is discharged from the container by entrainment with the desorbed lower hydrocarbon. The other water is left inside and in or on the surfaces of the porous material, and can be repeatedly utilized, as host compound, to form again the material containing the hydrate-like matter of the lower hydrocarbon.

Recently, there is known a method of positively adding moisture to a combustion atmosphere in order to reduce nitrogen oxides otherwise formed in combustion gas. When the desorbed, released lower hydrocarbon entraining water therewith as set out above is used as fuel in the practice of the invention, the effect of addition of water is realized by mere combustion of the lower hydrocarbon, contributing to environmental cleanup based on the reduction in amount of nitrogen oxides to be formed.

Hitherto known methane hydrate has a compositional ratio between methane and water of 1:5.75 (CH₄/H₂O \approx 0.174), thus water being present in major proportion. In contrast, the compositional ratio between methane and water in the material containing the methane hydrate-like matter inside the fine pores of the porous material, high-density methane hydrate, and high-density methane hydrate formed in the fine pores of the porous material of the invention ranges about 0.5 to 1.5:1 (CH₄/H₂O \approx 1/2 to 3/2). Thus, the content of methane is very large. This is true of lower hydrocarbons other than methane, carbon dioxide, and rare gases.

Conventionally known methane hydrate is in the form of sherbet or snow, and is an unstable substance. On the other hand, the material containing the methane hydrate-like matter in the fine pores of the porous material used in the invention keeps the shape of the porous material substantially as it is, in which methane and water are occluded, in hydrate form, inside the fine pores and the material is stable. This is true of the case using lower hydrocarbons other than methane, carbon dioxide, oxygen, nitrogen, and rare gases such as argon.

In the material containing the lower hydrocarbon hydrate-like matter inside the fine pores of the porous material used in the invention, a large volume of lower hydrocarbon gas is occluded in a small capacity of the porous material and can be released. Hence, the material is compact in size and is applicable to storage, transport and supply services of a large amount of one or more lower hydrocarbons, natural gas, city gas, petroleum gas and the like, and can be widely used in various fields. The invention makes use of such functions of occlusion and release.

The city gas tank of the invention is so arranged that a porous material is placed in a container, and city gas is caused to be adsorbed to the porous material in the presence of a compound serving as host. In a method of supplying city gas according to the invention, a compound serving as host and city gas to be adsorbed at the inside of the fine pores is brought in contact with the porous material placed in the city gas tank under mild conditions of ordinary temperature and of ordinary pressure or close to these temperatures and pressures. In this way, a large volume of city gas equivalent, for example, to not less than 180 times (converted to the standard state basis) an unit volume of the porous material can be stored in a very short time.

The temperature and pressure conditions at the time of storing in the city gas tank are similar to those conditions of producing the material containing the hydrate-like matter of the lower hydrocarbon. More particularly, the temperature ranges -40°C to 50°C, preferably -30°C to 40°C. and more preferably 0°C to 40°C. The pressure at the time of storage in the city gas tank is not limited to a pressure range of normal pressures to 10.68 atm (10 kg/cm² by gauge pressure), and city gas can be adsorbed to under a reduced pressure, for example, of 0.2 atm. Under a high pressure exceeding

10.68 atm (10 kg/cm² by gauge pressure), a larger amount of gas corresponding to the pressure can be stored in the tank. As stated hereinbefore, in view of the results of various experiments pertaining to the invention, the storage is probably possible from 0.1 atm, however, from the standpoint of pressure-reducing means and a material for reaction container, a pressure of 0.5 atm or above is preferred. The upper limit of pressure is not limited, and it is preferred from the viewpoint of legal regulations and security to use a range of 35 atm or below.

Thus, the city gas tank for supplying city gas in the invention does not need any special cooling device, or any special pressure equipment, thus being very effective in practical applications. It will be noted that urea or hydrogen sulfide may be used, for example, as a host compound, these generate sulfur dioxide or nitrogen oxides (NO_x) when combusted as fuel. These compounds, which emit the harmful gases on combustion, should be used after solving this problem.

In the city gas tank of the invention for supplying city gas, city gas is stored in the tank in the same manner as in the case of forming the material containing the hydrate-like material of a lower hydrocarbon inside the fine pores of the porous material. More particularly, (1) the porous material is placed in a tank vessel, after which a host compound is fed and adsorbed to the porous material, followed by further introduction of city gas; (2) the porous material to which a host compound has been adsorbed beforehand is placed in the tank vessel, into which city gas is introduced; (3) the porous material is placed in the tank vessel, into which both host compound and city gas have simultaneously introduced; and (4) two or more of the embodiments referred to under (1) to (3) above are used in combination. According to these embodiments, the hydrate-like matter of city gas is formed inside the fine pores of the porous material in the tank, and thus, city gas is stored in the tank.

In the case, since any embodiments enable city gas to be adsorbed and stored under low pressure, any high pressure container is not necessary. As a matter of course, a high pressure container may be used. In the city gas tank for supplying city gas or for controlling the feed of city gas according to the invention, city gas can be likewise stored under a pressure exceeding, for example, 10.68 atm (10 kg/cm² by gauge pressure). In this case, high pressure containers capable of withstanding such a high pressure are used.

The city gas tank of the invention may have any external forms as conventionally employed tanks for city gas or other various gases, such as a cylindrical form, round form, cubic form, rectangular form, and other appropriate forms. The constituting materials of the tank container are not critical, and materials usable for hydrocarbon fuels, such as stainless steels, may be used.

The porous material is filled inside the tank. The porous material can be filled as it is. Besides, it may be filled in an appropriate manner of forming a single layer or two or more layers. When the porous material is filled as layer, the material is supported with a meshwork or a perforated plate.

The city gas tank is provided with a feed pipe for host compound and a feed pipe for city gas. The two pipes may be separately provided. Alternatively, one pipe may be used for both gases. Any of these pipes may also be used as a discharge pipe when city gas is supplied. In the practice of the invention, the porous material, which has been once placed in the gas tank, may be repeatedly used.

The city gas tank of the invention may be (1) arranged at a city gas supply base (i.e. a satellite base) or on the way of a main pipe line. In this case, when the city gas tank is arranged in a city gas manufacturing plant or supply base, the manufacture of city gas in city gas manufacturing facilities can be flattened. For instance, the amount of manufacture of city gas can be so flattened that when its demand is small, city gas is stored in the city gas tanks and is released when the demand increases without increasing the city gas-manufacturing capacity in city gas manufacturing facilities in conformity with the peak of demand.

The city gas tank of the invention is (2) arranged on the way of a city gas feed pipe. In this case, the city gas tank is used for controlling the feed of city gas, and is employed for controlling the feed of city gas depending on seasonal variation of demand of city gas or the variation of demand such as daily variation.

The city gas tank of the invention is (3) arranged in a city gas feed pipe-extending laying operation region in which the tank is used for supplying city gas before completion of the operation.

The city gas tank of the invention is arranged such that (1) after city gas is stored in the tank, it is transported, shipped and set in position, and (2) the tank is set in position wherein city gas is stored. Especially, with a large-capacity tank used in case where the tank is arranged at a satellite base of city gas or on the way of a city gas main pipeline, the embodiment (2) above is preferably adopted.

The above-stated embodiments concerning the city gas tank are also applicable to the city gas tanks and fuel gas tanks other than city gas tanks according to the other embodiments of the invention.

In the practice of the invention, city gas can be supplied normally and emergently to individual consumers. City gas is supplied to individual consumers from a city gas main pipe via a pipe for individual consumer. According to the invention, the pipe for the consumer is provided with a branch pipe along with the city gas tank of the invention. If the feed of city gas from the city gas main pipe is short or is stopped in emergency, city gas is released from the city gas tank and supplied to individual consumers.

In the invention, fuel gas, such as city gas, petroleum gas or the like, can be supplied, normally or emergently, to a

gas turbine or gas engine for driving the generator assembled for use in a cogeneration system. In the cogeneration system, fuel gas is combusted, and the gas turbine or gas engine is run by the agency of the combustion gas to generate electric power with waste heat of the combustion gas being utilized as a heat source of air conditioning or hot water supply. City gas is normally used as the fuel gas, and is supplied via a pipe from a city gas main pipe.

5 According to the invention, a branch pipe is provided to the pipe from the main pipe, and the fuel gas tank is disposed at the branch pipe. In this arrangement, when the feed of city gas from the city gas main pipe is insufficient or is stopped in emergency, city gas is released from the city gas tank and supplied as fuel gas in the cogeneration system.

According to the invention, a fuel gas tank of the invention, which is not disposed at the branch pipe, is separately provided so that fuel gas from this tank is supplied to the cogeneration system.

10 As for portable and replaceable fuel gas tank according to the invention, fuel gas is stored in the tank in the following manner. (1) The porous material is placed in a tank container, after which a host compound is adsorbed to the porous material, followed by introduction of fuel gas. (2) The porous material, to which a host substance has been adsorbed beforehand, is placed in a tank container, followed by introduction of a gas to be stored. (3) The porous material is placed in a tank container, followed by simultaneous introduction of a host substance and a gas to be stored. (4)
15 The porous material is placed in a tank container, followed by introducing fuel gas first, and then a host substance. (5) Two or more of the embodiments referred to under (1) to (4) above are used in combination, and other various techniques may be used.

In any of the above embodiments, adsorption and storage are allowed to proceed under low pressure, and any high pressure container is not required. Of course, a high pressure container may be used. In the portable and replaceable
20 fuel gas tank, a pressure exceeding, for example, 10.68 atm (10 kg/cm² by gauge pressure) enables a gas to be likewise stored. In this case, high pressure containers capable of withstanding such a high pressure should be used.

The portable and replaceable fuel gas tank may take external forms, such as a cylindrical form, round form, cubic form, rectangular form and other appropriate forms, like portable LPG heaters or portable oil stoves conventionally employed in street stall or for cooking in campground, or oil fan-forced heaters or fuel tanks employed in natural gas
25 motor cars, for example. The constituting materials of the tank container are not critical, and materials usable for hydrocarbon fuels, such as stainless steels, may be used.

The tank is filled with the porous material therein. The porous material may be filled as it is. Besides, it may be filled in an appropriate manner of forming a single layer or two or more layers. The tank is provided with a feed pipe of fuel gas to be stored and filled and a discharge pipe therefor. These pipes may be separately provided. Alternatively, only
30 one pipe may be provided for both purposes. After storage and filling of the fuel gas in the tank, it is transported and shipped, followed by setting in position for use as a gas fan-forced heater, portable gas stove, or tank for gas fuel motor car, followed by connection to a fuel supply pipe via a connector. The pipe of the tank should have, at the end thereof, a structure matching with the connector used.

The fuel gas used in the fuel gas tank for automobiles according to the invention is not limitative so far as it is made
35 of lower hydrocarbons used as fuel gas for automobiles, and particularly includes methane or a lower hydrocarbon mainly composed of methane, natural gas, city gas, propane or a lower hydrocarbon mainly composed of propane, petroleum gas. The storage of fuel gas in the fuel gas tank for automobiles can be performed in the case of the afore-stated portable and replaceable fuel gas tank.

The fuel gas tank may take, in its external shape, a cylindrical form, round form, cubic form, rectangular form and
40 other appropriate forms, like the fuel tanks conventionally employed for natural gas motor cars. The constituting material for the tank container is not critical, and any material used for hydrocarbon fuels, such as stainless steels, may be used. The porous material is filled in the inside of the tank.

The fuel gas tank for automobiles may be (1) attached to the body of an automobile, and (2) arranged at a fuel gas stand for automobiles. The foregoing description concerning the fuel gas tank for automobiles is applicable to both
45 cases above. In case where a fuel gas formed in an ordinary fuel gas storage tank according to the high pressure compression method or liquefying-by-cooling method is supplied to the fuel gas tank of the invention attached to an automobile, a pipe from the gas storage tank is connected to a fuel feed pipe of the fuel gas tank, and the fuel gas in the gas storage tank is supplied in gaseous form. A connector is used for the connection, for which any known "one-touch" connector may be used.

50 In this regard, where a gas storage tank, in which fuel gas is stored to the porous material in the presence of a host substance, is stationed, as the gas storage tank, at the fuel gas stand for automobiles, the stored fuel gas in the gas storage tank is supplied in gaseous form by application of heat thereto. In this embodiment, the porous material once charged in the tank and gas storage tank can be repeatedly used. The same applies to the other embodiments of the invention.

55 We have proposed a method of transporting a gas, which is characterized by bringing a gas in contact with a porous material having fine pores and a large specific surface area in the presence of a compound serving as host at or close to ordinary temperature (about 0 to 40°C) to cause a large amount of the gas (methane, ethane, ethylene, propane or butane) to be adsorbed thereto, and transporting the adsorbed gas (EP Application No. 97 101 353.7).

In this invention, the transporting method is applied to the transport of a large amount of natural gas or petroleum gas. The transport is carried out by accommodating the porous material in a tank, causing a large amount of natural gas or petroleum gas to be stored in the porous material in the presence of a host compound, and transporting the tank through automobiles, railways or ship. The tank has such a shape and structure as set out before, and the manner of storage of gas to be transported and the manner of release are as described hereinbefore.

EXAMPLES

The invention is described in more detail based on examples, which should not be construed as limiting the invention thereto. First, the outline of an apparatus used in examples to form materials containing hydrate-like matters of lower hydrocarbons inside the fine pores of porous materials is described. Then, specific examples of forming the materials using the apparatus is described, and specific examples corresponding to the respective embodiments are shown.

Fig. 1 is a schematic view showing the outline of an apparatus of forming the materials used in Examples 1 to 3. In Fig. 1, reference numeral 1 indicates a high pressure cylinder for lower hydrocarbon gas, reference numerals 2, 4, 6, 8 and 10 are, respectively, a valve, 3 a regulator, 5 a gas pipe, and 7 a water vapor generator. Reference numeral 9 indicates a pressure gauge, 11 a pressure vessel, 12 a beam balance, 13 a mechanism for detecting downward displacement of one of the beams of the beam balance 12 and correcting such downward displacement by electromagnetic force, 14 a porous material to which a lower hydrocarbon gas adsorbs to form a hydrate-like matter, 15 a reference weight (to which gas does not adsorb), and 16 a vacuum pump.

When operating this apparatus, firstly air was evacuated from the pressure vessel 11 and the gas pipe 5 by use of the vacuum pump 16, and then water was caused to be adsorbed to the porous material 14. The adsorption of water was conducted in the following manner. Initially, water vapor generated from the water vapor generator 7 was fed into the pressure vessel 11 via the gas pipe 5 by opening the valve 6, thereby forming a saturated water vapor atmosphere in the vessel 11 to cause water to be adsorbed sufficiently to the porous material 14.

Thereafter, a predetermined water vapor atmosphere was formed by adequately reducing pressure further with the vacuum pump 16, and removing excess water adsorbed. Then, the valves 4 and 8 were closed to sufficiently decompress the inside of the gas pipe 5, and moisture inside the gas pipe 5 was completely removed. Subsequently, the lower hydrocarbon fuel gas was brought in contact with the porous material 14 prepared as above. While the lower hydrocarbon gas in the high pressure cylinder 1 was controlled by means of the regulator 3, it was fed into the system to form a gas atmosphere S with a predetermined pressure inside the pressure vessel 11.

Accurate measurement of amounts of the hydrate-like matter of water and the lower hydrocarbon gas that was adsorbed to the porous material 14 was made according to a method wherein an amount of water and the lower hydrocarbon gas, respectively, adsorbed to the porous material 14 was calculated from a quantity of electricity consumed to keep the beam of the beam balance 12 horizontal by the agency of electromagnetic force against a tendency of one end of the beam, on the side of the porous material 14, being displaced downward due to an increase in the weight of the water and the lower hydrocarbon gas adsorbed to the porous material 14. A temperature of the atmosphere was kept constant by housing the apparatus in whole in a thermostat. In Fig. 1, the thermostat is not shown.

Example 1

0.0320 g (0.0461 cc) of pitch-based active carbon fibers (hereinafter referred sometimes to ACF) having a specific surface area of 1765 m²/g, an average pore size of 1.13 nm (nanometers), a pore capacity of 0.971 cc/g, an intrinsic specific gravity of 2.13 g/cc, and an apparent specific gravity of 0.694 g/cc were set in position of the apparatus shown in Fig. 1. Subsequently, the pressure vessel 11 and the gas pipe 5 were set at 383 K, and were evacuated by use of the vacuum pump 16 for 2 hours in a vacuum of 1 mPa (milli-Pascal). followed by adsorption of 0.0083 g of water (a fine pore-filling rate, $\phi = 27\%$).

Next, methane gas under 0.2 atm (≈ 20.265 kPa) at 303 K was fed thereto. For comparison, the above procedure was repeated except that methane gas under the same conditions as mentioned above was fed thereto but without adsorption of water. In Fig. 2, variation in the weight of the methane gas adsorbed per 1 g of ACF is shown in relation to the variation in time. In Fig. 2, the variation in the weight when water was adsorbed to ACF prior to the methane gas being adsorbed thereto is plotted with the mark "○", whereas the variation obtained when methane gas was adsorbed straight to the active carbon is plotted with the mark "●".

As shown in Fig. 2, where water was adsorbed to ACF first and then the methane gas was fed thereto, ACF started to adsorb the methane gas henceforth at a rapid rate with an amount of the methane gas adsorbed after the elapse of 0.2 hours reaching more than 15 mmols per 1 g of ACF and the same after the elapse of 0.5 hours reaching around 17 mmols per 1 g of ACF, which was maintained thereafter. Considering the fact that the methane gas fed at this point was pressurized at 0.2 atm (temperature: 303 K), it can be seen that a rate, at which the methane gas is adsorbed, and an amount of adsorbed methane are remarkable, compared with conventional means.

The visual observation of the properties of ACF subjected to these measurements reveals that ACF keeps its own appearance, but becomes highly dense correspondingly to the amount of methane being adsorbed. On the other hand, when the methane gas was fed without water being adsorbed to ACF, only a minimal amount of the methane gas was adsorbed without showing any change in the amount of the methane gas adsorbed after the elapse of time in the same atmosphere as described above. When the properties of ACF not adsorbed with water were visually observed, they were similar to those prior to the adsorption.

Table 1 shows the results of comparison of the amounts of methane adsorbed per 1 g of ACF as shown in Fig. 2. As shown in Table 1, an amount of methane adsorbed was only 0.18 mmols after the elapse of 0.2 hours in the case where methane was adsorbed straight to ACF, whereas it was 12.08 mmols in the case where water was adsorbed to ACF beforehand, 67 times as much as the former case. After the elapse of 0.9 hours, an amount of methane adsorbed straight to ACF was 0.18 mmols, whereas it was 16.46 mmols in the case of water coexisting with methane, 91 times as much as the former case.

[Table 1]

Time Elapsed (Hours)	Amount of methane adsorbed per 1 g of ACF (mmols)		Ratio:A/B
	Methane adsorbed to ACF after water was adsorbed (A)	Methane adsorbed straight to ACF (B)	
0.2	12.08	0.18	67.1
0.9	16.46	0.18	91.4

A volume of methane adsorbed to 1 cc in an apparent volume of ACF in the presence of water is calculated as 183 cc on the standard state basis at 0°C under 1 atm. This result shows that methane was stored in a volume of exactly 183 times, on the standard state basis, as large as an unit volume of ACF under a pressure as low as only 0.2 atm. Then (after the elapse of 0.9 hours), an amount of methane adsorbed was found slightly reducing, and finally reached 11.77 mmols, at which a state of equilibrium was achieved without any change thereafter.

Example 2

In the same manner as in Example 1, 0.0083 g of water was adsorbed to 0.0320 g (0.0461 cc) of ACF of the same type as used in Example 1 (fine pore filling rate, $\phi = 27\%$). Thereafter, methane gas was fed under different pressures of 0 kPa (0 atm) to 2000 kPa (≈ 19.7 atm), respectively, at 303K, and amounts of methane gas adsorbed after a state of equilibrium was reached at the respective pressures were measured. Fig. 3 shows the results of the measurements. In Fig. 3, variation in the weight of methane adsorbed when water was adsorbed to ACF beforehand is plotted with the mark "○", whereas the variation obtained when methane gas was adsorbed straight to ACF is plotted with the mark "●".

As is clear from Fig. 3, in case of methane being adsorbed straight to ACF, the amount of methane adsorbed gradually increases with an increase of the pressure, and is as small as only approximately 5 mmols at 2000 kPa (≈ 19.7 atm). In the case where methane is fed after water is adsorbed to ACF beforehand, the amount of methane adsorbed under a pressure as low as 101 kPa (≈ 1 atm) is as much as 12 mmols per 1 g of ACF, which is not less than two times the amount of methane adsorbed under 2000 kPa (≈ 19.7 atm) in case of methane adsorbed straight to ACF in the absence of water.

Then, in the case where methane is adsorbed after water is adsorbed to ACF beforehand, volumes of methane adsorbed to 1 cc of ACF under different pressures according to Fig. 3, converted to respective volumes on the standard state basis, are equivalent to 191 cc under 71 kPa (≈ 0.7 atm), 203 cc under 152 kPa (≈ 1.5 atm), 271 cc under 507 kPa (≈ 5.0 atm), 290 cc under 1013 kPa (≈ 10 atm), and 326 cc under 2000 kPa (≈ 19.7 atm). In this way, according to the invention, not only good adsorption action under reduced pressure or under such a low pressure of normal pressures to 507 kPa (≈ 5.0 atm) is attained, but also a more effective adsorption can be expected under pressures of 1013 kPa (≈ 10 atm) or under 2000 kPa (≈ 19.7 atm) and higher.

Example 3

In the same manner as in Example 1, 0.0087 g of water was adsorbed to 0.0320 g (0.0461 cc) of ACF of the same type as used in Example 1 (fine pore filling rate, $\phi = 28\%$). Thereafter, methane gas was fed under different pressures

of 0 kPa (0 atm) to 30 kPa (\approx 0.3 atm), respectively, at 303K, and amounts of methane gas adsorbed after a state of equilibrium was reached at the respective pressures were measured. Fig. 4 shows the results of the measurements under these reduced pressures (low pressure methane adsorption isotherm). In Fig. 4, variation in the weight of methane adsorbed when water was adsorbed to ACF beforehand is plotted with the mark "○", whereas the variation obtained when methane gas was adsorbed straight to ACF is plotted with the mark "●".

As shown in Fig. 4 in the case where methane was fed after water was adsorbed to ACF beforehand, methane was stored at a rapid rate only under a very low pressure henceforth. The amount of methane adsorbed under 101 kPa (\approx 1 atm) is around 12 mmols. In the case where methane is adsorbed straight to ACF, the amount of methane adsorbed under a pressure of 152 kPa (\approx 1.5 atm) is around 1 mmol per 1 g of ACF. In the case where methane gas is fed after water is adsorbed to ACF beforehand, the amount of methane adsorbed under the same pressure of 152 kPa (\approx 1.5 atm) is as much as 13 mmols.

[Table 2]

Pressure (kPa)	Amount of methane adsorbed per 1 g of ACF(mmols)		Ratio:A/B
	Methane adsorbed to ACF after water was adsorbed (A)	Methane adsorbed straight to ACF (B)	
20	11.77	0.18	65.4
152	13.08	0.88	14.9

Table 2 shows the results of comparison of the amounts of methane adsorbed per 1 g of ACF as shown in Fig. 4. As shown in Table 2, in comparing the amounts of methane adsorbed when an equilibrium of adsorption was reached, for example, under 20 kPa (\approx 0.2 atm), an amount of methane adsorbed in the presence of water was 11.77 mmols as against the same of only 0.18 mmols when methane was adsorbed straight to ACF, representing a ratio of the former to the latter at 65. Further, in comparing amounts of methane adsorbed when an equilibrium of adsorption was reached under 152 kPa (\approx 1.5 atm), an amount of methane adsorbed in the presence of water was 13.08 mmols as against the same of only 0.88 mmols when methane was adsorbed straight to ACF, representing the ratio at 15.

These results of Examples 1 to 3 were similar to those attained by use of ethane, ethylene, propane, and butane, and were also true of the cases using mixed gases of methane and these lower hydrocarbons.

Example 4

The apparatus shown in Fig. 1 can be fundamentally used as an apparatus of forming the material of the invention. Fig. 5 is a view showing an apparatus of forming the material according to another embodiment. Reference numeral 17 indicates a pipe for lower hydrocarbon gas, which is connected to a gas storage tank, for example, of methane. Reference numeral 18 indicates a water vapor generator, and 19 a reaction container. A porous material 20 is packed in the container 19 and is held with a meshwork or perforated plate. In the operation of forming a hydrate-like matter, for example, a valve 21 is closed and valves 22, 23 are opened, under which water vapor is generated from the water vapor generator 18 and fed into the container 19 via pipes 24, 25. Next, the valve 21 is opened to feed the lower hydrocarbon gas into the container 19. It will be noted that the water vapor may be fed into the container 19 via a pipe other than the pipe 25. The water vapor may also be generated by application of heat as well as under reduced pressure. Both may be used in combination.

According to the aforesaid procedure, the lower hydrocarbon gas is rapidly adsorbed to the porous material to form a hydrate-like matter by the action of water serving as host. In the above procedure, the lower hydrocarbon gas is fed after the water vapor has been fed to the porous material beforehand, and it is a matter of fact that the lower hydrocarbon gas may be fed simultaneously with the water vapor. In this case, care should be taken in order not to cause any inconvenience such as of condensation of the vapor by controlling the flow rate, temperature and the like of the lower hydrocarbon gas or by appropriately designing the inner diameter of the pipe (e.g. pipe 25 in Fig. 5).

Example 5

Figs. 6(a), 6(b), 7(a) to 7(e), and 8 to 10 are, respectively, illustrative views showing examples concerning the feed of city gas and the control of city gas feed according to the invention.

Figs. 6(a) and 6(b) are, respectively, sectional views showing embodiments of city gas feed tank and gas feed con-

trolling city gas tank. Fig. 6(a) shows the porous material filled in the tank at it is, and Fig. 6(b) shows the porous material filled in the tank as layer. Fig. 6(b) shows the case of two layers being formed, and three or more layers may be used. This can be said of the case of a multi-layer embodiment described hereinafter.

In Figs. 6(a) and 6(b), reference numeral 26 indicates a tank container, 27 a porous material, and 28 a charge and discharge pipe for host compound and city gas in which the opening of the pipe 28 inside the container extends to an upper space 30 of the tank container. In Figs. 6(a) and 6(b), reference numeral 29 indicates a on-off valve. In Fig. 6(b), reference numeral 31 indicates an intermediate space between upper and lower layers. A member such as a perforate plate or a meshwork is arranged on the upper face of the porous material in Fig. 6(a) and on the upper and lower faces of the porous material in Fig. 6 (b). This can be said of embodiments appearing hereinafter.

The feed of a compound serving as host and city gas to the tank can be performed by use of an apparatus as shown in Example 4.

In order to separate and release city gas from the thus arranged tank. heating means is used, for example. In this case, appropriate heating sources including electric heaters, and heat mediums such as hot water, steam and the like may be used for this purpose. Heat can be applied to according to appropriate techniques including an internal heating technique where a heat source is built in the tank, an external heating technique wherein a heat source is arranged about the outer periphery of the tank, and a combination of both. These points can be said of examples which follow.

Example 6

Figs. 7(a) to 7(e) are, respectively, sectional views showing feed controlling city gas tanks according to further embodiments of the invention. Fig. (7a) shows a porous material which is arranged as a layer vertically formed with a through-hole. In Fig 7(a), reference numeral 32 indicates a through-hole, and 33 a lower space. The through-hole 32 is established, for example, with a meshwork or a hollow cylinder having a multitude of holes made therein. Only one through-hole 32 is provided in the figure, and two or more through-holes kept apart from each other may be provided, if necessary. A host compound and city gas fed from the inside opening of the pipe 28 extending to the upper space of the tank container are forced to enter not only from the upper and lower surfaces of the porous material layer, but also from the walls of the through-hole 32, and are more uniformly adsorbed to and stored in the porous material.

The thus stored city gas is released, for example, by application of heat toward the directions reverse to the directions in case of the gas being adsorbed and stored, and supplied from the pipe 28 to a city gas feed pipe. This is true of embodiments appearing hereinafter. Fig. 7(b) shows a modification of Fig. 7(a), in which the opening of the pipe 28 inside the container is arranged to extend to a lower space of the vessel. In this case, the compound serving as host and city gas fed from the inside opening of the pipe 28 inside the container enter from the walls of the through-hole 32 as well as from the upper and lower surfaces of the porous material layer, and are more uniformly adsorbed to and stored in the porous material.

In Fig. 7(c), two porous material layers are formed with a through-hole being made in vertical directions. In the figure, reference numeral 34 indicates a through-hole, and 35 an intermediate space between the layers. In Fig. 7(c), the two layers are formed, and three or more layers may be formed. The through-hole 34 may be constituted, for example, of a meshwork of a cylindrical form or a hollow cylinder having a multitude of pores. In the embodiment shown in the figure, one through-hole 34 is formed in each of the upper and lower layers. If necessary two or more through-holes may be formed as being kept apart from each other. In the case, the numbers of through-holes, which are made in the upper and lower layers, may be changed from each other. The compound serving as host and city gas, which are fed from the opening of the pipe 28 in the upper space of the tank container, enter from the walls of the through-holes 34 as well as from the upper and lower surfaces of the respective porous material layers, and are more uniformly adsorbed to and stored in the porous material.

Fig. 7(d) shows a modification of Fig 7(c) wherein the inside opening of the pipe 28 extends up to the lower space of the tank container. In this case, the compound serving as host and city gas, which are fed from the inside opening of the pipe 28, enter from the walls of the through-holes 34 as well as from the upper and lower surfaces of the respective porous material layers, and are more uniformly adsorbed to and stored in the porous material. The pipe 28 in the container may have a branch pipe with its opening extending to the upper space 30 and/or the intermediate space 35 in addition to the inside opening of the pipe 28 extending to the lower space.

Fig. 7(e) is a sectional view showing a further embodiment, in which a through-hole 36 is made vertically in the packing layer of the porous material. A plurality of branch pipes 37 are provided radially from the through-hole 36. The compound serving as host and fuel gas fed from the inside opening of the pipe 28 in the container enter not only from the upper surface of the porous material layer, but also from the walls of the through-holes 36 and the radial branch pipes 37, and are more uniformly adsorbed to and stored in the porous material.

Example 7

Figs. 8 and 9 are, respectively, a modification of Fig. 7(e). Fig. 8 shows an embodiment wherein the pipe 28 is extended from the through-hole 36 toward a plurality of branch pipes 37 provided radially, with its ends being opened at the branch pipes 37. In this case, the compound serving as host and city gas fed from the openings of the pipe 28 in the container enter not only from the upper and lower surfaces of the porous material layer, but also from the walls of individual branch pipes, and are more uniformly adsorbed to and stored in the porous material. Fig. 9 refers to an embodiment wherein a space 33 is formed at the lower portion of the packed layer. Like the case of Fig. 8, the pipe 28 may be provided with branch pipes corresponding to the radial branch pipes 37, with an opening thereof being made at the end of each radially branched pipe 37. The radially branched pipes 37 may have such a structure as of the lung of man passed through bronchial tubes.

Example 8

The city gas tanks thus arranged in accordance with the invention are disposed at or provided with city gas manufacturing plants or satellite bases (feed base), or arranged on the way of main feed pipes or branch pipes for city gas. Fig. 10 is a schematic view showing an embodiment of such an arrangement as mentioned above. In Fig. 10, reference numeral 38 indicates a city gas manufacturing plant or supply base using LNG or the like as starting material, and city gas is supplied via main feed pipes 39 and branch pipes 40 to various mills, facilities and homes. Numeral 41 indicates a city gas tank provided at the plant or base, and 42 a city gas tank arranged at the branch pipe.

Fig. 11 shows an example of a city gas tank being provided or disposed at a city gas supply main line or branch pipe. The city gas tank 26 used for city gas feed control is connected to a city gas feed main line 39 or branch pipe 40 via a control valve 43 and a pipe 44. If the demand relatively increases depending, for example, on seasonal variation thereof, or if the feed from a city gas manufacturing plant or supply base (= satellite base: a city gas storage base connected to the city gas supply main line) transiently becomes insufficient, the insufficiency is supplemented by releasing and supplying a required amount of city gas by application of heat or the like from the feed control city gas tank via the pipe 44 having the control valve 43 (on-off valve).

Example 9

Fig. 12 is an illustrative view showing an embodiment of normally or emergently supplying city gas to individual consumers according to the invention. In Fig. 12, numeral 45 indicates a city gas main pipe in section, and 46 a city gas pipe for individual consumer. The pipe 46 is provided with an intake check valve 47 for individual consumer and a weighing and emergency shutdown valve 48. Branch pipes 49,50 are provided between the check valve 47 and the weighing and emergency shutdown valve 48, and a container 53 of filling a porous material capable of storing and releasing a large amount of city gas, for example, under an ordinary pressure to a pressure not exceeding 10 ka/cm²G is connected to the branch pipe 49, 50 via pressure control valves, respectively. Needless to say, in an area where there is no legal regulation concerning the upper limit of gas pressure of 10 kg/cm²G, higher pressure may be used.

The container 53 has a porous material in which city gas is stored in the presence of a host compound such as water. Reference numeral 54 indicates a device of supplementing a host compound such as water. The container 53 may be of the replaceable type or of the regular locating type. In the latter type, the container 53 is normally set in position and wherein when city gas is released and consumed, a host compound such as water is supplemented, if necessary, and city gas is again adsorbed.

Normally, city gas is passed from the gas main pipe 45 via the intake pipe 46 for consumer, the intake check valve 47 for individual consumer and the weighing and emergency shutdown valve 48 for individual consumer to various gas appliances of consumer such as a boiler, a gas hot water supplier, gas burners and the like. Reference numeral 55 indicates branch pipes for such gas appliances.

When the city gas supply from the gas main pipe 45 is stopped due to earthquake or the like emergency, gas pressure inside the pipe 46 lowers, under which the city gas stored in the porous material-filled container 53 is fed to the city gas pipe 46 for individual consumer via the branch pipe 50 and pressure control valve 52, followed by supply via the weighing and emergency shutdown valve 48 to the respective gas appliances. In this case, the gas passing from the container 53 to the pipe 46 is stopped with the check valve 47, not causing the gas to flow backward to the gas main pipe 45.

At normal times, when the pressure of city gas passing through the pipe 46 is higher than a predetermined level at the pressure control valve 52, city gas runs toward the container 53 via the pipe 49 and pressure control valve 51 until city gas is stored to the full capacity of the container 53, invariably keeping the full capacity, while permitting city gas to be consumed with the respective gas appliances.

Further, where the pressure of city gas passing through the pipe 46 is lower than a predetermined level at the pres-

sure control valve 52 at normal times, the city gas stored in the container 53 is fed through the pressure control valve 52 and pipe 50, and also through the weighing and emergency shutdown valve 48, and the branch pipe 55 to the respective gas appliances, in the same manner as in emergency. PIC is a control device connected with these detection units and the control units, and any known one may be used.

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Example 10

Fig. 13 is a view showing an example wherein fuel gas, such as city gas, is supplied, normally or emergently, to a gas turbine or gas engine of driving a generator assembled in a cogeneration system of production mills, office buildings, hospitals and the like. City gas is used for illustration, which can be said of other fuel gases.

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Air is fed from an air pipe 56 via an air compressor 57 to a burner 58, in which city gas is combusted to generate a combustion gas. A gas turbine 59 is driven by means of the combustion gas with a generator 62 being driven along with the air compressor 57 by the agency of the revolving force of the gas turbine. The electric power obtained from the generator 62 is utilized as a power source of a cogeneration system. The combustion gas is further introduced into a waste heat utilizing boiler 60, in which water is heated to provide hot water or steam and exhausted from a chimney 61. The hot water or steam obtained in the boiler 60 is used for hot water supply or heating in the cogeneration system. T indicates a switch-over valve.

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Reference numeral 63 indicates a city gas-stored container (tank) according to the invention. The container 63 is connected with pipes 64, 65 for city gas, between which a bypass pipe 66 is provided. Normally, city gas is supplied through the bypass pipe 66 to the burner 58. In earthquake or other emergencies, city gas is fed from the stored container 63 to the burner 58. It is necessary to preliminarily store city gas in the container 63. The manner of the storage is similar to the cases of the foregoing examples. In Fig. 13, a feeder for a host compound such as water is not shown. The gas tank of this example may also be used for normally supplying fuel gas to gas turbines or gas engines in cogeneration systems.

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Example 11

Fig. 14 is a view showing a gas fan-forced heater using the Bunsen burner for city gas. Fig. 15 is a view showing an example of connecting a portable and replaceable fuel gas tank to a fuel gas feed pipe of the gas fan-forced heater as shown in Fig. 14.

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In Fig. 14, reference numeral 70 indicates a filter, 71 fan, 72 a combustion chamber, and 73 a burner. The burner 73 is provided with a fuel gas feed pipe 74, which is connected to a stopcock such as for city gas. In Fig. 14, the arrow (→) indicates the flowing directions of air and fuel gas. The portable and replaceable fuel gas tank of the invention is used by detachable connection, for example, to the fuel gas feed pipe 74 of the gas fan-forced heater.

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Fig. 15 shows the example of the connection. In Fig. 15, reference numeral 75 indicates a portable and replaceable fuel gas tank, and 76 a connector. The connector 76 is preferably a "one-touch" connector. In use, the portable and replaceable fuel gas tank 75 is connected to the gas fuel feed pipe 74 via the connector 76. The portable and replaceable fuel gas tank of the invention has a large amount of fuel gas filled therein, and can be used over a long time. At the time when the fuel gas is completely consumed or immediately before the complete consumption, the tank can be readily replaced at the connector 76. This is applicable (in case where the portable and replaceable fuel gas tank of the invention is used in place of conventional) tanks of gas fuel automobiles, liquid fuel tanks of petroleum fan-forced heaters, or LPG tanks or oil stoves ordinarily employed at home, campground, or stall (movable fast food shop).

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Fuel gas can be filled and stored in these portable and replaceable fuel gas tanks in a manner as shown, for example, in Fig. 5. The portable and replaceable fuel gas tank can be designed to have such structures as shown, for example, in Figs. 5, 6(a), 6(b), 7(a) to 7(e), 8 and 9.

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Example 12

Likewise, the fuel gas tank for automobiles of the invention can also be designed to have such structures as shown, for example, in Figs. 5, 6(a), 6(b), 7(a) to 7(e), 8 and 9. The manner of adsorption and storage of fuel gas in the tank is similar to the cases in the foregoing examples.

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The charge of fuel gas for automobiles in the tank is made in a manner as shown, for example, in Fig. 5. In this example, the manner of the storage is illustrated according to Fig. 5. Reference numeral 17 indicates a fuel gas pipe, which is connected, at one end thereof, to a fuel gas storage tank (not shown) installed at a fuel gas stand. Reference numeral 18 is a steam generator, 19 a fuel gas tank, in which active carbon is filled. In adsorption and storage operations, a valve 21 is closed, and valves 22, 23 are, respectively, opened, under which steam is generated from the steam generator 18 and is fed to the tank 19 via pipes 24, 25.

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Next, the valve 21 is opened, and fuel gas is fed to the tank 19. According to the above operation, the fuel gas is

rapidly adsorbed and stored inside the fine pores of the active carbon by the host action of water adsorbed inside the fine pores of the active carbon. Although, in the above operations, the fuel gas is fed after steam is generated and fed to active carbon beforehand, fuel gas may be fed simultaneously with steam. In this case, care should be paid in order not to cause any inconvenience such as of condensation or solidification of steam by controlling the flow rate or temperature of the fuel gas or by appropriately designing an inner diameter of the pipe 25.

The pipe 25 shown in Fig. 5 serves both as steam pipe and fuel gas pipe, and these pipes may be separately provided. In the latter case, both pipes are connected to the tank 19.

The fuel gas tank filled with fuel gas may be mounted in automobiles, or may be replaced with a tank which has been mounted beforehand and whose fuel gas is fully discharged (although the fuel gas in the tank to be replaced is not necessarily discharged to an full extent).

The fuel gas is released and gasified from a freshly mounted fuel gas tank by application of heat or the like, and supplied to an engine of an automobile.

The tank of the replaceable type has been described above. It is possible to mount a fuel gas tank by fixedly setting in position of an automobile and charge fuel gas at a fuel gas stand for automobiles. In this case, a device of charging fuel gas is furnished at the fuel gas stand. More particularly, this device is one which is, for example, shown in Fig. 5 and covers from the fuel gas pipe 17 to the valve 23, including the steam generator 18. The pipe 17 is connected to a conventional or ordinary type of fuel gas storage tank (not shown), which is installed at the fuel gas stand.

It is also possible to install the gas tank according to the invention in place of the conventional or ordinary type of fuel gas storage tank mentioned in the preceding paragraph.

The features disclosed in the foregoing description, in the claims and/or in the accompanying drawings may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Claims

1. A method of supplying city gas, characterized by comprising placing a porous material in a city gas tank, causing city gas to be stored in said porous material in the presence of a compound serving as host, and arranging the city gas tank in a city gas manufacturing plant or city gas supply base, or on the way of a city gas supply pipe.
2. A method of supplying city gas according to Claim 1, wherein said porous material is active carbon, a ceramic material or activated clay, and said compound serving as host is water, an alcohol, an organic acid or a quinone.
3. A method of controlling a feed of city gas, characterized by comprising placing a porous material in a city gas tank, causing city gas to be stored in said porous material in the presence of a compound serving as host, and arranging the city gas tank in a city gas manufacturing plant or city gas supply base, or on the way of a city gas supply pipe to control a feed of city gas.
4. A method of controlling a feed of city gas according to Claim 3, wherein said porous material is active carbon, a ceramic material or activated clay, and said compound serving as host is water, an alcohol, an organic acid or a quinone.
5. A city gas tank for supplying city gas or controlling a feed of city gas, characterized by comprising a container (11, 19, 26, 41, 42) having a porous material placed therein wherein city gas is stored inside said porous material (14, 20, 27) (in the presence of a compound serving as host).
6. A city gas tank for supplying city gas or controlling a feed of city gas according to Claim 5, wherein said porous material (14, 20, 27) has a specific surface area of 100 m²/g or over.
7. A city gas tank for supplying city gas or controlling a feed of city gas according to Claim 5, wherein said porous material (14, 20, 27) is active carbon, a ceramic material or activated clay, and said compound serving as host is water, an alcohol, an organic acid or a quinone.
8. A city gas tank for supplying city gas or controlling a feed of city gas according to Claim 5, wherein said porous material (14, 20, 27) is placed in said container (11, 19, 26, 41, 42) as one or more layers.
9. A method of supplying a fuel gas for individual consumer, characterized by comprising providing a fuel gas tank (11, 19, 26, 53) which is disposed at a branch pipe between a weighing and emergency shutdown valve and a check valve of a fuel gas pipe and which has a porous material (14, 20, 27) placed therein, said porous material (14, 20, 27) being adsorbed with a fuel gas containing one or more lower hydrocarbons selected from methane, ethane,

ethylene, propane and butane in the presence of a compound serving as host, and connecting said fuel gas tank (11, 19, 26, 53) to said branch pipe via a pressure control valve so that fuel gas can be released and supplied normally or emergently.

- 5 10. A method of supplying a fuel gas for individual consumer according to Claim 9, wherein said porous material (14, 20, 27) is active carbon, a ceramic material or activated clay, and the host compound is water, an alcohol, an organic acid, urea or a quinone.
- 10 11. A method of supplying a fuel gas for individual consumer according to Claim 9, wherein said fuel gas containing one or more lower hydrocarbons is city gas, natural gas or petroleum gas.
- 15 12. A method of supplying fuel gas to a gas turbine or gas engine of a cogeneration generator, characterized by comprising placing a porous material (14, 20, 27) in a fuel gas tank (63), causing a fuel gas containing one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in the presence of a compound serving as host to be adsorbed to said porous material (14, 20, 27), and invariably supplying the stored fuel gas to a gas turbine or gas engine of a generator in a cogeneration system.
- 20 13. A method of supplying fuel gas to a gas turbine or gas engine of a cogeneration generator according to Claim 12, wherein said porous material (14, 20, 27) is active carbon, a ceramic material or activated clay, and the host compound is water, an alcohol, an organic acid, a quinone or urea.
- 25 14. A method of supplying fuel gas to a gas turbine or gas engine of a cogeneration generator according to Claim 12, wherein said lower hydrocarbon is city gas natural gas or petroleum gas.
- 30 15. A method of supplying, at ordinary times or power stoppage, fuel gas to a gas turbine or gas engine of a cogeneration generator, characterized by comprising placing a porous material in a fuel gas tank, causing a fuel gas containing one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in the presence of a compound serving as host to be adsorbed to said porous material (14, 20, 27), and supplying the stored fuel gas, at normal times or in emergency, to a gas turbine or gas engine of a generator in a cogeneration system.
- 35 16. A portable and replaceable fuel gas tank (75), characterized by comprising a container having a porous material (14, 20, 27) placed therein, wherein a fuel gas made of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane is stored inside said porous material in the presence of a compound serving as host.
- 40 17. A portable and replaceable fuel gas tank (75) according to Claim 16, wherein said porous material (14, 20, 27) is active carbon, a ceramic material or activated clay, and the host compound is water, an alcohol, an organic acid, a quinone or urea.
- 45 18. A portable and replaceable fuel gas tank (75) according to Claim 16, wherein said fuel gas is city gas, natural gas or petroleum gas.
19. A portable and replaceable fuel gas tank (75) according to Claim 16, wherein said fuel gas tank is for gas fan-forced heater, gas heater or gas fuel automobile.
- 50 20. A portable and replaceable fuel gas tank (75) according to Claim 16, wherein said porous material (14, 20, 27) is accommodated as a single layer or two or more layers.
21. A fuel gas tank for automobiles, characterized by comprising a container having a porous material (14, 20, 27) placed therein, wherein a fuel gas made of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane is caused to store inside said porous material (14, 20, 27) in the presence of a compound serving as host.
- 55 22. A fuel gas tank for automobiles according to Claim 21, wherein said porous material (14, 20, 27) is active carbon, a ceramic material or activated clay, and the host compound is water, an alcohol, an organic acid, a quinone or urea.
23. A fuel gas tank for automobiles according to Claim 21, wherein said fuel gas being stored is city gas, natural gas

or petroleum gas.

24. A fuel gas tank for automobiles according to Claim 21, wherein said porous material (14, 20, 27) is accommodated as a single layer or two or more layers.

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25. A fuel gas stand for automobiles, characterized by comprising a container having a porous material (14, 20, 27) placed therein, wherein a fuel gas made of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane in the presence of a compound serving as host is stored in said porous material (14, 20, 27), said container being arranged in said gas stand as a fuel gas tank for automobiles.

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26. A fuel gas stand for automobiles according to Claim 25, wherein said porous material (14, 20, 27) is active carbon, a ceramic material or activated clay, and the host compound is water, an alcohol, an organic acid, a quinone or urea.

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27. A fuel gas stand for automobiles, characterized by comprising a storage tank for a fuel gas made of one or more lower hydrocarbons selected from methane, ethane, ethylene, propane and butane, a pipe connected to said storage tank, and a mechanism of feeding a host compound for said fuel gas.

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28. A method of transporting a large amount of natural gas or petroleum gas, characterized by comprising causing a large amount of natural gas or petroleum gas to be stored inside a porous material, placed in a container, in the presence of a compound serving as host, and transporting said container by automobile railway or ship.

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FIG. 1

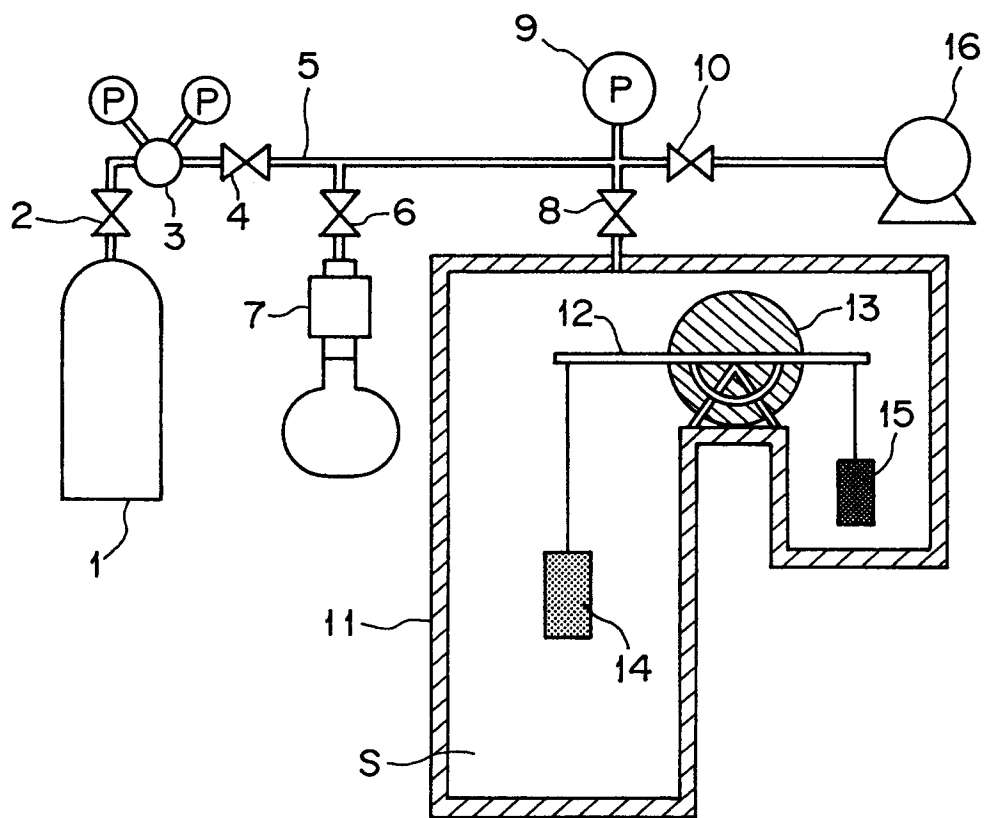


FIG. 2

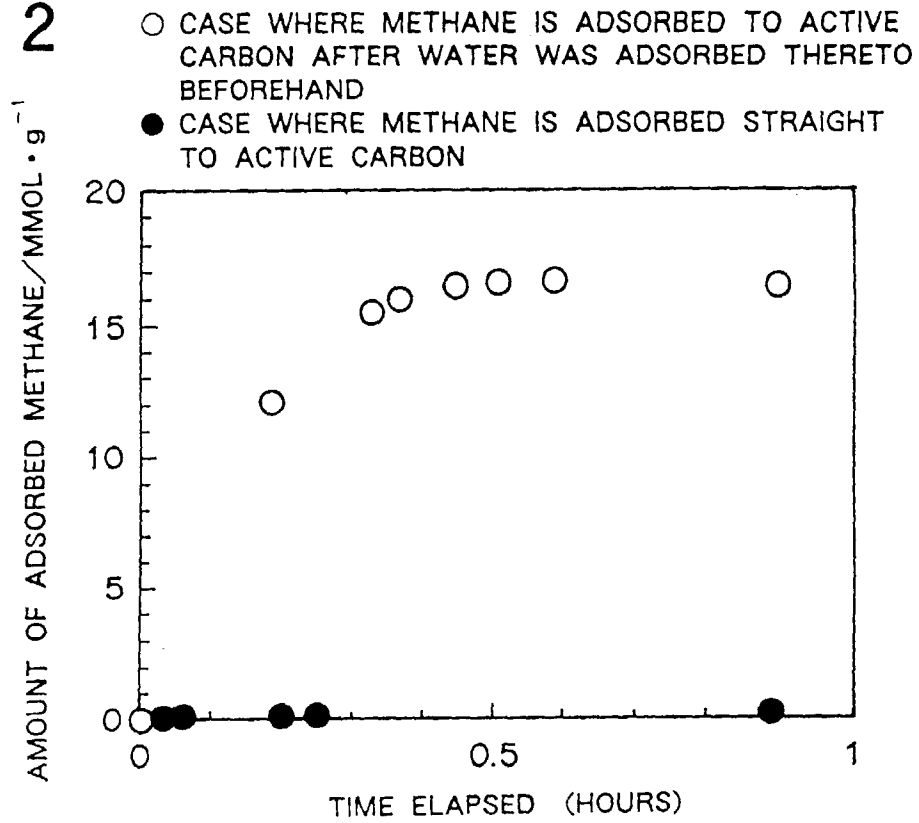


FIG. 3

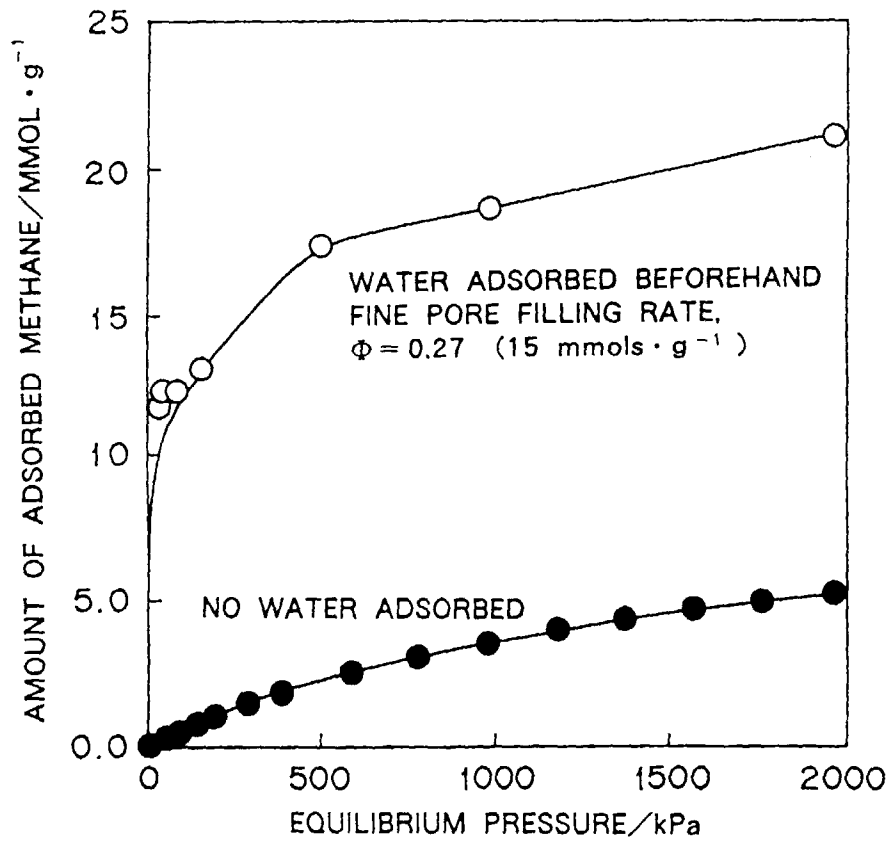


FIG. 4

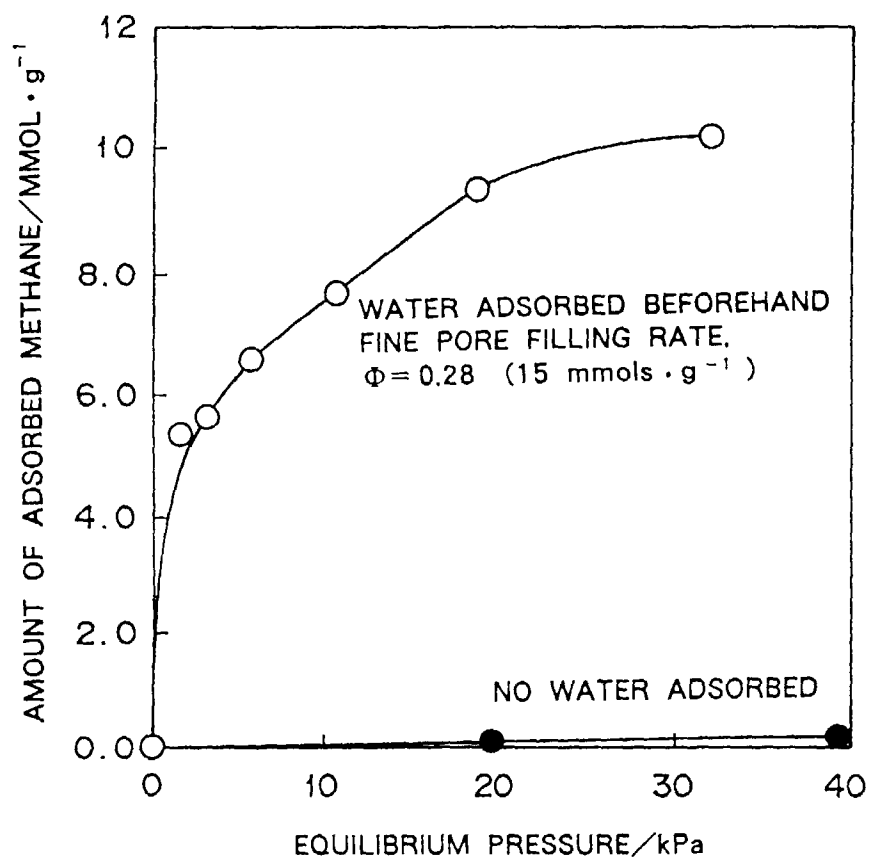


FIG. 5

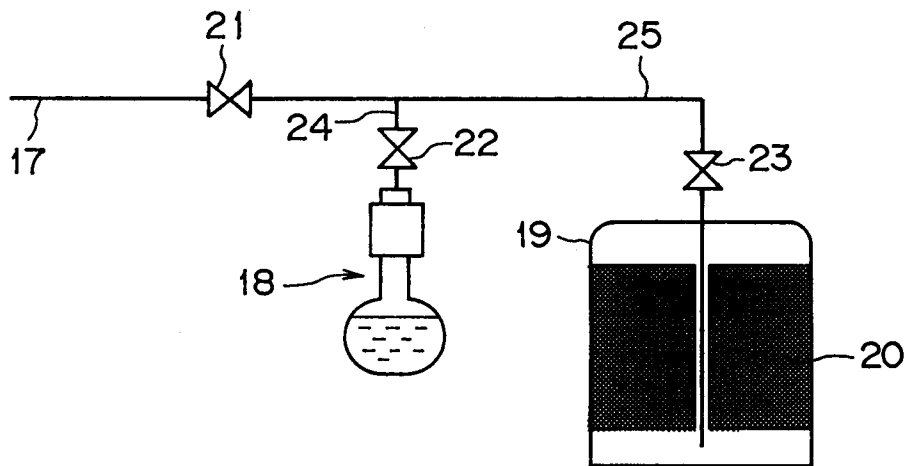


FIG. 6 (a)

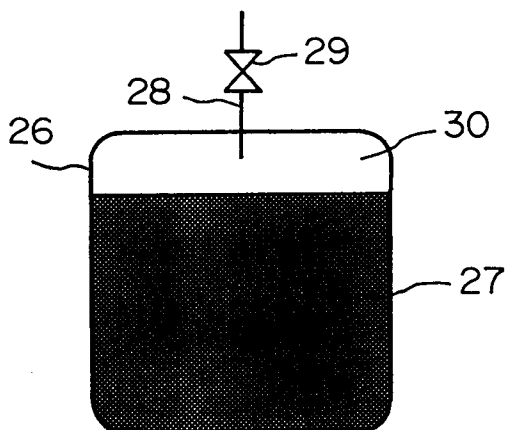


FIG. 6 (b)

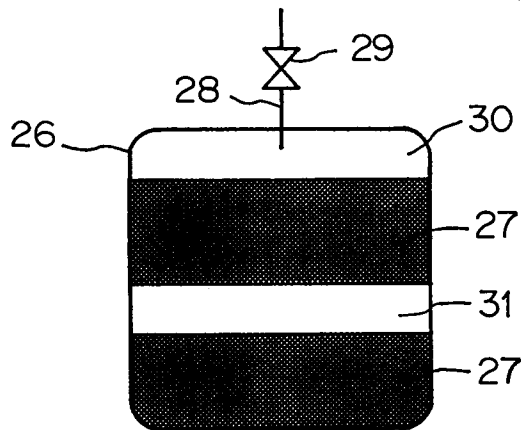


FIG. 7 (a)

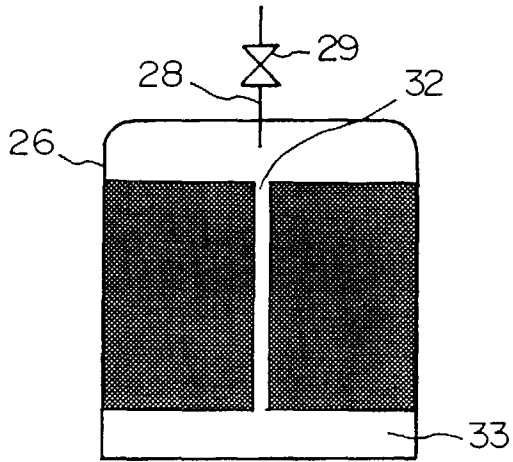


FIG. 7 (b)

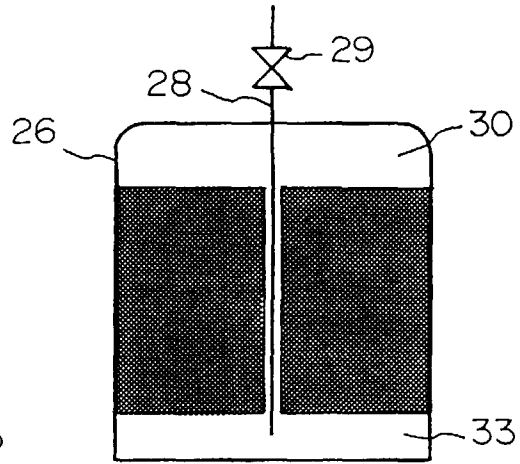


FIG. 7 (c)

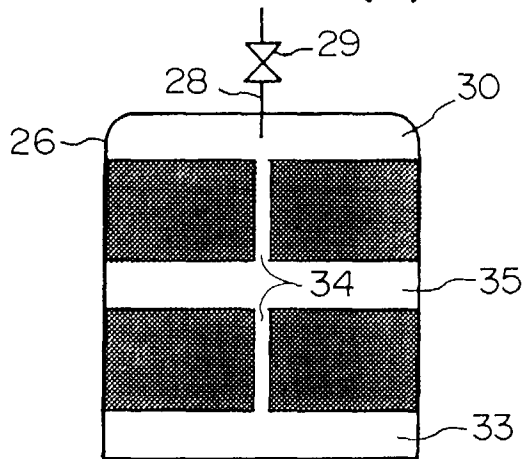


FIG. 7 (d)

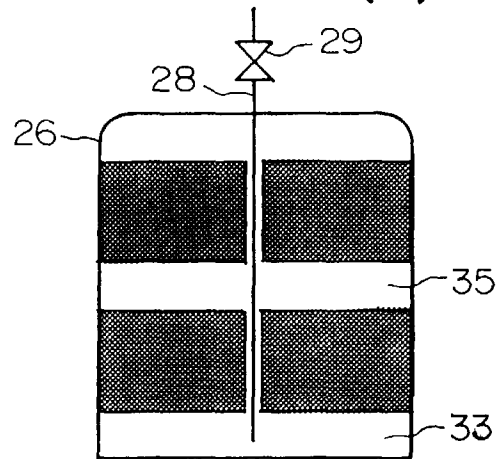


FIG. 7 (e)

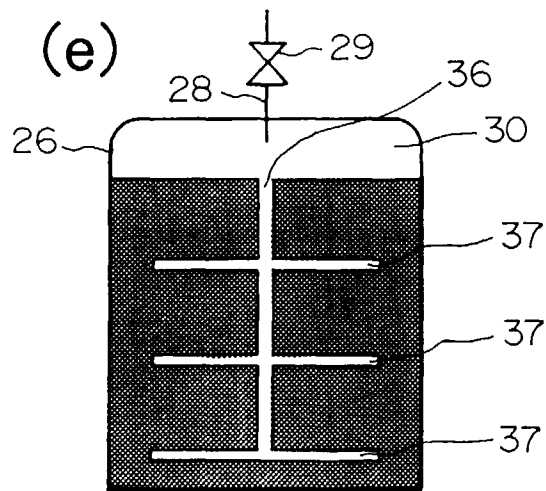


FIG. 8

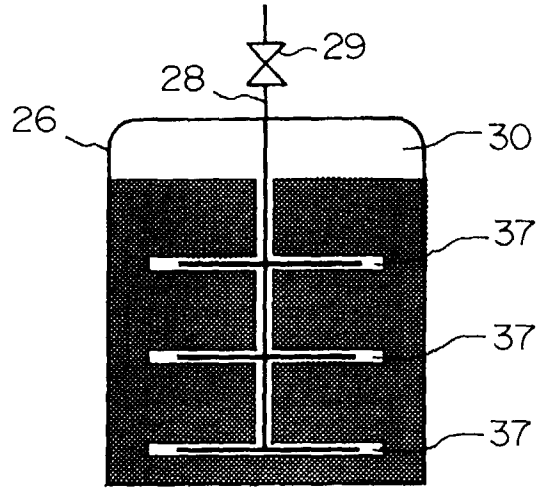


FIG. 9

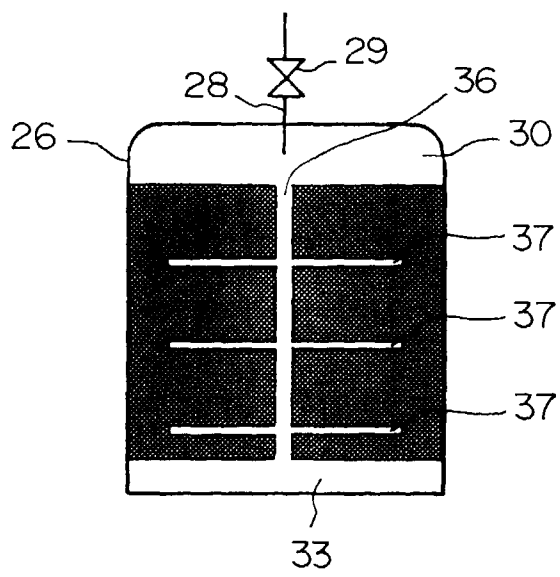


FIG. 10

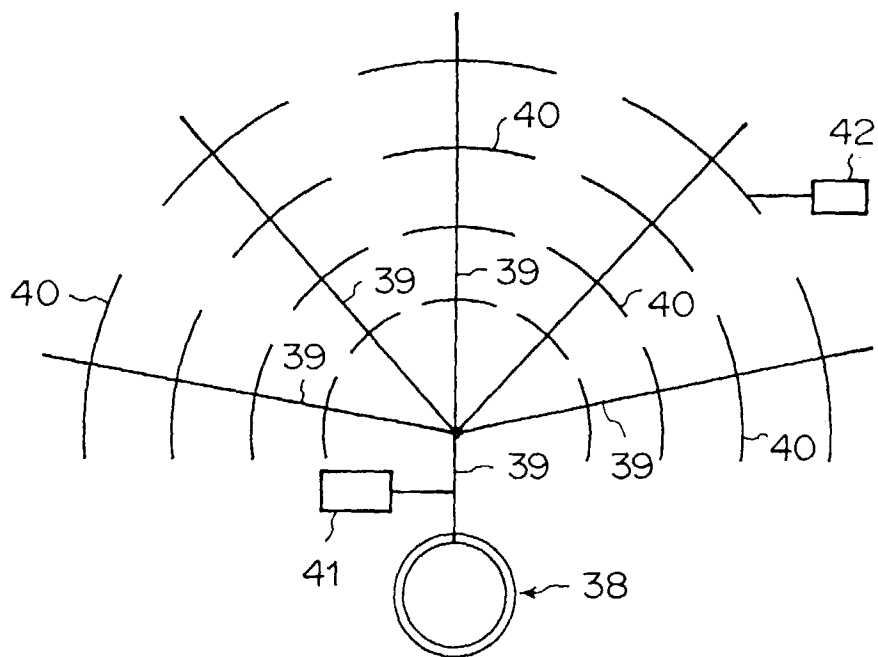
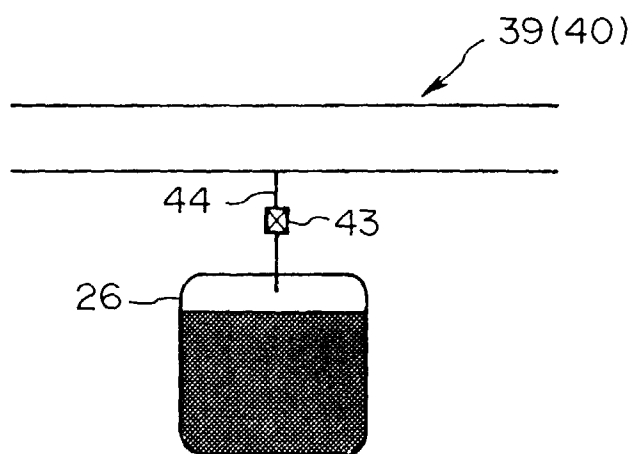


FIG. 11



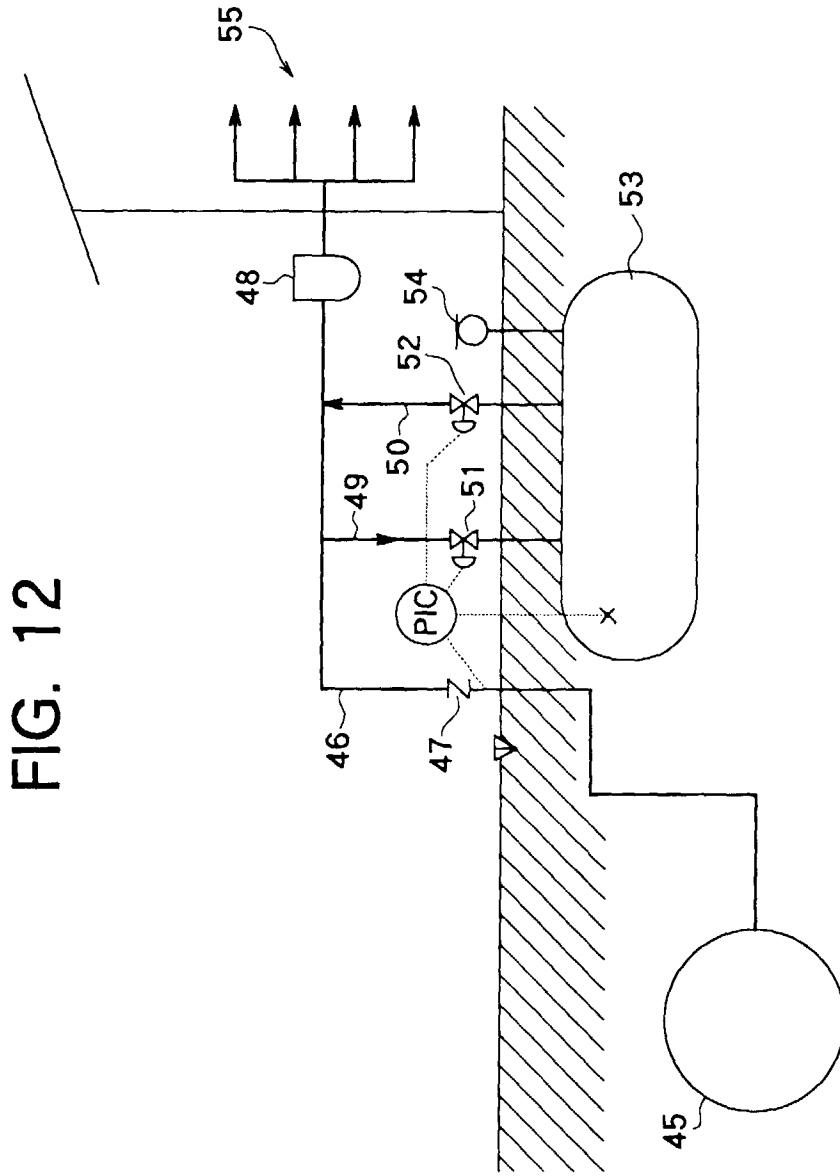


FIG. 12

FIG. 13

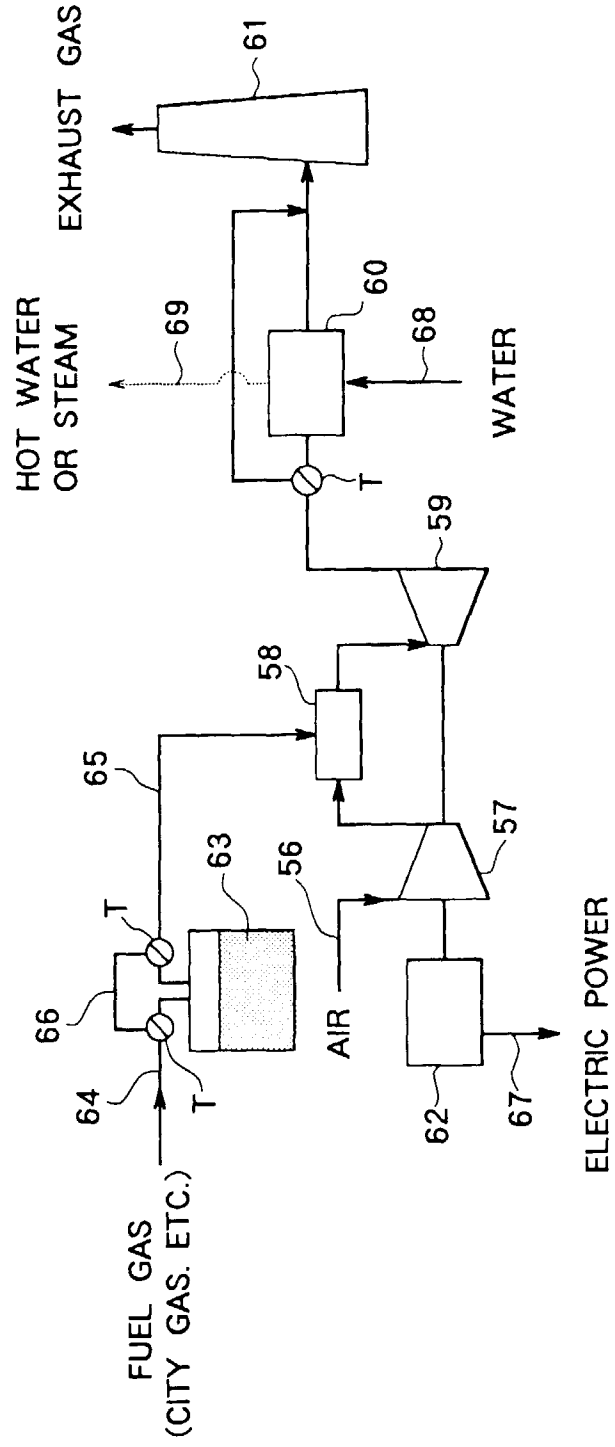


FIG. 14

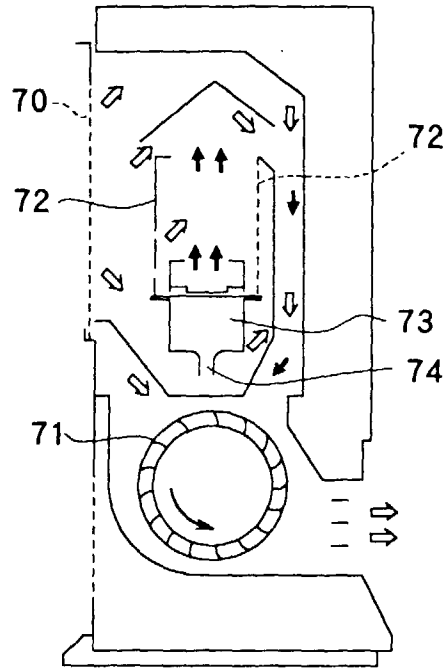
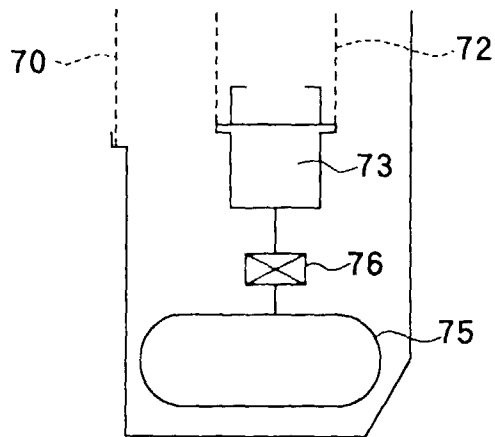


FIG. 15





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 10 7557

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 903 498 C (HASSEL)	1-7, 27, 28	F17C11/00 C10L3/00
Y	* claims *	8-11	
Y		12-26	
Y	--- PATENT ABSTRACTS OF JAPAN vol. 012, no. 222 (M-712), 24 June 1988 & JP 63 019500 A (OSAKA GAS CO LTD), 27 January 1988, * abstract *	8-11	
Y	--- US 5 473 904 A (GUO BOYUN ET AL) 12 December 1995 * claims; figure 3 *	12-26	
A	--- CHEMICAL ABSTRACTS, vol. 80, no. 3, 1974 Columbus, Ohio, US; abstract no. 28958, HASHII, KAZUO: "Rare Gas Cathrates" page 121; column 1; XP002070265 * abstract * & JP 73 023 795 A (JAPAN OXYGEN CO)		TECHNICAL FIELDS SEARCHED (Int.Cl.6) F17C
A,D	--- PATENT ABSTRACTS OF JAPAN vol. 018, no. 288 (C-1207), 2 June 1994 & JP 06 055067 A (OSAKA GAS CO LTD), 1 March 1994, * abstract *		
A,D	--- PATENT ABSTRACTS OF JAPAN vol. 004, no. 002 (C-069), 9 January 1980 & JP 54 135708 A (MITSUBISHI HEAVY IND LTD), 22 October 1979, * abstract *		
A	--- US 2 663 626 A (2663626) 22 December 1953 --- -/--		
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		13 July 1998	Meertens, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (F04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 7557

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 2 535 148 A (MARTIN ET AL) 26 December 1950 -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	13 July 1998	Meertens, J	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention	
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Y : particularly relevant if combined with another document of the same category		D : document cited in the application	
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