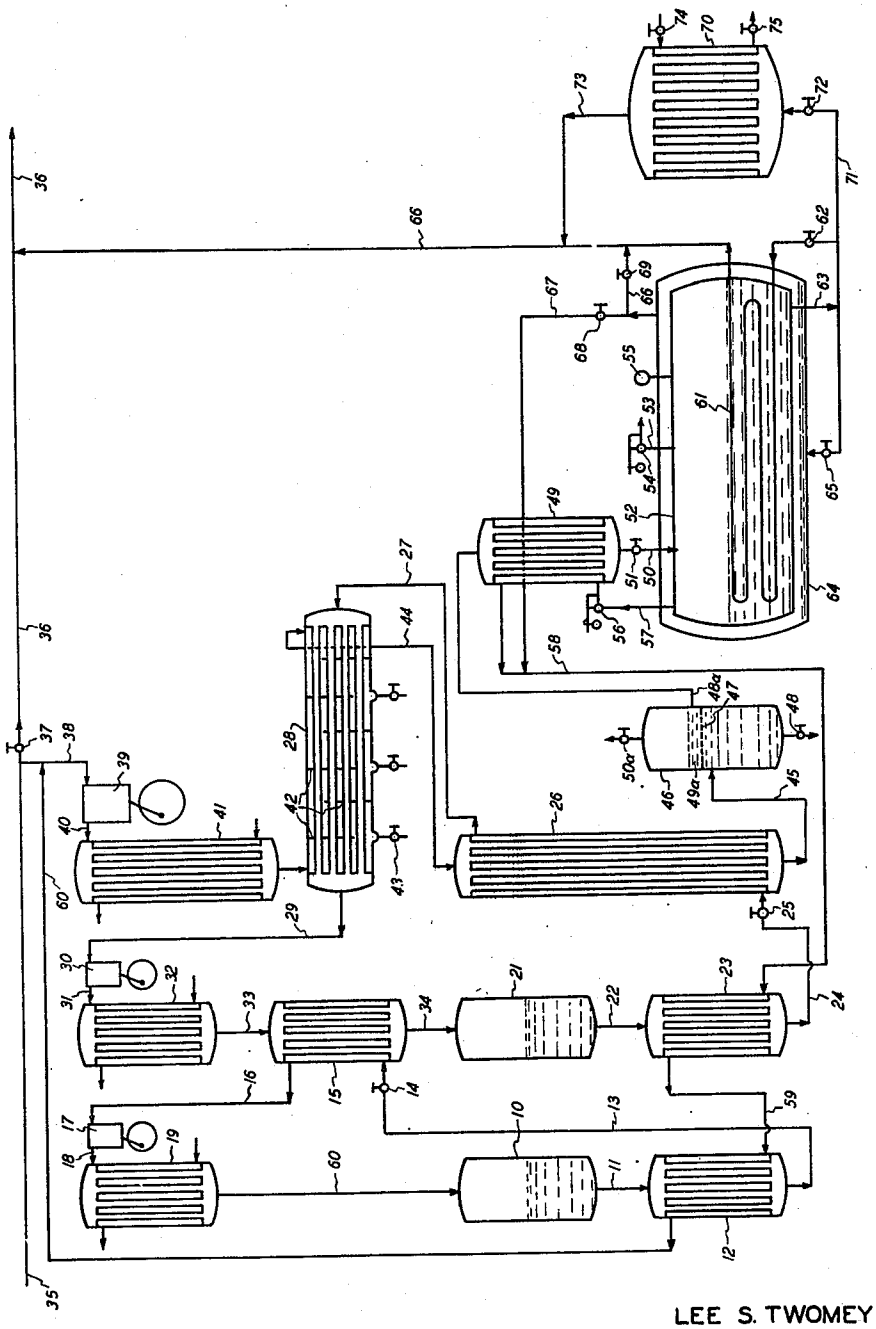
June 1, 1937. L. S. TWOMEY 2,082,189

METHOD OF LIQUEFYING AND STORING FUEL GASES

Filed May 9, 1934



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Patented June 1, 1937 2,082,189

UNITED STATES PATENT OFFICE

2,082,189

METHOD OF LIQUEFYING AND STORING FUEL GASES

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Application May 9, 1934, Serial No. 724,693

6 Claims. (Cl. 62—175)

The object of my invention is to provide means and a method for economically reducing hydrocarbon gases to the liquid condition, for maintaining them in storage at a slight superatmospheric pressure, and for converting them back to the gaseous state at such times as they may be required.

It is well known that at the present time many large cities rely largely on gas for household heating and for industrial purposes and that this gas is in large part of natural origin and is brought to the point of consumption over great distances.

The pipe lines through which this gas is conducted, often hundreds of miles in length, are enormously costly to build and to operate. The demand for gas naturally fluctuates with weather conditions, the variation between peak load and low load being in many cases as high as ten to one. As it is commercially impossible to provide an adequate amount of storage for gas at atmospheric temperature and pressure, or even for gas compressed to a fraction of its original volume, it has been necessary to adopt one or the other of two alternatives: either to provide production, pipe lines and pumping facilities having a normal capacity adequate for normal loads, crowding these lines to their limit during times of peak load and often leaving an excess demand unsupplied, or to so proportion the production and transportation facilities as to provide for maximum load, with the result that a very large investment is standing idle the greater part of the time.

Further, in most oil fields gas flow is utilized as a means for producing or is concomitant with the production of petroleum, and as the daily output of wells is limited by law or agreement and the wastage of gas is forbidden, a reduction in the demand for gas often results in a direct loss of allowable oil production. From the standpoint of the oil producer it is highly desirable that the requirement for gas be the same throughout the seasons.

My proposal is to operate pipe lines conducting gas in the most economical manner, at their normal load constantly maintained, to reduce the excess delivery during periods of low load to the liquid form, to maintain this liquefied gas in storage at substantially atmospheric pressure, and to draw on this liquid storage during peak load periods. By this procedure, which is made possible by the methods herein disclosed, existing lines may be made to transport much greater quantities of gas throughout the rotation of seasons than is now possible, the excessive cost of pumping at maximum pressure during peak load periods is avoided as is also acute shortage during times of extreme cold, and new installations of pipe lines and pumps may be based on average annual loads rather than on the maximum seasonal load.

It is now common practice to store limited quantities of fuel gas in pressure vessels, at from 100 to 500 pounds gauge. When it is reflected that any unit of space will hold approximately eight volumes of gas compressed to 100 pounds gauge or thirty five volumes compressed to 500 pounds, while it will hold approximately six hundred and forty volumes of the same gas when reduced to liquid form, and further that the liquid gas does not necessarily require the use of pressure vessels, the extreme advantages incident to storage in the liquid phase will be evident.

Natural gas, while quite variable in the proportions of its constituents, is qualitatively constant, being composed in almost all cases of varying proportions of the first four members of the normal series of paraffins—methane, ethane, propane, and butane. The pentanes and other constituents which may profitably be put into commercial liquid products are now, as a rule, closely fractionated from the constituents normally gaseous, and sold with the gasoline which accompanies most gas produced from oil wells.

The temperatures and pressures at which hydrocarbon fuel gases may be liquefied will vary from place to place and from time to time with the quantitative composition of the gas delivered by any pipe line. The plant in which it is reduced to the liquid state must therefore be reasonably flexible as to both temperature and pressure possibilities, but should in any case be capable of liquefying pure methane, which is the most refractory constituent of most natural gases. The required plant will have apparatus for liquefying and suitable vessels for storage without waste, the latter being provided with means for withdrawing the liquid and for reconverting it to the gaseous form without fractionating it by evaporation of its lighter constituents.

The method steps making up my invention are best described in connection with the attached drawing, which diagrammatically illustrates various combinations of apparatus suitable for putting them into effect.

In the following description all temperatures are in degrees Kelvin, or centigrade degrees absolute. Pressures stated in atmospheres are ab-

solute, those given in pounds gauge are plus one atmosphere absolute.

Referring to the drawing; 10 is a receiver containing a quantity of liquefied anhydrous ammonia, at atmospheric temperature and under a pressure equivalent to its vapor pressure at that temperature. The liquid ammonia passes through pipe 11 to and through the tubes of interchanger 12 where it is brought to a temperature somewhat below atmospheric in a manner which will be described. It then passes through pipe 13 and a regulating valve 14 to the shell (the space surrounding the tubes) of a condenser 15, the shell being maintained at or about atmospheric pressure by regulation of the valve. In this shell the ammonia vaporizes at an initial temperature about 240°, being its boiling point at atmospheric pressure. Absorbing heat from gaseous ethylene flowing downwardly through the tubes of condenser 15, the ammonia gas leaves the shell through pipe 16 at substantially atmospheric temperature. Passing then to compressor 17, it is raised to its condensation pressure at atmospheric temperature, then through pipe 18 to and through the tubes of a condenser 19, these tubes being cooled by water. In the condenser it is brought back to substantially atmospheric temperature and thereby condensed, the liquefied ammonia passing through pipe 20 to receiver 10. This completes a closed ammonia cycle.

Numeral 21 indicates a receiver containing a quantity of liquefied ethylene, at a temperature about 240° and at a pressure corresponding to its vapor pressure at that temperature. The liquid ethylene passes through pipe 22 and the tubes of interchanger 23 where it is brought to a temperature somewhat below 240° in a manner which will be described. It then passes through pipe 24 and a regulating valve 25 to the shell of a condenser 26, the shell being maintained at or about atmospheric pressure by regulation of the valve. In this shell the ethylene vaporizes at an initial temperature about 168°, being its boiling point at atmospheric pressure.

Withdrawing heat from partly cooled fuel gas flowing downwardly through the tubes of condenser 26, the gaseous ethylene leaves the shell through pipe 27 at substantially atmospheric pressure and flows to the tubes of a dehydrating interchanger 28 in which it is heated to atmospheric temperature in cooling compressed fuel gas. Passing then through pipe 29 to compressor 30 it is raised to its condensation pressure at the temperature of the ammonia cooled tubes of condenser 15. From the compressor the hot compressed gas flows through pipe 31 and the tubes of a cooler 32 which is supplied with cold water. In cooler 32 the compressed gas is returned to atmospheric temperature but is not liquefied, the compressed and cooled gas flowing through pipe 33 and the tubes of condenser 15 which, as already stated, are cooled by evaporating ammonia to 240°. At this temperature the ethylene condenses and passes through pipe 34 to receiver 21, thus completing the ethylene cycle.

A continuous stream of the fuel gas to be liquefied is introduced to the system through a pipe 35, which may be the pipe line through which gas is brought from the field and which may extend to connect with the distribution system as a pipe 36, a regulating valve 37 being interposed to maintain a substantially constant but usually slight pressure in the compressor intake. A branch pipe 38 conducts the gas stream to the suction side of a compressor 39 by which it is raised to a pressure at which it will condense at a temperature of 168°. The hot compressed gas passes through pipe 40 and the tubes of a cooler 41 which is supplied with cold water. In this cooler the compressed gas is returned to atmospheric temperature but is not entirely liquefied, the compressed and cooled gas flowing to the shell of dehydrating interchanger 28.

This interchanger is cooled by cold ethylene gas, as described, to a temperature at which water vapor is condensed and in part frozen. It should be provided with baffles 42 by which it is divided into pockets, these pockets being drained by valves 43. The entire unit should be duplicated and provided with suitable diversion pipes and valves so that one may be cut out of the system and freed from ice while the other is being used.

From the dehydrator the partly cooled gas passes through pipe 44 into the tubes of condenser 26 which, as said, are cooled by liquid ethylene evaporating at atmospheric pressure at 168° K. In this condenser the entire gas liquefies unless it contains hydrogen or nitrogen which, if present, may be separated in the next unit. Any carbon dioxide which may be present in the original gas is frozen at the temperature existing in this condenser but is not deposited in the tubes because of the rapid flow of liquid hydrocarbons over them, and the entire condenser output, consisting of liquid hydrocarbons, suspended solid carbon dioxide and gaseous nitrogen and hydrogen pass through pipe 45 to the trap 46.

The trap which, like the dehydrator, should be provided in duplicate to permit of thawing when choked, is a vertically arranged shell into which pipe 45 enters at a medial height. Above this level a filtering disc 47 is disposed across the shell, this disc being of cloth supported by a perforated plate or of fine mesh metal filter cloth, or other known filtering material. Carbon dioxide crystals entering with the liquefied gas may settle into the lower part of the shell from which they may be withdrawn as a slimy suspension through valve 48, or they may pass upwardly with the liquid and be retained by the screen. The liquid and gaseous portions of the stream pass through the screen and the liquid is withdrawn from a point above the screen, as by pipe 48*a*, a space 49*a* being provided above the liquid level for the accumulation of incondensible gas which may, from time to time, be vented through valve 50*a*.

The pressure in the various receivers, using the refrigerating gases above described will be approximately 110 pounds gauge in ammonia receiver 10 and approximately 250 pounds gauge in ethylene receiver 21. The pressure in the trap will vary with the constitution of the particular gas, but if we assume the gas to consist entirely of methane, which is an extreme condition, it will be about 290 pounds gauge. With most natural gases the pressure will be materially lower. All the above temperatures assume perfect interchange, which is hardly realized, and in practice the outlet temperatures will usually be about 5° above those stated.

The above described method of cooling and liquefying gases is substantially that described and claimed in my copending application entitled "Method of producing low temperature refrigeration", filed May 9, 1934, under Serial No. 724,691.

As fully set forth in the copending application, any one of a number of other gases may be sub-

stituted for ammonia in the first cycle, as for example propylene, propane, allylene, methyl chloride, sulphur dioxide, and carbon dioxide, while ethane and nitrous oxide may be substituted for ethylene in the second, all these changes involving some changes in temperatures and pressures. It is also possible to raise and lower the evaporating temperatures of the refrigerant gases by varying the pressure to which they are expanded. Air cooled apparatus may be substituted for the water cooled units 19, 32, and 41, and other changes in structure and operation may be made without departing from the spirit of the disclosure.

As above described, the product (liquefied fuel gas) continuously passes into trap 46 at a temperature approximating 168° absolute and a pressure ranging downward from 290 pounds gauge. As it would be unduly expensive to store the liquid under such conditions of temperature and pressure, I first reduce its temperature to that at which its vapor pressure is only slightly superatmospheric, preferably not in excess of 15 pounds gauge. If the liquid fuel gas should consist solely of methane, the temperature at 15 pounds gauge would be 122°, but in practice it will usually be somewhat higher.

To accomplish this result I permit a portion of the liquefied gas to evaporate and expand either to atmospheric pressure, at which pressure methane will be reduced to 112°, or to the pressure at which it is to be stored.

The liquid product is allowed to flow from the trap through pipe 48*a* and the tubes of an interchanger 49, in which its temperature is somewhat reduced as will be described. Thence the liquid flows through pipe 50 and valve 51, by which the volume of flow is regulated, into a storage tank 52 so proportioned as to have a safe working pressure of say 15 pounds gauge. This tank should be provided with a blow-off pipe 53 having a safety valve 54 set for a pound or two over working pressure, but this valve is provided for emergencies only.

The pressure on this tank may be read on a pressure gauge 55 and should be maintained at the working pressure by manipulation of a valve 56 in a return gas line 57. This valve may conveniently be a weighted or spring relief valve set for the working pressure.

On the passage of the liquid product through control valve 51 into the zone of lower pressure within storage tank 52 a portion of the liquid will flash into the gaseous form and the temperature will be reduced to the boiling point of the liquid at the pressure within the tank. The portion which does not so flash and return to the gaseous condition is stable at tank pressure so long as leakage of heat into the tank is prevented. It may be said at this point that all parts of this apparatus which are materially below atmospheric temperature are heavily heat insulated, but as this practice is entirely conventional it need not be described in detail.

The gas produced by the above described flashing operation leaves the tank through pipe 57, at the temperature of the liquid in the tank, and is thus materially colder than any of the liquids collected in the receivers. To recover the cooling effect of this relatively large volume of cold gas I pass it back through a series of interchangers already referred to: thus it passes through pipe 57 to the shell of interchanger 49 where it somewhat reduces the temperature of the stream of liquid product leaving trap 46, then through pipe 58 to the shell of interchanger 23 where it reduces the temperature of the stream of liquid ethylene leaving receiver 21, then through pipe 59 to the shell of interchanger 12 where it reduces the temperature of the liquid ammonia leaving receiver 10, and finally returns through pipes 60 and 38 to the intake side of the fuel gas compressor at substantially atmospheric temperature.

The liquefied fuel gas being now in storage at a preferred superatmospheric pressure and at a temperature at which its vapor pressure does not exceed the preferred storage pressure, it is necessary to maintain it at that temperature so long as it is stored, and as even the most effective insulation will permit some infiltration of atmospheric heat toward the storage vessel, it becomes necessary to constantly withdraw this heat either from the stored contents or from a fluid layer interposed between the vessel itself and the interior of the insulation.

The first of these alternatives is shown in the drawing as a pipe coil 61 sealed into the upper portion of the vessel and supplied with a liquefied gas such as methane. The interior of the coil is maintained at a pressure below that on the liquefied refrigerant and the evaporation of the liquid as it is admitted through control valve 62 reduces the temperature of the coil below the temperature of the stored liquid and thus provides for absorption of the heat which passes through the insulating layer into the liquefied contents of the vessel. The supply of liquid is shown as being drawn from tank 52 through a pipe 63 but it may be provided from any other source of liquid of the same or lower boiling point.

The second of these alternatives is shown in the drawing as a jacket 64 surrounding the vessel and spaced a few inches from it, this jacket being gas tight at atmospheric pressure. The liquefied cooling gas is admitted to this jacket through a valve 65, in such quantity as to maintain at least a small pool of liquid in the jacket, which is maintained at atmospheric pressure. This liquefied gas is regasified at a rate determined by the rate of heat infiltration, and maintains around the vessel a temperature slightly below the normal storage temperature, thus preventing atmospheric heat from reaching the stored contents. The gas thus produced passes through pipe 66 into distribution pipe 36, or during operating periods it may be diverted into pipe 58 through pipe 67 for recovering its cooling effect, valve 68 being then open and valve 69 closed. While not functionally identical, these two methods for maintaining the stored liquids at a stable temperature are practically equivalent.

The object in maintaining even a slight superatmospheric pressure on tank 52 is to provide a heat head between the contents of the tank and a liquid of the same boiling point expanding to atmospheric pressure. By expanding the cooling liquid to a slightly subatmospheric pressure, or by using a cooling liquid of lower boiling point, the requirement for pressure on the tank contents may be avoided.

On the other hand it may be economically desirable to store the liquid product at much higher pressures, as from 100 pounds to 400 pounds gauge, in which case the initial pressure on the gas is increased and the condensing temperature is correspondingly raised. At 100 pounds gauge the boiling point of methane is 142° K., at 400 pounds gauge it is 171° K., and at these temperatures the heat head between the atmosphere and

the contents of the tank is materially lowered, with a consequent reduction in the amount of refrigeration required to maintain a constant temperature within the tank. At 400 pounds pressure the cooling may be effected by the atmospheric pressure evaporation of liquid ethylene.

In returning stored gas into the distribution system it is necessary to supply the heat rendered latent in evaporation and for returning the gas to atmospheric temperature. For this purpose a device is provided comprising a shell 70 into which liquefied gas passes from storage vessel 52 through pipe 71 controlled by a valve 72, the gasified material flowing from the upper part of the shell through pipes 73 and 66 into distribution pipe 36. If the pressure in the tank is below that of distribution, the liquid may be pumped into the gasifying device. The requisite heat is supplied by steam or other heating fluid admitted to the space around the tubes through a pipe and valve 74 and the space may be drained by means of a pipe and valve 75.

I claim as my invention:

1. The method of increasing the operative capacity of hydrocarbon fuel gas distribution systems which comprises: raising a stream of said fuel gas to a material superatmospheric pressure; effecting a first cooling of said fuel gas stream to atmospheric temperature; effecting a second cooling of said stream to a temperature below the freezing point of water whereby said stream is substantially dehydrated; effecting a third cooling of said stream by heat interchange with an evaporating liquid refrigerant to a temperature at which the hydrocarbon constituents of said stream are liquefied at compression pressure; separating from said stream any gaseous and any solid substances accompanying said liquid stream; introducing said stream into a storage vessel maintained at a desired subatmospheric temperature; returning any gases evolved in said storage vessel to be recompressed, and maintaining the desired temperature in said vessel by the evaporation of a controlled quantity of the liquid collected in said vessel in heat exchange relation with the liquid contents of said vessel.

2. In the liquefaction of a stream of fuel gas by means involving the evaporation of liquid refrigerants, the steps comprising the reduction of pressure on the liquefied stream, whereby a cold gas is produced, and the utilization of said cold gas in reducing the temperatures of said liquid refrigerants below their respective condensation temperatures prior to the evaporation of said refrigerants in liquefying said stream.

3. In a liquefaction of fuel gas involving the evaporation of a stream of liquefied refrigerant and the subsequent passage of said liquefied gas into a vessel, the step of utilizing cold gases evolved in said vessel in cooling said refrigerant prior to the evaporation of said refrigerant in liquefying said gas.

4. In the liquefaction of a gas having a lower boiling point than that of ethylene by heat interchange between said gas and an evaporating stream of liquid ethylene, the step of cooling said liquid ethylene stream prior to said evaporation by heat interchange against cold gases resulting from evaporation of first said gas from the liquefied condition.

5. The method of manipulating a fuel gas which comprises: liquefying said gas by compression and by cooling in heat interchange relation with a succession of liquid refrigerants; introducing said liquefied gas into a substantially closed vessel; withdrawing from said vessel any gases evolved therein, and returning said gases in heat interchange relation with said succession of liquid refrigerants.

6. In the liquefaction of a stream of fuel gas, the steps of effecting dehydration of said stream, prior to said liquefaction, by heat interchange with a cold gas resulting from the evaporation of a liquid refrigerant used in an external refrigerating cycle in effecting said liquefaction and of removing from said stream, in the liquid condition, a substantial proportion of the water condensed in said heat interchange dehydration.

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