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REMOVAL OF AROMATICS FROM LIQUEFIED NATURAL GAS

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FIG. 1

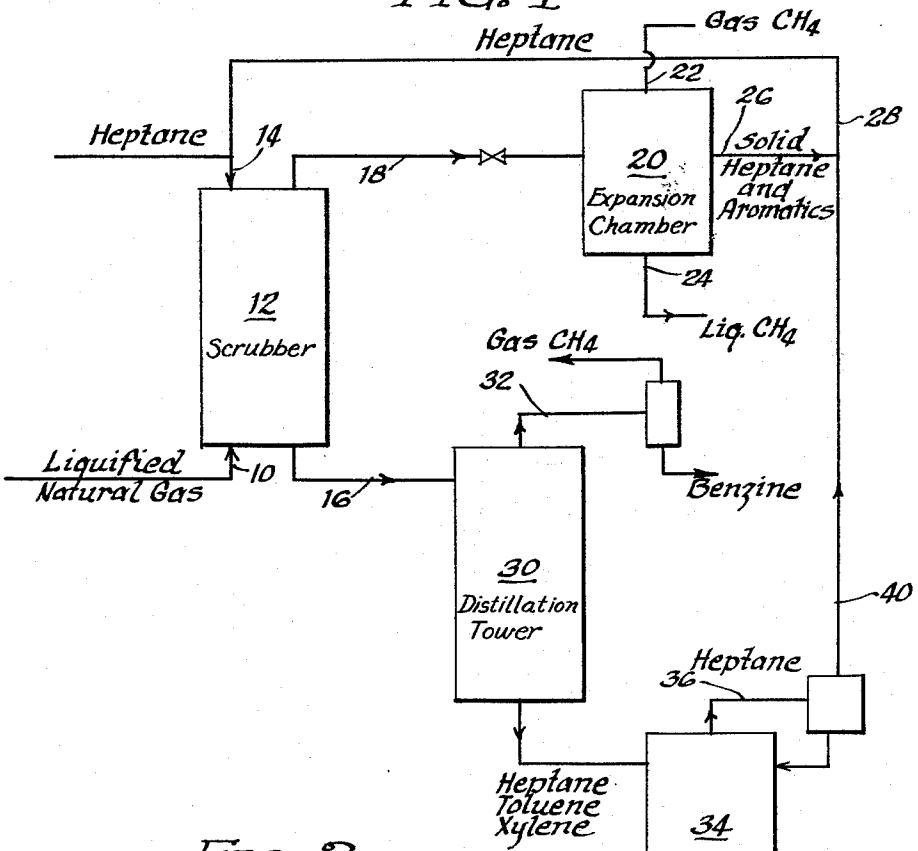
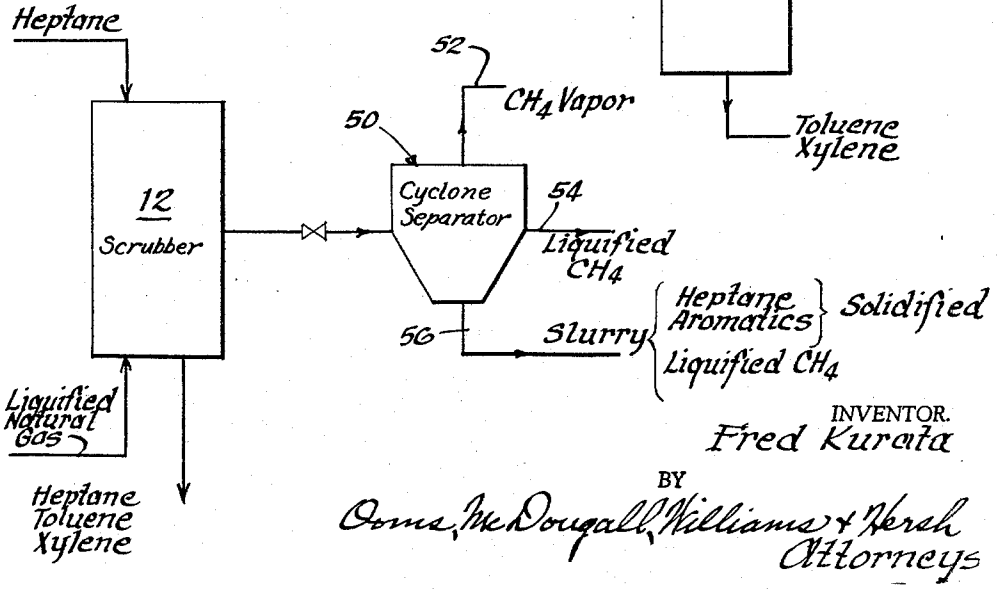



FIG. 2




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# REMOVAL OF AROMATICS FROM LIQUEFIED NATURAL GAS

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This invention relates to the processing of natural gas in the liquefaction thereof and it relates more particularly to the removal of aromatics and higher hydrocarbons from a liquefied natural gas in a gas liquefaction process for the recovery of the aromatics and higher hydrocarbons and for the improvement of the process as well as protection of the equipment in the liquefaction process.

To a variable extent, depending on location or source, natural gas will be found ot contain aromatics and higher hydrocarbons having a freezing point higher than the boiling point of methane. These materials, especially the aromatics, have been found to be harmful in the process for the liquefaction of natural gas because they condense at temperatures considerably higher than the liquefaction temperature for the methane component of the natural gas and they tend to plate out on the surfaces of process equipment, such as turbine blades, heat exchanger surfaces and the like, thereby to interfere with the efficiency and operation of the equipment. When, for example, the liquefied natural gas is processed through a heat exchanger, the aromatics and higher hydrocarbons that plate out on the surface of the heat exchanger, greatly reduce the heat transfer characteristics of the unit to reduce the efficiency thereof and throw the entire system out of balance.

Thus, it is desirable to effect the removal of as much of the higher hydrocarbons and aromatics as possible from the natural gas during the liquefaction process or in advance thereof. As a matter of further practicability, the aromatics and some of the higher hydrocarbons have a value in their separated state which is far greater than their value as an inclusion in the liquefied natural gas. As a result, their separation is desirable also from the standpoint of economy and use.

Therefore, it is an object of this invention to provide a method and means for the removal or separation of aromatics and higher hydrocarbons from methane, and it is a related object to provide a method and means for the removal of such aromatics and higher hydrocarbons from natural gas when processed to a liquefied state.

More specifically, it is an object of this invention to provide a means and method for the efficient and economical removal of aromatics and higher hydrocarbons from a system composed chiefly of methane, as represented by natural gas; which requires the use of a minimum amount of equipment and labor; which does not interfere with the continuity or the mass production process for the liquefaction of natural gas; which produces a relatively pure aromatic or higher hydrocarbon and correspondingly results in a liquified natural gas which is relatively free of such materials; which achieves maximum recovery of aromatics and higher hydrocarbons present in the natural gas, and which makes use of inexpensive and readily available material in the separation and makes possible the recovery thereof for reuse in substantially continuous operation.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, embodiments of the invention are shown in the accompanying drawing, in which—

FIGURE 1 is a flow diagram showing the process steps employed in the practice of this invention, and

FIGURE 2 is a partial flow diagram showing a modified system which may be used in the practice of this invention.



The inventive concepts will hereinafter be decsribed with reference to the treatment of natural gas in a liquefied state to effect the removal of aromatics and/or higher hydrocarbons which may be included in the natural gas. Liquefaction may be achieved initially by an expansion process or by a cascade process or by combinations thereof well known to the art. Such aromatics and higher hydrocarbons will usually be found to be present in the liquefied natural gas in amounts less than 10 percent by weight and more often in an amount less than 2 percent by weight. The principal component of natural gas is methane which will be present in an amount greater than 80 percent by weight and usually in an amount greater than 90 percent by weight. Thus the concepts hereinafter described with reference to the removal of aromatics and higher hydrocarbons from liquefied natural gas will be applicable also for the separation of the same materials from liquefied methane, the only difference being that the boiling point temperature for liquefied methane at atmospheric pressure will be —258° F. instead of about —240° F. to —258° F. for liquefied natural gas and the critical temperature for liquefied natural gas may be a few degrees higher than the critical temperature of —116° F. for pure methane.

The concepts of this invention reside in the removal of aromatics and higher hydrocarbons from liquefied natural gas by extraction with a liquid which has little solubility in the liquefied natural gas and is only partially miscible with the liquefied natural gas and in which the aromatics and higher hydrocarbons are preferentially soluble by comparison with natural gas. It is preferred to make use of a liquid-liquid system wherein the scrubbing liquid is insoluble and immiscible with the liquefied natural gas, although partial miscibility is not disadvantageous from the standpoint of wetting out one liquid with the other for transfer of aromatic components.

The successful practice of this invention depends upon the presence of a number of conditions during processing. Contact between the two materials for extraction should be carried out while the methane is in the liquefied state. Thus the extraction process can be practiced at any temperature below the critical temperature, which for methane is about —116° F. and possibly higher (10°–20° F.), for natural gas. The lower limitation from the standpoint of the natural gas is the temperature at which the extracting liquid or the constituents in the natural gas begin to freeze out. The process is independent of pressure from the standpoint of natural gas, with the exception that the process should be carried out above the minimum pressure, which is that required to keep the methane and the scrubbing liquid in a liquefied state during process. This pressure is fixed by the temperature at which the natural gas is liquefied. In general, it is advantageous to liquefy the natural gas at a temperature slightly above the temperature at which the scrubbing liquid or higher hydrocarbons begin to freeze out.

Contact between the two liquids should be carried out while the extracting material is also in a liquid phase. Thus it becomes necessary to make use of a liquid which has a freezing point below the critical temperature for the liquefied gas, or below —116° F. for a methane system. In addition, the temperature conditions existing in the process, while below the critical temperature for methane, should also be above the freezing temperature for the methane system and the extraction liquid. Thus, it is often necessary from the standpoint of wider selection of extraction liquids and maintenance thereof in a liquefied state, to make use of positive pressure conditions during operation to enable the use of temperatures above —258° F. (the boiling point temperature for pure methane at atmospheric pressure), but below —116° F.

The lower the freezing point of the scrubbing liquid, the lower the pressure required for operation since a lower temperature means less pressure is required to keep the methane in a liquefied state.

Briefly described, the process embodying the features of this invention can be operated under any pressure and temperature conditions which will be below the critical temperature for liquefied methane (−116° F.) or natural gas and above the freezing point of the scrubbing liquid and the natural gas system.

Further, the best practice of this invention resides in the use of an extraction liquid which is insoluble and immiscible or at most partially miscible with the liquefied methane, and in which the aromatic and higher hydrocarbons in the natural gas are preferentially soluble.

The described conditions are capable of being met by normal heptane, for example, which has a freezing point of −131° F. This is below the critical temperature of −116° F. for the methane and above the freezing temperature of methane. It is partially miscible with the methane and is soluble in liquefied methane to the extent of about 0.92 mol percent, and the aromatics and higher hydrocarbons are preferentially soluble in normal heptane by comparison with liquefied methane.

The normal hydrocarbons below heptane, such as N-hexane, N-pentane and the like, are incapable of use in the practice of this invention because they are substantially miscible or soluble in liquefied methane whereas the higher homologues, as represented by N-octane, for example, have freezing points which are above the critical temperature of methane. In addition to heptane, use can be made of toluene (FP–139° F.), methylcyclohexane (FP–195.6° F.), 2,2,4-trimethylpentane (FP–170° F.), and 2,2,3-trimethylpentane (FP–161° F.). It will be understood that the foregoing are given by way of illustration and not by way of limitation because any liquid can be employed which meets the described specifications. It will be understood that combination of liquids can be employed to provide a material which fits into the specification as described. For example, a mixture of iso-pentane and iso-octane, or a mixture of hexane and heptane, or a mixture of octane and toluene can be employed. Any aromatic present in natural gas, as represented by benzene, toluene, xylene and naphthalene, would preferentially dissolve in these materials by comparison with methane. The same applies to hydrocarbons heavier than heptane, such as octane, decane and the like, thereby simultaneously to effect their removal on the same principles as are employed in the removal of aromatics.

To illustrate the practice of this invention, description will be made with reference to a system employing normal heptane as the extracting liquid and methane as the main component of a liquefied natural gas containing about 1 percent by weight of aromatics and higher hydrocarbons. For this purpose, reference will now be made to the flow sheet of FIGURE 1.

Liquefied natural gas, which will be assumed for purposes of illustration to have about 1 percent by weight aromatics and higher hydrocarbons, is fed from line **10** into a scrubbing tower **12** at the bottom at a pressure of about 500 pounds per square inch and at a liquefaction temperature of about −130° F. Normal heptane, soluble in the methane in an amount of about 0.9 mol percent, is fed through the inlet **14** into the tower **12** at the top in countercurrent flow with the liquefied natural gas in an amount corresponding to about 10 mols of heptane per 100 mols of natural gas, or an amount corresponding to about 50 percent by weight of the liquefied natural gas. The effluent **16** from the bottom of the tower **12** will consist essentially of heptane containing about 90 percent of the aromatics and the higher hydrocarbons originally present in the natural gas, and about 10 percent by weight of methane, while the effluent **18** at the top will be a relatively clear liquid containing mostly methane, about 0.0092 mol of heptane per mol of methane, and less than 10 percent by weight of the aromatics and higher hydrocarbons originally present in the natural gas, or about 1 percent by weight heptane and less than 0.1 percent of the aromatics.

With this reduced amount of aromatics, the liquefied natural gas component **18** can now be expanded stepwise from the high pressure at which the liquefaction process was carried out to a lower pressure, such as atmospheric pressure, without fear of the aromatics plating out on the surfaces of the process equipment.

When the effluent issuing from the top of the tower **12** is subsequently expanded to lower pressure, either stepwise or in a single step, as to atmospheric pressure, for example, in an expansion chamber **20**, the temperature will be reduced to about −258° F. Some of the liquefied natural gas component will be flashed off as a vapor upon expansion but the greater majority of the liquefied natural gas component (mostly methane) will remain in the liquefied state at the lower temperature conditions existing. However, at this temperature, the heptane, which solidifies at −131° F. when pure and at a temperature of −151° F. to −156° F. in the presence of methane, will become solidified so that separation of the heptane and aromatics dissolved therein from the remainder can be effected by filtration or other conventional separating means. Thus, relatively pure methane vapor at about one atmospheric pressure and about −258° F. will be removed from the outlet **22** at the top of the flash chamber, and relatively pure liquefied natural gas component (mostly methane) at one atmospheric pressure and −258° F. will be removed from the outlet **24** at the bottom of the flash chamber, while solidified heptane and aromatics will be separated out, as indicated by the numeral **26**.

The vapor issuing from the outlet **22** can be recycled to the liquefaction cycle for reliquefaction in advance of the scrubbing step, or it can be processed in a separate liquefaction step. In the alternative, it can be used as a fuel or the like, but preferably after the refrigeration available in the vapor has been beneficially employed and the vapor consequently raised in temperature. The solidified heptane **26** and the small amount of aromatics filtered out in the flash-chamber can be remelted and recycled through lines **28** for reuse as feed in the scrubbing tower, or the solidified product may be processed through a stripper to separate the heptane from the aromatics for reuse of the heptane in the process, while other desirable use can be made of the aromatics, as in chemical synthesis or the like.

The effluent issuing in line **16** from the bottom of the scrubbing tower **12** can be processed through a stripper to separate the natural gas component (mostly methane), heptane and aromatic components. It will be assumed that, under the most exaggerated conditions, the aromatic component of the material would be composed of a mixture of benzene (B.P. 80° C.), toluene (B.P. 110° C.), and xylene (B.P. 139° C.). A stripper in the form of a distillation tower **30** can be employed wherein the materials having a boiling point below 90° C., for example, are distilled off. This will cause the natural gas component (methane) and benzene to be distilled off at the top **32** while the residue, coming off at the bottom, will be made up of the heptane (B.P. 98° C.), toluene and xylene. The vapors distilled off at the top can thereafter be processed through a condenser operating below the boiling point of benzene but above the boiling point of methane (−258° F.) to separate the benzene by condensation from the methane. The latter may be collected as a vapor for use as described with respect to the methane or natural gas component flashed from the expansion chamber **20**.

The heptane can be separated from the toluene and xylene in a stripper **34**, such as a distillation tower, operating at 105° F. to drive off the heptane **36** as a vapor, while the toluene and xylene **38** are drained off as a liquid.

The heptane can be condensed for recycling through line 40 for reuse as feed in the scrubbing tower 12.

It will be understood that the processing steps employed subsequent to the scrubber may be varied depending upon the boiling point temperatures and the quantity of aromatics removed from the natural gas as compared to the boiling point temperature of the scrubbing liquid.

The amount of heptane or other scrubbing liquid introduced for contact with the liquefied natural gas or methane can be varied from a minimum amount where all of the heptane is dissolved in the liquefied methane, to a maximum where all of the liquefied methane is dissolved in the heptane. The preferred ratio lies somewhere between these two extremes. If excessive amounts of heptane are employed, the process becomes impractical because it would lead to a condition wherein an excessive amount of liquefied natural gas would be removed with the heptane. Excessively small amounts of heptane are also impractical because then almost all of the heptane with the aromatics dissolved therein would remain with the natural gas removed as a clear liquid from the scrubbing tower.

As the scrubber, use can be made of conventional packed towers or spray towers for continuous operation. Instead, use can be made of batch systems for contact between the two liquids, as in a mixer and decanter or the like.

Instead of removing the clear methane liquid or natural gas component 18 at the top and the heptane and extract at the bottom, the liquid-liquid system from the scrubber or contact tower can be directed in its entirety to a cyclone separator 50, as illustrated in FIGURE 2, as the liquid is expanded to a lower pressure, with resulting reduction in temperature to a level where the heptane will exist in a solidified or frozen state. The flash of relatively pure methane will be removed as a vapor 52 from the cyclone. Liquefied natural gas component (mostly methane) 54 will be separated from the solidified heptane, the latter of which will be removed as a slurry 56 from the bottom of the cyclone separator. The slurry, which will be formed of liquefied natural gas or methane, solidified heptane, and other higher hydrocarbons and aromatics, can be stripped, as by vaporization, to remove the methane component, leaving substantially pure heptane and the aromatics and higher hydrocarbons.

It will be apparent from the foregoing that I have provided a liquid-in-liquid system which operates efficiently and effectively to remove such amounts of aromatics and higher hydrocarbons as would subsequently plate out on the surfaces of process equipment as the liquefied methane or liquefied natural gas is reduced in temperature as by expansion or heat exchange. It will be apparent, further, that the removal of the aromatics and the higher hydrocarbons will permit substantially complete recovery of these materials as a relatively pure compound for subsequent use as a chemical in synthesis or the like.

It will be understood that changes may be made in the details of construction, arrangement and operation without departing from the spirit of the invention, especially as defined in the following claims.

What is claimed is:

1. A process for the removal of aromatics and higher hydrocarbons from a liquefied natural gas comprising the steps of scrubbing the liquefied natural gas with a liquid hydrocarbon having at least 7 carbon atoms and having a freezing point temperature below the critical temperature for the natural gas and relatively insoluble and immiscible with the liquefied natural gas and in which the aromatics and higher hydrocarbons are preferentially soluble by comparison with the liquefied natural gas, maintaining the conditions during the scrubbing operation between the critical temperature for the liquefied natural gas and the freezing point temperature for the scrubbing liquid and the liquefied natural gas, and then separating the scrubbing liquid from the remainder.

2. A process for the removal of aromatics and higher hydrocarbons from a liquefied methane comprising the steps of scrubbing the liquefied methane with another liquid hydrocarbon having at least 7 carbon atoms and having a freezing point temperature below the critical temperature for liquefied methane and which is relatively insoluble and immiscible in the liquefied methane and in which the aromatics and higher hydrocarbons are preferentially dissolved by comparison with the liquefied methane, maintaining the conditions during the scrubbing operation between the critical temperature for the liquefied methane and the freezing point temperature for the scrubbing liquid and the liquefied methane, and then separating the scrubbing liquid from the remainder.

3. A process for the removal of aromatics and higher hydrocarbons from a liquefied natural gas comprising the steps of contacting the liquefied natural gas with a liquid hydrocarbon having at least 7 carbon atoms and having a freezing point temperature below —116° F. and which is relatively insoluble and immiscible with the liquefied natural gas and in which aromatics and higher hydrocarbons are preferentially soluble by comparison with the liquefied natural gas, and maintaining the conditions during contact between the liquids below —116° F. but above the freezing point temperature for the scrubbing liquid and the liquefied natural gas and then separating the contacting liquid from the remainder.

4. A process for the removal of aromatics and higher hydrocarbons from a liquefied natural gas comprising the steps of contacting the liquefied natural gas with a liquid hydrocarbon having at least 7 carbon atoms and having a freezing point temperature below —116° F. and which is relatively insoluble and immiscible with the liquefied natural gas and in which the aromatics and higher hydrocarbons are preferentially dissolved by comparison with the liquefied natural gas, maintaining the conditions during operation below —116° F. and above —258° F., and then separating the contacting liquid from the remainder.

5. A process for the removal of aromatics from a liquefied natural gas comprising the steps of scrubbing the liquefied natural gas with a liquid hydrocarbon having at least 7 carbon atoms and having a freezing point temperature below the critical temperature for the liquefied natural gas and which is relatively insoluble and immiscible with the liquefied natural gas and in which aromatics are preferentially dissolved by comparison with the liquefied natural gas, and maintaining the conditions during scrubbing below —116° F. and above —258° F. and at pressures such that the natural gas is maintained as a liquid and separating the scrubbing liquid from the remainder.

6. A process for the removal of aromatics and higher hydrocarbons from a liquefied natural gas comprising the steps of bringing a liquid into contact with the liquefied natural gas wherein the liquid is a hydrocarbon having at least 7 carbon atoms and which is characterized by a freezing point temperature below the critical temperature for the liquefied natural gas and relative insolubility and immiscibility with the liquefied natural gas and in which aromatics and higher hydrocarbons are preferentially dissolved by comparisons with the liquefied natural gas, said liquids being brought into contact with each other in the ratio of 1 part by weight of the scrubbing liquid to 100 parts by weight of the natural gas as a minimum and 50 parts by weight of the scrubbing liquid to 50 parts by weight of the liquefied natural gas as a maximum, and maintaining the conditions during operation below the critical temperature for the liquefied natural gas and above the freezing point temperature for the scrubbing liquid and separating the contacting liquid from the remainder.

7. A process for the removal of aromatics and higher hydrocarbons from a liquefied natural gas comprising the steps of contacting the liquefied natural gas with nor-

mal heptane in an extraction step in the ratio of 1 part by weight of heptane to 100 parts by weight of liquefied natural gas as a minimum and 50 parts by weight of heptane to 50 parts by weight of liquefied natural gas as a maximum, maintaining the conditions during extraction below −116° F. and above −131° F., and then separating heptane and materials dissolved therein from the remainder.

8. The process as claimed in claim 3 in which the liquids are contacted one with the other while at super-atmospheric pressure.

9. The process as claimed in claim 3 wherein the liquids are contacted one with the other while at super-atmospheric pressure and which includes the step of separating the immiscible portion from the remainder of the liquefied natural gas while under super-atmospheric pressure.

10. The process as claimed in claim 9 which includes the steps of expanding the separated immiscible component to a lower pressure to vaporize off one component from the other, and then separating the vaporized



portion from the remainder to recover the scrubbing liquids and heavier hydrocarbons.

11. The process as claimed in claim 1 in which the scrubbing liquid comprises normal heptane.

12. The process as claimed in claim 11 which includes the step of separating the normal heptane from the material dissolved therein following separation of the scrubbing liquid from the remainder.

13. The process as claimed in claim 11 in which the temperature is maintained below −116° F. and above −131° F. during the scrubbing operation.

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