May 23, 1961 V. C. GARBARINI 2,984,989

VAPORIZING APPARATUS

Filed Sept. 2, 1958 2 Sheets-Sheet 1

FIG. - 1

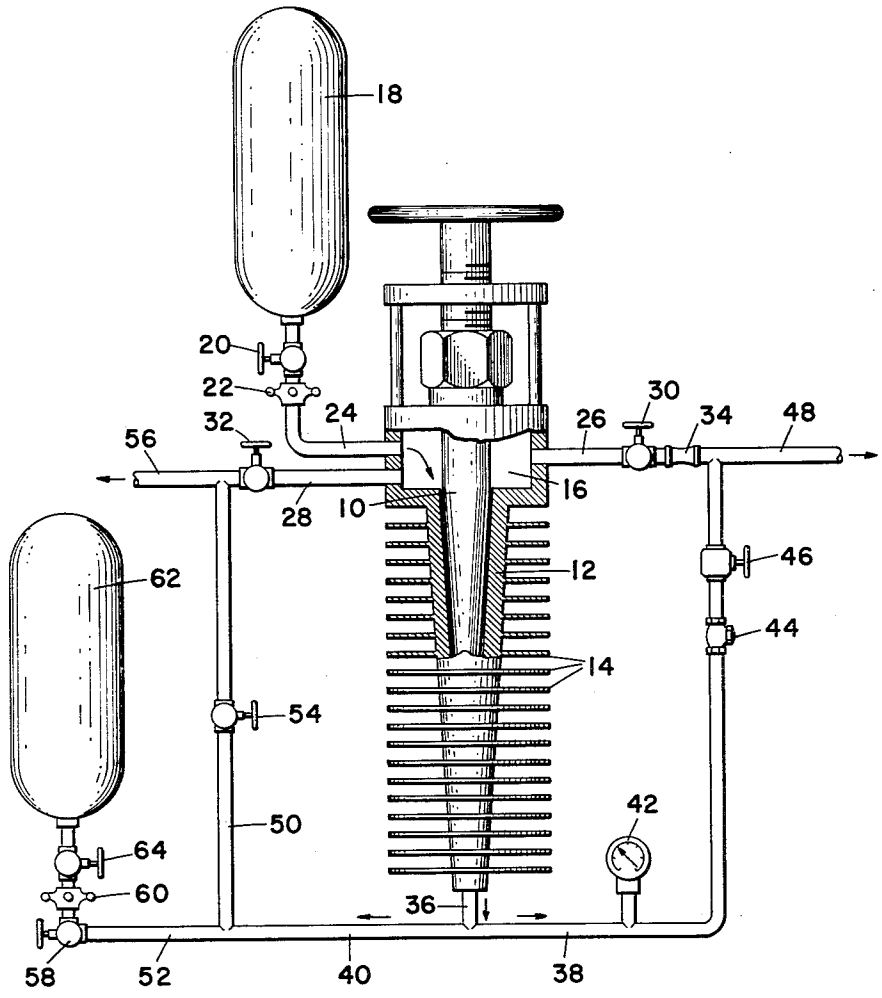

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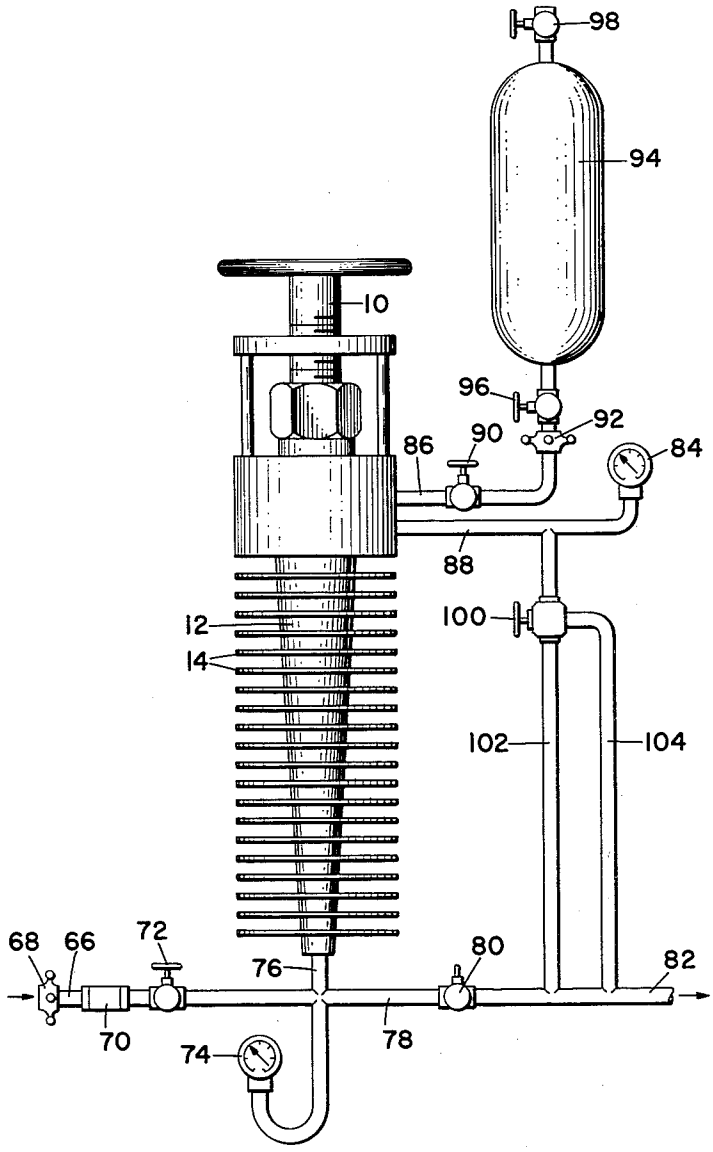
FIG. - 2



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VAPORIZING APPARATUS

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5 Claims. (Cl. 62—52)

This invention relates to apparatus for vaporizing liquid mixtures at ambient temperatures. It relates particularly to apparatus for vaporizing light hydrocarbon liquids such as liquified gas mixtures of which representative samples are desired to be taken for analytical purposes.

Present methods of analysis for light hydrocarbons (C_2—C_5+) by mass spectrometry and gas-liquid or gas-solid chromatography require gaseous samples. A simple way of effecting vaporization of a liquid sample is to allow it to throttle through a needle valve into an evacuated receiving container with the sample material that actually passes the valve flashing completely from the liquid to the vapor state.

A potential disadvantage of this simple vaporization technique is that there will be cooling of the sample material passing the valve. Some heavy ends so cooled will tend to be left behind in the valve and connecting piping as liquids. The working sample finally collected after the valve has been shut may not, therefore, be truly representative of the main body of hydrocarbon liquid from which it was drawn.

This disadvantage might, in theory, be overcome by applying heat to the valve. Heating of a throttle valve using conventional means, however, is both inconvenient and unreliable, and also creates a potential hazard when highly inflammable or thermally unstable fluids are being handled. Accordingly, vaporizing valves have been constructed with extended external surfaces intended to act as means for gathering heat from the atmosphere and transferring it to fluid flowing through the valve to obtain a substantially isothermal expansion of this fluid. A fabricator of such valves is the Manufacturers Engineering and Equipment Company of Hatboro, Pa., whose products bear the trade name "MEECO." The MEECO vaporizing valve comprises a long needle in a body or casing formed or fitted externally with a plurality of heat absorbing fins.

Another potential disadvantage of the simple vaporization technique even when a MEECO valve is used, however, is that of accumulation of liquid in the receiving chamber downstream of the needle valve as the pressure builds up in this chamber. Once the valve is opened, there will, of course, be an increase in pressure in the initially evacuated receiving chamber. As the pressure therein rises the pressure drop across the needle valve may decrease significantly, and liquid materials arriving at the inlet to the valve be only partially flashed to vapor in their passage through the valve with some liquid carrying over to the receiving chamber.

Likewise, as pressure builds up in the receiving chamber with fluid flowing thereinto, some sample constituents initially vaporized may be condensed again; that is, there may be reliquefaction. When the needle valve is fully shut off, therefore, the material in the receiving chamber may comprise a vapor above a liquid, and this vapor, the actual substance for subjection to analysis, will be significantly different in composition from the parent body of hydrocarbon liquid.

According to this invention the foregoing potential disadvantages of the throttle valve vaporization apparatus and process are substantially eliminated by employing a valve adapted to give substantially isothermal expansion of fluid passing therethrough, and limiting back pressure on this valve to prevent pressure downstream of the valve, that is, in the sample receiving chamber, from building up to a level that would permit any constituent of the material being sampled to exist as a liquid.

It is a principal object of this invention to provide a method and means for obtaining vapor samples from gases which have been liquefied under pressure.

It is a particular object of this invention to provide a method and means according to the aforesaid principal object wherein and whereby a step of vaporizing liquid samples shall be performed substantially isothermally and said vapor samples be gathered only up to a certain limiting and predetermined pressure.

It is another particular object of this invention to provide a method and means according to the aforestated principal object wherein and whereby said vapor samples may be obtained for routine analytical use quantitatively, rapidly, and with minimum liquid sample requirements.

These and other objects may be perceived and a fuller understanding of this invention obtained by referring to the following description and claims taken in conjunction with the accompanying drawings in which:

Fig. 1 represents a layout of an apparatus embodiment of this invention which is particularly adapted for the vaporizing of comparatively small liquid samples on an intermittent basis as in laboratory use.

Fig. 2 represents a layout of an apparatus embodiment of this invention which is particularly adapted for the vaporizing of comparatively large liquid samples on a semi-continuous or continuous basis as in field or plant use.

Referring now to Fig. 1, 10 designates the needle member of a needle valve for liquified gas vaporization. This needle is enclosed in a long sleeve or valve body **12** in which the valve seat is formed. Surrounding valve body **12** is a plurality of fins **14** either formed integrally with the valve body, or, if formed separately, so attached thereto that heat may flow freely from the fins to the valve body. At the sample inlet end of the valve body and below the valve packing region there is a chamber region **16** wherein supply, vacuum, and dumping connections are made to the valve. Desirably this chamber will be as small as practicably possible. The packing and needle adjusting means of the illustrated valve may be considered conventional.

Fluid supply to the needle valve comes from a sample source such as a bomb cylinder **18** containing a body of gas liquified under pressure. This cylinder is provided with a shutoff valve **20**, and may have a short nipple-like extension therebeyond to enter a quickly manipulable coupler **22** on supply line **24** to the needle valve. While line **24** is shown of appreciable length for purposes of illustration and description, in practice it will be kept as short as possible and coupler **22** may effectively be fitted directly to chamber **16**.

Leading away from valve chamber **16** are dumping line **26** and vacuum line **28**. Line **26** which is provided with a dumping valve **30** is the means for discharging unused portions of liquid samples after vaporizing operations have been concluded. Line **28** which is provided with vacuum shutoff valve **32** is used for the evacuation of valve chamber **16** and lines **24** and **26** before vaporizing operations are commenced; that is, before valve **20** is opened. Lines **26** and **28** like line **24** are shown of appreciable length for disclosure purposes, but also like line **24** will be kept as short as possible in practice and

may simply comprise direct connections from valve chamber **16** to dumping and vacuum valves **30** and **32**.

In the course of a vaporizing operation which will be described in detail presently, valve chamber **16** and lines **24**, **26**, and **28** to the extent that these lines exist must be maintained full of liquid material at all times. As a check on this condition a pipe or tubing section **34** of transparent or translucent plastic or glass is provided on the downstream side of dumping valve **30**. The function of this tubing section is to allow observation of the rapid boil-off of unused liquid sample material after conclusion of a vaporizing run. This is indicated by a momentary fogging inside the tubing. Failure to obtain such boil-off will be information to an operator that insufficient sample material was supplied or that the vaporizer was not used properly, and in any case that the preceding vaporizing run was invalid.

The outlet line **36** of the needle valve branches into two lines **38** and **40**. Line **40** is provided with a compound pressure gauge **42**, a vacuum-tight check valve **44**, and a back pressure regulating valve **46**, which is, in effect, a relief valve with an adjustable setting. The outlet end of regulating valve **46** is joined with that of sight tube **34** in a common vent line **48**. In many appartus embodiments of this invention, regulating valve **46** may be eliminated as an individual piece of equipment with its function being obtained through spring loading within check valve **44**.

Branch line **40** leading away from the outlet end of the needle valve is itself branched into two lines **50** and **52**. Line **50** is provided with a vacuum shutoff valve **54**. The outlet end of this valve is joined with that of valve **32** in a common vacuum line **56**. Line **52**, the other branch of line **40**, may be provided with an anti-dumping valve **58** as shown closely adjacent a quick coupler **60** through which attachment to the line is made of an evacuated bomb cylinder **62** for vaporized sample reception. This cylinder is provided with a shutoff valve **64**. The function of anti-dumping valve **58** is to hold vapor pressure in the system substantially up to the point of receiving cylinder attachment, so that neither need wastage of vapor be tolerated nor re-evacuation of the system performed if a succession of pre-evacuated receiving cylinders **62** are to be filled. Valve **58** may be omitted in apparatus embodiments of this invention where the foregoing effects are not considered important or bothersome. Fine mesh screens or other filtering devices may be incorporated into the quick couplers **22** and **60** to prevent solid contaminants from entering the apparatus.

The apparatus embodiment of this invention illustrated in Fig. 1 having been described, its operation will now be considered. For this consideration assume that supply cylinder **18** and receiving cylinder **62** are in place on the apparatus as shown. Valve **20** of cylinder **18** will be closed, and valve **64** of cylinder **62** may be open although it need not be if cylinder **62** has been evacuated prior to installation on the vaporizing apparatus. Assume also that the back pressure regulating valve **46** has been set to open at some pressure less than that which would allow any constituent of the fluid material in cylinder **18** to exist as a liquid. For liquefied petroleum gas mixtures C_4 or lighter, the regulated back pressure could conveniently be 1 pound per square inch above atmospheric pressure. For less volatile fluids such as gasoline, the back pressure could be as low as ½ pound per square inch absolute provided that line **48** is connected to a region of reduced pressure such as the suction side of a vacuum pump.

Initially the needle member **10** of the needle valve assembly will be off its seat in valve body **12**; that is, the needle valve will be open. Dumping valve **30** will be closed, and anti-dumping valve **58** will be open. Vacuum shutoff valves **32** and **54** will be open also. Upon operation of whatever vacuum producing means is connected to line **56**, valve chamber **16** and all lines of the apparatus except those beyond vacuum-tight check valve **44** and dumping valve **30** in the direction of vent line **48** will be evacuated. This includes receiving cylinder **62** if it has not been evacuated previously and its shutoff valve **64** is open. Compound gauge **42** will indicate the lowering of pressure in the system.

After a satisfactory condition of evacuation of the apparatus has been achieved, the needle member **10** is seated again in valve body **12**; vacuum shutoff valves **32** and **54** are closed, and receiving cylinder valve **64** opened if it has been closed up to this time. Any rise of pressure in the system as shown on gauge **42** as valve **64** is opened indicates that not all of the gas or gas producing material originally in cylinder **62** has been removed. Assuming a satisfactory conditon of evacuation, however, supply cylinder valve **20** will be opened next to admit liquefied gas under pressure to valve chamber **16**. Needle member **10** may then be backed off its seat in valve body **12** an appropriate amount to allow the flow of fluid through the needle valve assembly.

As liquefied gas to be vaporized flows down the long, narrow annular space between the needle member and the valve body, it will be dropping in pressure and tending to drop in temperature according to the usual throttling process in the course of flashing to a vapor. However, as soon as temperature of fluid in the throttle valve drops below the environmental temperature of the valve or atmospheric temperature, the difference in temperature across the valve body will cause a flow of heat therethrough toward the fluid.

Such flow of heat will be at a significant rate because of the large heat transfer area of valve body fins **14**. This flow will tend to restrict the temperature drop taken by fluid flowing through the needle valve from supply cylinder **18**, and will furnish heat of vaporization to that portion of the fluid flowing through the valve which might otherwise remain a liquid if the throttling process were adiabatic. Accordingly, fluid arriving at valve outlet line **36** will be completely vaporized, having not only been expanded to a reduced pressure level from its condition of liquefaction under pressure in supply cylinder **18**, but also been substantially sustained in temperature during the expansion process.

From outlet line **36** vapor flows through line **38** toward check valve **44** and back pressure regulating valve **46**, and through line **40** toward receiving cylinder **62**. As operation of the apparatus is continued, pressure will rise in cylinder **62**, and, check valve **44** having opened, against regulating valve **46**. At some time a pressure level will be reached corresponding to the setting of valve **46**, and upon opening of this valve there will be flow of vapor out the vent line **46** and no further pressure rise in cylinder **60**.

After valve **46** has opened, needle member **10** may be seated in valve body **12** to end the flow of liquified gas, and anti-dumping valve **58** and receiving cylinder valve **64** be closed. Coupler **60** may be manipulated to release cylinder **62** for the latter to be removed from the apparatus. If another previously evacuated cylinder is to be filled with vapor it may be coupled to the apparatus in place of the one just removed; its shutoff valve **64** and the anti-dumping valve **58** opened, and needle member **10** backed off its seat to allow further flow and vaporization of liquified gas. On the other hand, if no more vapor samples are to be taken at the time, shutoff valve **20** on supply cylinder **18** may be closed and dumping valve **30** opened to vent residual high pressure fluid from valve chamber **16** and lines connected thereto, observation of boiling off of the vented fluid being taken through sight tube **34**.

It might appear that the foregoing process of taking vapor samples could be carried out simply by manipulating needle member **10** while gauge **42** was observed, and shutting off flow through the needle valve upon

achievement of a particular pressure. That is, it might appear that the function of pressure regulating valve **44** to limit the pressure level in the system automatically could be replaced in practice with a manual function. Actually, the vaporization of a liquid sample with consequent build-up of pressure in the receiving cylinder for vaporizing equipment of laboratory size will be extremely rapid, and once the needle valve has been opened human agency cannot be relied upon to shut it at just the right time. Closing needle valve too late will allow over pressuring of the receiving cylinder, while closing it too early may result in collection of a vapor sample at sub-atmospheric pressure. Most apparatuses for the analysis of light hydrocarbons require vapor samples at some positive pressure. By having a back pressure regulating valve in the vaporizing system, not only is a convenience factor supplied but also and more important a considerable possibility for human error in operation of the equipment is removed.

Another benefit of the back pressure regulating valve is that it will allow fluid to flow through the system while temperature conditions in receiving cylinder **62** are becoming stable. The first vapor particles arriving in the cylinder will be at substantially atmospheric temperature but very low pressure, and will be compressed with corresponding rise in temperature by succeeding vapor particles flowing into cylinder **62**. At the moment that valve **46** opens, the vapor in the cylinder will be at the regulated pressure but at a temperature at least somewhat higher than atmospheric.

Continued flow of vapor through the needle valve and the back pressure regulating valve for a short while will allow heat to flow from the vapor in cylinder **62** to the atmosphere through the cylinder wall, while external vapor pressure is maintained on the cylinder contents with a little more material flowing in as these contents cool. When cooling has been substantially completed, cylinder **62** may be shut off and removed from the vaporizing apparatus according to procedures given already with confidence that the pressure and temperature of the vapor within it are stable.

A slight variation of the foregoing operating procedure for the apparatus of Fig. 1 will be to leave receiving cylinder valve **64** closed after the system has been pumped down, vacuum shutoff valves **32** and **54** closed, and the needle valve opened. Pressure will build up rapidly in the various open lines of the system until the predetermined limiting back pressure has been achieved, and valve **46** has opened to vent the total vapor flow out line **48** before any material has entered the receiving cylinder. This venting may be continued for any period necessary to allow the internal surface of the various lines and fittings of the system to become saturated with adsorbed hydrocarbon heavy ends. When valve **64** is finally opened, therefore, the fluid flowing from the supply to the receiving cylinder will not be altered in composition along the way by adsorption of any components on intermediate pipe or valve surfaces.

Referring now to Fig. 2, what is shown is a vaporizing apparatus arrangement which will be particularly useful in the following circumstances: when vacuum is not available; when high pressure and/or large volume liquid samples are available as in plant or field use, and when semi-continuous or continuous vaporizing is required as in gathering a large number of individual vapor samples or generating a vapor stream for calibrating continuous flow type gas analyzers.

In Fig. 2 the high pressure liquid inlet line to the vaporizing apparatus is designated **66**. This line may be provided with any suitable coupling means such as quick coupler **68** for attachment to the liquid sample source. Line **66** leads to a filter **70** which may be employed to arrest the flow of any foreign matter carried over from the liquid sample source. Downstream of the filter is a sample inlet shutoff valve **72**. From this valve the inlet line proceeds to a cross to which are connected an inlet pressure gauge **74**, the inlet fitting **76** of the vaporizing needle valve, and an excess liquid outlet or high pressure blow-through line **78**.

Pressure gauge **74** is not compounded, and should be capable of indicating relatively high pressures, 400 pounds per square inch for example. The vaporizing valve for the apparatus of Fig. 2 may be just the same as that shown in Fig. 1 comprising a needle member **10**, a valve body **12**, and heat absorbing fins **14**. Inlet connection **76** for the needle valve supplies fluid for flow therethrough in a direction in reverse of the vaporizing flow in the apparatus of Fig. 1.

In Fig. 1 the relatively high pressure liquid sample is supplied to the valve at the end adjacent the packing, and any liquid which may be left accidentally to vaporize in valve chamber **16** after the valve has been shut may seep out through the packing as gas to relieve any potentially dangerous condition of high pressure. In the apparatus of Fig. 2 such relief is provided by a safety valve **80** in the excess liquid outlet line **78**. Valve **80** may be conveniently of the spring-loaded toggle type susceptible to opening by external manipulation of the toggle mechanism or internal pressure of about 350 pounds per square inch. The outlet side of valve **80** is connected through a series of fittings to a vent line **82**.

Connected to the chamber region of the needle valve assembly are a vapor product outlet line **86** and a vapor product pressure regulating valve inlet line **88**. Vapor product pressure gauge **84** connected to line **88** need not be a compound gauge since it is contemplated that the low pressure side of the apparatus of Fig. 2 will always operate at a positive pressure. Product outlet line **86** leads to an outlet shutoff valve **90**. Beyond this valve are appropriate coupling means such as quick coupler **92** whereby the vaporizing apparatus may be connected to a desired vapor receiving device. Shown in place on the apparatus is a receiving cylinder **94** which is provided with shutoff valves **96** and **98**, one at either end. With both of these valves open, vaporized material may be blown through cylinder **94** to purge it of air or any other prior contents. When purging is complete, valves **98** and **96** may be closed in the order stated for vapor sample collection.

Line **88** leads to the inlet side of a vapor product back pressure regulating valve **100**. This valve may be of the spring-loaded diaphragm type and need not be vacuum tight. Desirably valve **100** may be adjusted to open or relieve over a range of inlet pressures, and it is by means of such adjustment that the pressure of the vapor product of the apparatus of Fig. 2 available in line **86** is set. When valve **100** opens in the regular way, fluid flowing through it will leave by way of relief line **102** which is connected to vent line **82**.

As a protective feature for the low pressure side of the apparatus, regulating valve **100** may be provided with an emergency relief line **104** which is connected to it in the region above the diaphragm. In case of any unexpected pressure build up on the downstream side of the vaporizing valve, the diaphragm of regulating valve **100** will rupture and the high pressure material escape safely through emergency line **104** and vent **82** with no damage to any low pressure parts other than the diaphragm which may be replaced easily.

Operation of the apparatus of Fig. 2 will be similar in principle to that of the apparatus of Fig. 1, although somewhat different in detail. With the needle valve closed and sample inlet shutoff valve **72** open, safety valve **80** may be lifted by hand to allow high pressure fluid to blow through to vent line **82** as a check that there is indeed liquid material under pressure available at the sample source. Valve **80** should then be closed, and, after opening valves **90**, **96**, and **98**, the needle valve be opened to allow fluid to flow therethrough to be vapor-

ized at substantially constant temperature and to purge the system of air and any other contaminants.

During the purging process, the vapor product pressure regulating valve **100** should be so adjusted that at least a slight positive pressure in line **88** will be required to open it. This is to insure that there will be appreciable vapor flow through product line **86** and receiving cylinder **94**. At the conclusion of purging, valve **98** on cylinder **94** will be closed. This will divert all vapor flow through valve **100** and cause an increase in the reading of product pressure gauge **84**. The pressure regulating valve may then be adjusted in accordance with observations of gauge **84** to give the desired back pressure on the system which will be the limiting pressure of accumulation of vapor in receiving cylinder **94**.

Although this invention has been described with a certain degree of particularity, it is to be understood that the present disclosure has been made only by way of example, and that numerous changes in the details of construction and the combination and arrangement of parts may be resorted to without departing from the spirit and scope of this invention as hereinafter claimed.

What is claimed is:

1. An apparatus for vaporizing gases which have been liquefied under pressure comprising a needle valve having a needle member and a body member characterized by inlet and outlet ends, supply means whereby gas liquefied under pressure is furnished to the inlet end of said valve body member for passage through said needle valve, fins affixed to said valve body member whereby heat flow through said valve body member from the environment of said needle valve to fluid passing through said valve is facilitated, receiving means at said outlet end of said valve body wherein vapors of gases liquefied under pressure and revaporized during passage through said needle valve are statically gathered, and pressure regulating means in gas line connection with said needle valve at said outlet end whereby pressure of vapor in said receiving means and the outlet end of said valve is prevented from rising above a predetermined value.

2. An apparatus according to claim 1 in which said pressure regulating means comprises a relief valve.

3. A process for vaporizing gases which have been liquified under pressure comprising passing said gases through a needle valve having a body member wherein a reduction in pressure of said gases is effected; transferring heat to said gases through said body member of said valve during the passage of said gases therethrough at such rate to maintain these gases at substantially constant temperature; statically gathering vapors of said gases which have been revaporized during passage through said needle valve, and limiting to a predetermined value the pressure up to which said vapors may be gathered.

4. A process according to claim 3 in which said gases comprise hydrocarbons in the range of C_2 to C_5.

5. A process according to claim 3 in which said predetermined value of pressure is lower than the pressure at which any constituent of said gases can exist as a liquid at the gathering temperature.

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