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LIQUEFACTION AND PURIFICATION OF LOW TEMPERATURE GASES

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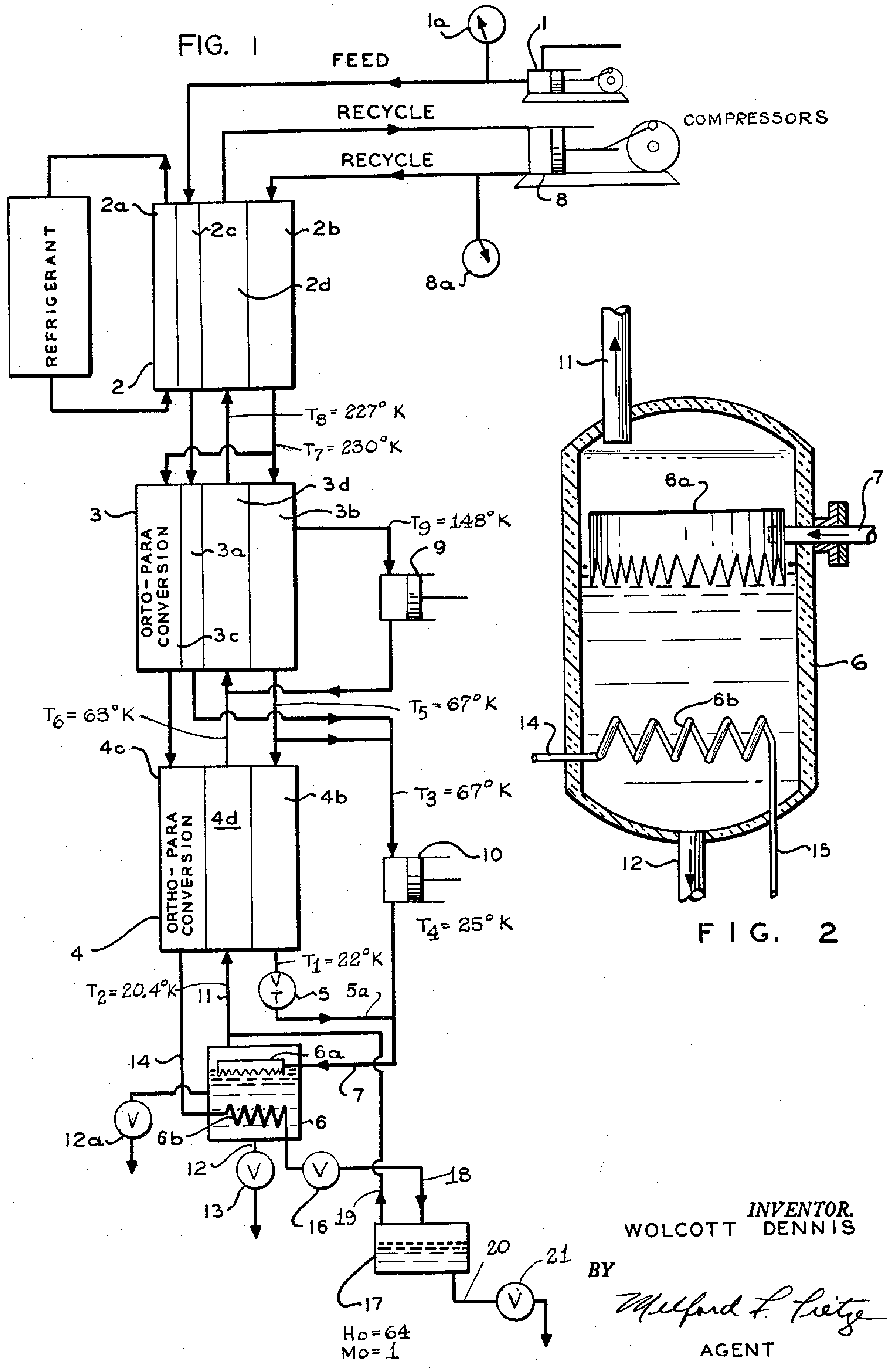

FIG. 1

FIG. 2

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LIQUEFACTION AND PURIFICATION OF LOW TEMPERATURE GASES

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This invention relates in general to the liquefaction of gases; and more particularly, to the purification of gases undergoing liquefaction in a temperature range below that of liquid nitrogen. As specifically disclosed, this invention relates to the removal from the feed-stream of hydrogen undergoing liquefaction, of remnant impurities which solidify below the temperature range of liquid nitrogen.

During the liquefaction of hydrogen or helium which take place at temperatures below 35 degrees Kelvin, concentrations of the order of one percent by volume of contaminating gases, including primarily nitrogen, remaining in the feed-stream after conventional methods of purification, have a deleterious effect, in that they freeze-up and clog the expansion valves and heat-exchangers at the lowest temperature levels of the liquefaction systems. Such cloggings not only impede the operation of the liquefaction systems, but in certain cases, where solid oxygen is involved, raise a danger of explosion. Moreover, it has been found that the applications of conventional prior art methods for the removal of such impurities from the feed-stream gases by drying, scrubbing, and absorption-filtering means prior to the final stages of the liquefaction process are cumbersome and expensive.

Accordingly, it is a general object of this invention to improve the liquefaction of gases in the range below the temperature range of liquid nitrogen.

A more specific object of the invention is to render conventional systems for liquefying hydrogen more efficient by providing simplified means for purging the feed-stream of small concentrations of impurities such as nitrogen or oxygen which solidify and clog the systems at the lowest temperature levels.

In accordance with the present invention, these and other objects are accomplished in a gas liquefaction system operating through a cycle in which the gas is compressed, cooled, partly reduced to the liquid phase, and the remainder returned to the compressor for recycling, by expanding the impure gas in the feed-stream at a low temperature level with the production of external work to freeze out the impurities, separating the solidified impurities from the gas, such as by entraining them in the liquid phase, and delivering the thus treated feed-stream to the recycle stream.

More specifically, in the system which is presently disclosed as an illustration of the invention, the feed-stream of hydrogen, which may contain up to about one percent by volume of nitrogen impurity, is first compressed to a pressure within the range 20 to 100 atmospheres, and then cooled through successive stages, including heat-exchangers, to a temperature not far above the freezing point of nitrogen. At this point, the feed-stream, together with a portion of recycled gas which has already been purified, is by-passed around the lowest level heat-exchanger, and is diverted through a low-level expansion device where it expands with the performance of external work. This lowers the temperature of the gaseous mixture below the freezing point of the nitrogen impurity, causing the latter to snow-out, forming a finely divided suspension of impurity particles in the gas. The exhaust from this low-level expander bearing the finely divided impurities is further combined with the fluid output from the lowest-level heat-exchanger, which is substantially free of the condensable impurities and which has been partially liquefied by Joule-Thompson expansion through a throttle valve. As a result, the solid impurities become entrained in the liquid. The combined fluid stream passes into a receptacle where the vapor-phase is separated from the liquid, and returns through a series of heat-exchangers to the compressor for recycling. The impurities entrained in the liquid fall to the bottom of the receptacle to form a slurry which is periodically drawn off through a valve.

In accordance with a further step which is desirable, although not necessary to the process, the last stage of the recycled gas passes at high-pressure through a series of ortho-para conversion chambers associated with the heat-exchangers, the converted output from the cold-end of which is further cooled and condensed to liquid in a coil of pipe which is surrounded by the liquid from the throttle-valve. This final product is drawn off at intervals, and placed in another storage receptacle. The primary function of this last step is to facilitate storage of the liquid hydrogen by expediting the ortho-para conversion and absorbing the heat which it generates.

The principal advantage of the improved system of the present invention is that it enables adequate removal of those remnant impurity gases which tend to freeze and clog the lowest levels of the heat exchangers and expansion valves in systems for the liquefaction of hydrogen and helium, by a method which is structurally simpler and more convenient than the absorption-filter systems and other prior art techniques for removing such impurities at higher temperature levels.

The operation of the present invention will be described in detail hereinafter with reference to the drawings, in which:

FIG. 1 is a schematic showing of a typical system for the liquefaction of hydrogen which has been modified in accordance with the present invention for the removal of solidified impurities at the lowest temperature levels; and

FIG. 2 is an enlarged schematic of the liquid receptacle 6 of the system of FIG. 1, showing a convenient form which the bubble-cap *6a* may assume.

It will be apparent to those skilled in the art that the teachings of the present invention are not restricted to the particular type of refrigeration cycle employed in the disclosed, illustrative embodiment; but may be used advantageously in conjunction with any suitable refrigeration cycle in which similar problems are encountered.

Referring to the drawing, a stream of hydrogen containing up to about one percent by volume of nitrogen, and not more than a few parts per million of oxygen or carbon dioxide, is passed into the conventional feed-compressor 1. It will be assumed that at some time prior to compression, or alternatively, immediately following compression, the hydrogen involved has been submitted to conventional purification means, not here shown or described, which as generally employed have been found to leave small residues of nitrogen and other impurities, such as oxygen and argon, the removal of which at a low temperature level, is the subject of the present invention.

The disclosed liquefaction system includes a pair of conventional compressors 1 and 8 which serve to raise the hydrogen from atmospheric pressure to a pressure within the range of 20 to 100 atmospheres. For the purposes of the present illustrative embodiment, 30 atmospheres has been selected as an optimum pressure. The compressor 1 is adapted to accommodate the incoming hydrogen stream before purification and the unit 8 is adapted to operate on the recycled stream of hydrogen which has already passed through a complete cycle of the liquefaction system, including the low temperature expander and purification unit which has been added in accordance with the teachings of the present invention. Standard pressure gauges *1a* and *8a* are respectively connected to measure the pressures of the exhaust gases of each of the compressors **1** and **8**.

The high pressure output stream from each of the compressors **1** and **8** is led through pipes of any suitable material, such as one of the nonferrous metals, to the inner chambers of the fore-cooler-heat-exchanger **2**, which is a convenient, but not indispensable adjunct of the system under description. A suitable refrigerant, such as dichlorodifluoromethane, which is known in the art by the trade name "Freon 12" is circulated through the outer shell of the fore-cooler-heat-exchanger **2**. The latter may comprise carbon steel, or one of the nonferrous metals such as copper, suitable for use at medium-low temperatures. Moreover, fore-cooler **2** may assume any of the forms well known in the art, such as that indicated in Fig. 2.11, page 21 of Cryogenic Engineering by Russell B. Scott, D. Van Nostrand Co., Princeton, New Jersey, 1959. The refrigerant evaporates in the outer shell **2***a* of the fore-cooler **2**, extracting heat from two separate incoming streams of high pressure hydrogen, the recycled, purified stream passing through pipe **2***b*, and the impurity-bearing feed-stream passing through pipe **2***c*. Simultaneously, the cold, low-pressure hydrogen stream, which is returning after expansion to the compressor **8** for recycling in the system, also passes through the fore-cooler-heat-exchanger **2** by way of the pipe **2***d*, absorbing heat from the high pressure streams passing the opposite direction in pipes **2***b* and **2***c*. By this process, the incoming streams of high pressure hydrogen in the system under description are cooled to a temperature of 230 degrees Kelvin at the outlet of the fore-cooler **2**, at which point the low pressure, returning stream is about 3 degrees below, at 227 degrees Kelvin.

From the fore-cooler **2**, the two high-pressure streams are passed into the relatively warm heat-exchanger stage **3**, which is constructed of any of the metals suitable for medium-low temperature application, such as stainless steel, aluminum or copper, and which may assume any of the forms usually employed for such components, such as, for example, that shown in Figure 2.8 and described on page 18 of Cryogenic Engineering by Russell B. Scott, supra.

Heat-exchanger **3** includes channel **3***a* which carries the high pressure, impurity-bearing feed-stream, channels **3***b* and **3***c* which carry the recycled streams of purified hydrogen, and channel **3***d* which carries the low temperature, low pressure stream returning to the compressor.

It will be noted that the recycle stream **2***b* from the heat-exchanger **2** is divided at the intake of heat-exchanger **3** into two parts, **3***b* and **3***c*, for the purpose of submitting one of the streams which passes through the final cycle of the system, to ortho-para conversion.

At room temperature, the two molecular varieties, ortho- and para-hydrogen, which are distinguished by their opposing nuclear spins, make up 75 and 25 percent, respectively, of the hydrogen composition under equilibrium conditions. However, almost the entire mass of the hydrogen converts to para at its boiling point, the reaction being exothermic, and producing sufficient heat to evaporate about one percent of the liquid per hour. In order to avoid this heat loss in the liquid hydrogen storage vessel, it is desirable to catalyze the ortho-para conversion, and effect the conversion during the liquefaction process prior to storage, so that the final liquefied product is almost entirely para-hydrogen. This is carried out by employing in channel **3***c* of heat-exchanger **3**, about 1 liter of hydrous ferrous-oxide to expedite the reaction in a manner described on page 50 of Cryogenic Engineering, supra.

As noted from FIG. 1, part of the high pressure recycle stream **3***b* is further diverted at a temperature level of, say, 148 degrees Kelvin to pass through the expander **9**, where it is cooled by expanding with the performance of external work to a temperature of 67 degrees Kelvin. An expansion engine of a form suitable for this purpose was recently constructed by S. C. Collins, and is described with reference to Fig. 2.16 on page 32 et sequor of Cryogenic Engineering by Russell B. Scott, supra. At this level, the expansion engine **9** serves as an efficient and simple method for cooling down the hydrogen to be liquefied, although it is not essential when employing the teachings of the present invention, to have an expander at this point. The exhaust from the expansion engine **9** passes at a temperature of about 67 degrees Kelvin into the low pressure, low temperature stream returning to the compressor through the passage **3***d* of the heat-exchanger **3**.

In order to further reduce its temperature to below the critical temperature of hydrogen, the high pressure streams of gas at the cold outlets of channels **3***b* and **3***c* of heat-exchanger **3** are passed through still another heat-exchanger **4**, which is similar in form to the heat-exchanger **3**, except for the fact that it is designed for a lower temperature range, and accommodates only three streams of gas, instead of the four accommodated by the latter. There are the two high pressure recycle streams, **4***b*, which passes ultimately to the Joule-Thompson throttle-valve **5**, and **4***c*, the final-cycle purified stream, which passes through channel **4***c* for ortho-para conversion in a manner previously described with reference to channel **3***c* of heat-exchanger **3**. In addition, the returning low pressure stream passes through the inner channel **4***d* and serves to cool the incoming streams.

At the cold end of the heat-exchanger **4**, the high pressure gas in the chamber **4***b* is permitted to expand freely through a throttle-valve **5** to a pressure of one atmosphere, without the performance of external work, whereby Joule-Thompson cooling occurs, lowering the temperature to the liquefaction point, causing a portion of the gas to liquefy. The mixture, part in liquid and part in vapor phase, passes into the connecting pipe **5***a*. Valve **5**, through which the Joule-Thompson expansion takes place, may be constructed, for example, of stainless steel, and so formed, that for normal flow, the needle has to be considerably withdrawn from its closed position, thereby providing an opening which is not critical, and in which the tendency to clogging is lessened. The valve-stem extends through the top of the liquefier, and is subject to control by any suitable means, such as manual control through a system of pulleys.

As pointed out in the early part of the specification, a particular feature of the presently disclosed system lies in the use of an expansion engine at a low temperature level, through which the incoming, high pressure stream of impure hydrogen is diverted, together with a portion of the purified stream, and permitted to expand with the performance of external work, thereby rapidly lowering the temperature of the expanded gas, and resulting in the solidification of impurities. The expansion engine **10**, which is provided for this purpose, may be similar in form to that recently constructed by S. C. Collins, such as described with reference to FIG. 2.16, page 32, of Cryogenic Engineering by Russell B. Scott, supra, and as pointed out with reference to the earlier description of expansion engine **9**.

The high pressure stream of gas, bearing up to one percent by volume of nitrogen, and certain other trace impurities, such as argon and oxygen, which has passed through channel **3***a* of heat-exchanger **3**, is by-passed around the heat-exchanger **4**, together with a portion of the high pressure stream of pure gas from channel **3***b*. These merged streams pass through the expansion engine **10**, where they expand with the performance of external work, causing the temperature to drop from 67 degrees Kelvin to 25 degrees Kelvin, the latter being considerably below the temperature at which nitrogen solidifies. Consequently, the nitrogen impurities "snow out" during the course of the expansion, forming a fine suspension of tiny, snow-like particles in the purified gas.

The exhaust from the expansion device **10**, carrying a suspension of finely divided particles of solid nitrogen, or such other impurities as have a freezing point within the temperature range 67 to 25 degrees Kelvin, is mingled with the part-vapor, part-liquid output of the throttle-valve **5** at the junction with pipe *5a*, the mingled streams passing at substantially atmospheric pressure through inlet pipe **7** into the receiving flask **6**. The receptacle **6** may be a dewar bottle of any of the forms well-known in the art, having an inner shell, and an outer shell, the space between which is evacuated, the surface facing the evacuated portion being silvered to reflect away the heat. Alternatively, and in addition, other methods of insulation may be employed, such as an enveloping layer of polystyrene foam.

The receptacle **6** is provided with a vacuum-sealed inlet **7** which serves to introduce the mingled gas and liquid from the throttle-valve **5**, together with the exhaust gas including solidified impurities from the expander **10**, into the bubble-cap *6a*.

The bubble-cap *6a*, which is shown in enlarged schematic in FIG. 2 of the drawings, is disposed within the liquid-receiving flask **6** so that it is supported just above the surface of the liquid, with a portion projecting down into the liquid as indicated in the drawing. Although the bubble-cap *6a* may assume any one of a number of forms well known in the art, in the present illustrative embodiment it has the form of an inverted crown, closed at the top. The cylindrical rim is slightly smaller than the inner circumference of the flask **6**, the upper end being closed with a flat, circular closure disposed parallel to the surface of the liquid, and the lower end being open, and cut in a series of triangular slots about two inches deep and a half-inch across at the bottom. The bubble-cap *6a* is adjusted with reference to the surface of the liquid so that only a small area of each of the slots projects above, serving as a vent for escaping vapor. Bubble-cap *6a* may be formed of any of the materials which are known in the art to be ductile at low temperatures, and which are not corroded by the forming liquid. Metals which have been found suitable for this purpose are copper, brass, aluminum, cupro-nickel, 18–8 stainless steel, and those metals known by the trade names Monel and Everdur.

When the intermingled stream, including liquid, vapor, and suspended solid impurities, enters the bubble-cap *6a* at the inlet **7** of flask **6**, the solid impurities become entrained in the liquid, and fall to the bottom of the flask **6**, while the vapor portion escapes through the vents in bubble-cap *6a*, and rises above the surface of the liquid, passing out through the outlet pipe **11**, and passing, substantially at atmospheric pressure, through channel *4d* of heat-exchanger **4**, channel *3d* of heat-exchanger 3, and channel *2d* of fore-cooler-heat-exchanger 2, in each of which devices it serves to cool the incoming high-pressure streams. From channel *2d*, the low-pressure gas finally returns to the recycle compressor **8** for recycling through the system.

The flask **6** is provided with an outlet **12**, closed with a vacuum sealed valve **13**, which is opened from time to time to remove the slurry formed when the solid impurities fall to the bottom of the liquid hydrogen. A valve controlled draw-off *12a* is provided on the vessel **6** to permit normal liquid hydrogen to be drawn off if this is desired. It will be understood that the tap *12a* preferably is located in the upper portion of the vessel **6** in the region where the liquid hydrogen strata are relatively free of the impurities which tend to collect at the bottom of the vessel.

During the final phase of the liquefaction process, the recycled gas passes at high pressure, for example, thirty atmospheres, through channel *2b* of heat-exchanger **2**, and in succession, ortho-para conversion channels *3c* and *4c* of heat exchangers **3** and **4**, respectively, passing from the cold end of heat-exchanger **4** through pipe **14** into the copper coil *6b*, which is vacuum sealed into the lower portion of the liquid-receiving flask **6**, where it is surrounded by liquid hydrogen, which causes the converted para-hydrogen vapor to condense and form liquid. The latter passes through outlet **15** of the condenser pipe *6b* under control of valve **16**, from which it is led into a second liquid-receptacle **17**, through inlet pipe **18**. The receptacle **17** is a dewar bottle, and has a highly insulating jacket such as described with reference to receptacle **6**. A vapor-vent **19** is provided at the top, to permit that portion of the hydrogen which is not liquefied to return through the heat-exchangers **4**, **3**, and **2** to the recycle compressor **8**.

A vacuum-sealed outlet **20** is provided at the bottom of the receptacle **17** to draw off the para-hydrogen liquid product for storage, under control of the valve **21**.

All calculations for the present illustrative embodiment are based on data extracted from the temperature-entropy diagram for hydrogen published in Research Paper #RP 1932 by Wooley, Scott and Brickwedde, which is reproduced as FIG. 9.16 on pages 294–297, Cryogenic Engineering by Russell B. Scott, supra.

An operating pressure of 30 atmospheres at the compressors has been assumed. If a much lower pressure is employed, an increase of cycle flow-rate results with attendant increase in exchanger losses. Accordingly, the choice of 30 atmospheres is approximately optimum, although the operative range may be said to extend from about 100 to around 20 atmospheres.

Using 30 atmospheres pressure for the compressor, and one atmosphere for the receiver, as convenient values, and selecting convenient temperature ranges for the operation of the various heat exchangers and expanders, one consults the temperature-entropy diagram referred to above for the location of enthalpy values in calories per gram to correspond to each temperature point. From this information, one may compute the heat transferred per unit mass from the warmer to the cooler stream through any element of the system by setting up enthalpy balances.

For the purposes of calculation, certain assumptions have been made. It will be assumed that the forecooler **2** cools the high pressure stream to a temperature T_7 of 230 degrees Kelvin; and that there is a temperature difference ΔT of 3 degrees between the high pressure and low pressure streams at the warm end of the heat-exchanger **3**, making the temperature T_8 of the returning, low pressure stream 227 degrees Kelvin. It will be further assumed that the ortho-para conversion of the product fraction of hydrogen is completed to equilibrium at each temperature level in exchangers **3** and **4**. A heat leak loss of 10%, 70 calories per gram, will be assumed to be distributed below 140 degrees Kelvin. Moreover, all of the high pressure streams in the heat exchangers **3** and **4** have been assumed to be combined in one stream. The exhaust temperature of the lowest level expander **10**, has been fixed at 25 degrees Kelvin.

The sample calculations which follow are based on a liquid product of one gram. The subscripted T's indicate the temperatures at the various points in the system, as indicated on FIG. 1. Corresponding values of enthalpy and relative flow for these same points are indicated by similarly subscripted values of H and M, respectively. K represents Kelvin, and S, entropy.

EXPANDER 10

M_3—Hight pressure input stream (30 atmospheres pressure):

H_3=270 calories per gram.
$T_3=T_5$=67 degrees K.
S=8.85 calories per gram per degrees K.

M_4—Low pressure exhaust stream (about one atmosphere pressure):

At atmospheric pressure—
H_A=162 calories per gram.
ΔH (theoretical drop through expander **10**)$=H_3-H_A$=108 calories per gram.

But expander **10** has a Rankine efficiency of 80%; therefore, the actual enthalpy drop

$$\Delta H' = \Delta H \times .80 = 108 \times .80 = 86 \text{ calories per gram}$$

$$H_4 = H_3 - \Delta H' = 184 \text{ calories per gram.}$$
$$T_4 = 25 \text{ degrees K.}$$

This value was worked out empirically by finding a value for H_3 which would give the desired value of T_4.

EXCHANGER 4 (Flow From Exchanger 3)

[Minimum difference in temperature at warm end of exchanger 4 (4 degrees K.)]

M_2—Low pressure vapor, saturated at cold end of Exchanger **4** (about one atmosphere pressure):

H_2=172 calories per gram.
T_2=20.4 degrees K.

M_1—High pressure fluid stream, cold end (30 atmospheres pressure): H_1=75 calories per gram.

T_1 is assumed to be 1.6 degrees warmer than T_2; therefore, T_1=22 degrees K.

M_5—High pressure fluid stream at cold end of Exchanger **3** (about 30 atmospheres pressure):

$H_5=H_3$=270 calories per gram.
$T_5=T_3$=67 degrees K.

Assumed ortho-para conversion load-factor, distributed through exchanger **4**=62 calories per gram.

Distributed heat leak load factor, exchanger **4**=30 calories per gram.

Assumed heat leak factor, into receiving receptacle **6**, =10 calories per gram.

M_6—Low pressure output, warm end, heat-exchanger **4**:

Let H_6=281 calories per gram.
Let T_6=63 degrees K.

These latter values are selected empirically, in order to arrive at suitable heat-exchange relations in the heat-exchanger **4**.

Heat balance of heat-exchanger **4**:

$$(H_5-H_1)M_1 + \text{ortho-para conversion factor} + \text{heat leak factor} = (H_6-H_2)M_6 \quad (1)$$

Substituting values from foregoing analysis in Equation 1:

$$(270-75)M_1+62+30=(281-172)M_6$$
$$195M_1+92=109M_6 \quad (2)$$

Over-all balance of heat-exchanger **4**, liquid receiver **6**, and expander **10**:

$$H_5M_1+H_4M_3+102=281M_6+64$$
$$M_1+M_3-1=M_6$$
$$M_3=M_6+1-M_1 \quad (2.5)$$

$$270M_1+184M_6+184-184M_1+102=281M_6+64 \quad (3)$$
$$86M_1-97M_6=-222 \quad (4)$$

Substituting (2) in (4):

$$86M_1-173.5M_1-82=-222$$
$$87.5M_1=140$$
$$M_1=1.6$$

From Equation 4:

$$97M_6=222+1.6\times 86=359.5$$
$$M_6=3.71$$

But since the total liquid product M_0=1, then:

$$M_6=M_5-1$$
$$M_5=4.71$$

Substituting in Equation 2.5:

$$M_3=3.11$$

EXCHANGER 3

M_5—High pressure fluid stream at cold end (30 atmospheres pressure):

H_5=270 calories per gram
T_5=67 degrees K.

M_6—Low pressure output from warm end of exchanger **4** (about one atmosphere pressure):

Let H_6=281 calories per gram.
Let T_6=63 degrees K.
} Values selected empirically.

M_7—High pressure input stream, warm end exchanger **3** (30 atmospheres pressure):

H_7=775 calories per gram.
T_7=230 degrees K.

M_8—Low pressure output stream, warm end exchanger **3** (one atmosphere pressure):

H_8=765 calories per gram.
T_8=227 degrees K.

M_9—High pressure input into expander **9** (30 atmospheres pressure):

H_9=510 calories per gram.
T_9=148 degrees K.

This value for T_9 was determined empirically, to provide an enthalpy of 281 at the exhaust of expander **9**, the efficiency of which is 80%.

Ortho-para conversion loss factor=57 calories per gram.

Heat leak loss factor=30 calories per gram.

Heat balance of heat-exchanger **3**:

$$(H_7-H_5)M_5 + \text{ortho-para conversion factor} + \text{heat leak factor} + (H_7-H_9)M_9 = (H_8-H_6)M_8 \quad (5)$$

Substituting values from foregoing analysis in Equation 5:

$$(775-270)4.71+57+30+(775-510)M_9=(765-281)M_8$$
$$505M_5+87+265M_9=484M_8 \quad (6)$$

But $M_8=M_6+M_9=3.71+M_9$; and $M_5=4.71$

Substituting these values in Equation 6:

$$505\times 4.71+87+265M_9=484M_9+484\times 3.71$$
$$-219M_9=1795-85-2380=-670$$
$$M_9=3.06$$

$$M_7=M_5+M_9=4.71+3.06=7.77$$
$$M_8=M_7-1=6.77$$

Summary of flows:

Liquid product	$M_0=1.00$
High pressure output, heat-exchanger **4**	$M_1=1.6$
Low pressure input, heat-exchanger **4**	$M_2=M_6=3.71$
Input, expander **10**	$M_3=3.11$
Exhaust, expander **10**	$M_4=3.11$
High pressure output, heat-exchanger **3**	$M_5=4.71$
Low pressure output, heat-exchanger **4**	$M_6=3.71$
High pressure input, heat-exchanger **3**	$M_7=7.77$
Low pressure output, heat-exchanger **3**	$M_8=6.77$
High pressure input, expander **9**	$M_9=3.06$

Summary of power consumption:

Assumed production rate=30 standard cubic feet per minute.
=60 liters per hour.
Feed+recycle=30×7.77 =233 standard cubic feet per minute.

Expanders, work done:
Expander 9—229×3.06=700 calories per gram;
Expander 10—86×3.11=267 calories per gram.

Total work product=967 calories per gram.
=1740 B.t.u. per number of product
=16,300 B.t.u. per hour.
=4.4 kilowatts.

This is an efficiency of 90 percent.

Compressor power (2 stage)	= 64.5 kilowatts.
Fore-cooler, refrigeration	= 1.3 kilowatts.
	65.8 kilowatts.
Expander credit	−4.4 kilowatts.
Net power consumed	61.4 kilowatts.
Kilowatt hours per liter	= 1.02
Kilowatt hours per gallon	= 3.98

Table

[*Heat exchanger 4;* Enthalpy values at selected temperature levels of the high pressure stream (30 atmospheres), and corresponding enthalpy values and resultant temperatures of the low pressure returning stream. For mass flow values $M_1=1.6$ and $M_6=3.71$]

No.	High pressure stream		ΔH, cal./g.	$M_1\Delta H$, cal.	Ortho-para factor, cal.	Heat leak factor	Total heat exchange ΔQ, cal.	$\Delta Q/M_6$ equals L.P.ΔH, cal./g.	Low pressure stream		Temp. diff. ΔT, ° K
	Temp., ° K	Enthalpy H, cal./g.							Enthalpy H, cal./g.	Temp., ° K	
1	22	75	--------	--------	--------	--------	--------	--------	172	20.4	1.6
2	27	88	13	20.8	--------	4	24.8	6.7	178.7	23.0	4.0
3	30	97	9	14.4	--------	4	18.4	5.0	183.7	25.0	5.0
4	35	118	21	33.6	3	4	40.6	10.9	194.6	29.0	6.0
5	40	151	33	52.8	7	4	63.8	17.2	211.8	35.5	4.5
6	45	184	33	52.8	10	4	66.8	18.0	229.8	43.0	2.0
7	50	204	25	40.0	10	4	54.0	14.5	244.3	48.5	1.5
8	55	228	19	30.4	10	4	44.4	11.9	256.2	53.0	2.0
9	60	246	18	28.8	10	2	40.8	11.0	267.2	57.0	3.0
10	67	270	24	38.8	12	--------	50.4	13.6	281.0	63.0	4.0

From the foregoing table, it is apparent that the values which have been assumed for T_1 and T_6 in heat-exchanger **4** produce a minimum spread of 1.5 degrees at 50 degrees Kelvin, which is satisfactory between the incoming and outgoing streams. A similar calculation for heat-exchanger **3** has shown that the values selected for that unit also give a satisfactory temperature spread between incoming and outgoing streams.

It will be seen that in the embodiment hereinabove described in detail, the solidified impurities in the expanded feed stream from the expander **10** are effectively removed by entrainment in the liquid phase delivered from the cold end of the exchanger **4** through valve **5**. In an alternative embodiment, however, the solidified impurities from the expander may be effectively removed from the expanded feed-stream by passage through a suitable filter device which may be, for example, a sintered or porous metal element of stainless steel or nonferrous metal or of a ceramic material which is provided with openings of sufficiently small dimensions to effectively retain the finely divided particles of solidified impurities. In such embodiment, the expanded feed-stream thus removed of its solidified impurities may be directly combined with the cold vapor from the vessel **6** delivered to the cold end of the heat exchanger compartment **4***d* inasmuch as it will not be necessary to contact the expanded stream with the liquid from expansion valve **5** to effect the separation of the impurities. It will be evident, of course, in this embodiment that the recycled stream from the expansion valve **5** may then advantageously be delivered directly to the vessel **6** where the purified, normal, liquid hydrogen may be accumulated. The desired liquid hydrogen product, of course, may then be readily drawn off either from the vessel **6** or from the vessel **17** in the para-form in substantially the identical manner described previously in connection with the operation of the cycle in FIG. 1. It will be seen that in such alternative embodiment the heat balance described in connection with the specific embodiment of FIG. 1 will be altered. However, the adjustment of the various flows and the control thereof to obtain a desired thermodynamic balance in such alternative form of the liquefaction cycle will be obvious to those skilled in the art. The employment of such alternative embodiment of the invention, while effective for the production of liquid hydrogen, necessarily involves suitable provision for the periodic replacement or recharging of such filter means such as, for example, by parallel switching filters or other similar expedients. It will be seen that the former embodiment, which is described in greater detail as utilizing a liquid entrainment for the separation of solidified impurities, is more amenable to a continuous uninterrupted operation and is considered to be more advantageous for the purposes of the present invention.

It will be apparent to those skilled in the art that whereas the present invention has been described with reference to specific apparatus, and whereas specific values for the parameters of the system have been assumed in order to teach the practice of the disclosed invention, the scope of the invention, as embraced in the appended claims, is not limited or circumscribed by the particular forms of apparatus shown, or the specific values disclosed by way of illustration.

I claim:

1. In the liquefaction of gas in a liquefaction system through a cycle and recycle which includes the steps of compressing the said gas including a feed-stream and a recycled stream, cooling the said stream of compressed recycled gas, and freely expanding the cooled, compressed recycled gas through a throttle-valve to produce a partially liquid output, the method of removing small amounts of low-boiling impurities which tend to freeze within a temperature-pressure range above the liquefaction point of said gas and clog the low temperature stages of said liquefaction system including said throttle-valve, said method including the steps of cooling the compressed feed-stream of the gas including said impurities to a temperature slightly above the freezing point of said impurities, diverting the entire compressed feed-stream into a path which by-passes said low-temperature stages including said throttle-valve, expanding said diverted feed-stream in an expansion device with the performance of external work to lower the temperature of said feed-steam below the freezing point of said impurities at the output pressure of said expansion device causing said impurities to freeze in said feed-stream, and thereafter causing said expanded feed stream including said frozen impurities to mingle with a portion of the partially liquid output derived from said throttle-valve, permitting said impurities to become entrained in said liquid, and permitting the gaseous residue of said expanded feed-stream purged of said impurities to return in said system through a path whereby it cools said compressed gas including said feed-stream and said recycled stream, and is subsequently compressed as said recycled stream.

2. In the liquefaction of gas in a liquefaction system through a cycle and recycle which include the steps of compressing the said gas including a feed-stream and a recycled stream, cooling the said stream of compressed recycled gas, and freely expanding the cooled, compressed recycled gas through a throttle-valve, to produce a partially liquid output, the method of removing small amounts of low-boiling impurities which tend to freeze within a temperature-pressure range above the liquefaction point of said gas and clog the low temperature stages of said liquefaction system including said throttle-valve, said method including the steps of cooling the compressed feed-stream of the gas including said impurities to a temperature slightly above the freezing point of said impurities, diverting the entire compressed feed-stream into a path which by-passes said low-temperature stages including said throttle-valve, expanding said diverted feed-stream together with a portion of purified recycled gas in an expansion device with the performance

of external work to lower the temperature of said feed-stream below the freezing point of said impurities at the output pressure of said expansion device causing said impurities to freeze in said feed-stream, and thereafter causing said expanded feed-stream including said frozen impurities to mingle with a portion of the partially liquid output derived from said throttle-valve, permitting said impurities to become entrained in said liquid, and permitting the gaseous residue of said expanded feed-stream purged of said impurities to return in said system through a path whereby it cools said compressed gas including said feed-stream and said recycled stream, and is subsequently recompressed as said recycled stream.

3. In a process for liquefying hydrogen in a liquefaction system through a cycle and recycle which include the steps of compressing said gas including a feed-stream and a recycled stream to a pressure within the range of 20 to 100 atmospheres, cooling the said stream of compressed recycled gas to a temperature below the critical temperature of hydrogen, and freely expanding said compressed, cooled recycled hydrogen through a throttle-valve to produce a partially liquid output, the method of removing small amounts of impurities which tend to freeze within the temperature-pressure range above the liquefaction point of said gas and clog the low temperature stages of said liquefaction system including said throttle-valve which comprises the steps of cooling the compressed feed-stream of hydrogen including said impurities to a temperature slightly above the freezing point of said impurities, diverting the entire compressed feed-stream into a path which by-passes said low-temperature stages including said throttle-valve, expanding said diverted feed-stream in an expansion device with the performance of external work to substantially atmospheric pressure to lower the temperature of said feed-stream below the freezing point of said impurities at said pressure causing said impurities to freeze out in said feed-stream, and thereafter causing said expanded feed-stream including said frozen-out impurities to mingle with a portion of partially liquid hydrogen derived from said throttle-valve, permitting said impurities to become entrained in said liquid, and permitting the residue of gaseous hydrogen from said feed-stream purged of said impurities to return in said system through a path whereby it cools said compressed gas including said feed-stream and said recycled stream, and is subsequently recompressed as said recycled stream.

4. In a system for liquefying a gas having a critical temperature below about 35 degrees Kelvin, said system operating through a cycle and recycle in which the gas including a feed-stream and a recycled stream is compressed and a portion of said recycled stream cooled and converted to the liquid phase in a throttle-valve, and the remainder of said recycled stream returned for recompression and recycling in said system, the method of removing from the low-temperature stages of said system including said throttle-valve small amounts of impurities which solidify in the mixture of said gas below the temperature range of liquid nitrogen but above the liquefaction temperature of said gas, which comprises the steps of cooling the high pressure feed-stream of said gas including said impurities separately from the high-pressure recycled gas to a temperature slightly in excess of the freezing temperatures of said impurities, diverting the entire compressed feed-stream into a path which avoids said throttle-valve, expanding said diverted feed-stream in an expansion device with the performance of external work thereby causing said impurities to freeze out of said feed-stream in a fine suspension at a temperature-pressure point above the liquefaction point of said gas, and thereafter passing said expanded feed-stream including said frozen-out impurities in suspension into the liquid phase formed in said system, whereby the purified gas bubbles through said liquid and returns through a path whereby it cools said compressed gas in said system and is subsequently compressed as said recycled stream, and permittings said impurity particles to be entrained in said liquid.

5. In a system for liquefying hydrogen through a cycle and recycle in which the recycled stream of hydrogen is compressed and a portion of said recycled stream cooled and converted to liquid phase in a throttle-valve, and the remainder returned for recycling and recompression, the method of removing small amounts of impurities which solidify in the hydrogen mixture below the temperature range of liquid nitrogen but above the liquefaction temperature of hydrogen which comprises the steps of compressing and cooling the feed-stream of said hydrogen containing said impurities to a low temperature in excess of the freezing point of said impurities separately from said hydrogen recycle stream, expanding all of said feed-stream in an expansion device with the performance of external work causing said impurities to freeze-out in a fine suspension at a temperature-pressure point above the liquefaction point of said hydrogen, thereafter passing said expanded stream containing the frozen-out particles of said impurities into the liquid phase formed in said system, permitting the purified portion of said expanded hydrogen stream to bubble through said liquid and return through a path whereby it cools said compressed hydrogen in said system and is subsequently compressed as said recycled stream, and permitting said impurity particles to be entrained in said liquid for subsequent removal.

6. The method of removing impurities which solidify below the temperature range of liquid nitrogen and above the liquefaction temperature of hydrogen from the feed-stream of hydrogen in a system for liquefying hydrogen wherein said hydrogen undergoes a cycle and recycle in which it is compressed, cooled, a portion of the recycled purified hydrogen converted to liquid-phase through a principal liquefaction path, and the remainder of said recycled hydrogen returned for recompression and recycling, said method comprising the steps of compressing and cooling the impure feed-stream of said hydrogen to a temperature slightly above the freezing temperature of said impurities, diverting the entire said impure feed-stream away from the principal liquefaction path of the recycled purified hydrogen, similarly diverting a portion of the purified recycled stream of said hydrogen after compression and cooling to said same temperature above the freezing temperature of said impurities, forming a mixture of said diverted purified portion with said impure feed-stream, expanding said mixture in an expansion device with the performance of external work causing said impurities to freeze-out in a fine suspension at a temperature-pressure point above the liquefaction point of said hydrogen, and thereafter intermingling said mixture including said frozen-out impurities in suspension with the liquid-phase of said hydrogen, permitting the purified gas of said mixture to escape from said liquid phase and return through a path whereby it cools said compressed hydrogen for recompression in said recycle compression step where it becomes a part of said recycled hydrogen in said system, and permitting said impurity particles to become entrained in said liquid for subsequent removal.

7. In a system for liquefying hydrogen through a cycle and recycle in which said recycled stream of hydrogen is compressed to a pressure in excess of 20 atmospheres, cooled to about the liquefaction temperature of hydrogen, and a portion converted to liquid by expansion without the performance of external work, and the unliquefied remainder of said recycled stream is returned to be recompressed and recycled in said system, the method of removing small amounts of impurities which solidify in the hydrogen mixture below the temperature range of liquid nitrogen but above the liquefaction temperature of hydrogen in said system, which comprises the steps of compressing the feed-stream of hydrogen to said pressure and cooling said

feed-stream containing said impurities to a point below the liquefaction temperature of nitrogen but above the freezing point of said impurities, forming a mixture of the entire said feed-stream with a portion of said recycled remainder at substantially the same temperature and pressure, expanding said mixture including the entire said feed-stream in an expansion device with the performance of external work to substantially atmospheric pressure causing said impurities to freeze-out from the gaseous portion of said mixture in a fine suspension, and thereafter mingling said mixture including said frozen-out impurities in suspension with said liquid, permitting said gaseous portion to escape from said liquid and return with said unliquefied remainder for recompression as said recycled stream of hydrogen and recycling in said system through a path whereby it cools said compressed hydrogen, and permitting said impurity particles to become entrained in said liquid for subsequent removal.

8. The process of liquefying and purifying hydrogen through a cycle and recycle which includes the steps of separately compressing the feed-stream, including nitrogen and other low-boiling impurities, and the returning, recycled streams of said hydrogen to a pressure within the range of 20 to 100 atmospheres in compressing means, cooling a portion of the recycled streams to about the liquefaction temperature of hydrogen, freely expanding a portion of the recycled streams through a throttle-valve to substantially about atmospheric pressure, causing the said portion to be partially converted to liquid, separately cooling the compressed feed stream to a temperature above the freezing point of nitrogen, expanding said entire compressed, cooled feed-stream, together with a portion of said compressed, cooled recycled stream, to substantially atmospheric pressure below the freezing point of said impurities and above the liquefaction point of said hydrogen with the performance of external work in an expansion device through a path which avoids said throttle-valve, thereby causing said impurities to freeze-out and form a suspension in said streams, thereafter causing said feed-stream including gaseous hydrogen and said suspended impurities to mingle with the partially liquid recycled stream, permitting said impurities to become entrained in the liquid of said recycle stream, permitting said purified, gaseous hydrogen to return to said recycle compressing step thereby cooling the compressed feed stream and recycled streams enroute, and in the final stage of said process, after recompressing and cooling said purified gaseous stream of hydrogen as one of said recycled streams, submitting a portion of said recycled stream to ortho-para conversion, cooling the para-hydrogen product of said conversion to a final low temperature below the liquefaction temperature of hydrogen and condensing said product to liquid by the step of passing said portion through a cooling bath of liquid formed in the earlier stages of said process.

9. An apparatus for the liquefaction and purification of hydrogen through a cycle and recycle which comprises in combination means for separately compressing to a pressure within the range of 20 to 100 atmospheres both the incoming feed-stream of said hydrogen including up to about one percent by volume of nitrogen, oxygen and other low-boiling impurities and the recycled stream of said hydrogen gas, means for cooling the compressed, recycled stream to about the liquefaction temperature of hydrogen, means including a throttle-valve for permitting said compressed, cooled, recycled stream to expand freely partially forming liquid, a receptacle connected to receive and store the liquid so formed, means for cooling said compressed feed-stream including said impurities to a temperature-pressure range slightly above the freezing point of nitrogen, means for diverting the entire said feed-stream through a path which avoids said throttle-valve, said path including an expansion engine connected to receive said compressed, cooled feed-stream together with a portion of said compressed, cooled recycled stream to permit said streams to expand with the production of external work to substantially atmospheric pressure whereby said impurities snow-out and form a suspension in said streams, means including said liquid receptacle for permitting said expanded streams exhausted from said expansion engine and including said suspension of solidified impurities to mingle with the liquid formed in said throttle-valve, means including a bubble-cap disposed in said receptacle for entraining the suspended impurities in said liquid and permitting the escape of the gaseous portions of said streams, and means including said cooling means for returning said gaseous portions at substantially atmospheric pressure to said recycle compression means, whereby the incoming, compressed streams are cooled by said returning gaseous portions, and an outlet valve in said receptacle for periodically removing the slurry formed by said impurities entrained in said liquid.

10. An apparatus for the liquefaction and purification of hydrogen through a cycle and recycle which comprises in combination means for separately compressing to a pressure within the range of 20 to 100 atmospheres both the incoming feed-stream of said hydrogen including up to about one percent by volume of nitrogen and other low-boiling impurities and the recycled stream of said hydrogen, means for cooling the compressed recycled stream to about the liquefaction temperature of hydrogen, means including a throttle-valve for permitting said compressed, cooled, recycled stream to expand freely partially forming liquid, a receptacle connected to receive and store the liquid so formed, means for cooling said compressed feed-stream including said impurities to a temperature-pressure range slightly above the freezing point of nitrogen, means for diverting said entire feed-stream through a path which avoids said throttle-valve, said path including an expansion engine connected to receive said compressed, cooled feed-stream together with a portion of said compressed, cooled, recycled stream to permit said streams to expand with the production of external work to substantially atmospheric pressure whereby said impurities are caused to snow-out and form a suspension in said streams, means including said liquid receptacle for permitting said expanded streams exhausted from said expansion engine and including said suspension of solidified impurities to mingle with the liquid formed in said throttle-valve, means including a bubble-cap disposed in said receptacle for permitting said suspended impurities to become entrained in said liquid and for permitting the gaseous portions of said streams to rise out of said liquid, means including said cooling means for returning said gaseous portions at substantially atmospheric pressure to said recycle compressing means whereby the incoming, compressed streams are cooled by said returning gaseous portions, ortho-para conversion means connected to receive a portion of the recycled stream from said cooling means in the final stage of liquefaction and to convert ortho to para-hydrogen, cooling and condensing means including a coil of pipe disposed in said receptacle and surrounded by the liquid stored therein for partially liquefying the para-hydrogen product of said conversion means, means for storing the para-hydrogen liquid so formed, and means for returning the unliquefied portion of said para-hydrogen product to said compression means for recompression and recycling.

11. The method of liquefying and purifying a hydrogen stream containing minor amounts of low boiling impurities including nitrogen which comprises compressing the impure hydrogen stream, cooling said stream to a temperature-pressure range substantially above the point at which said impurities are solidified, expanding said entire impure stream in a work-expansion step to a temperature-pressure range below the freezing point of said impurities and obtaining said impurities as finely divided

solid particles in the fluid exhaust of said expansion, maintaining a body of liquid hydrogen containing impurities precipitated therein, introducing said expanded hydrogen fluid containing said solid particles into said body of liquid hydrogen, segregating the said solidified impurities in said liquid hydrogen body, withdrawing vaporized hydrogen from said body of liquid substantially free of said impurities, compressing said withdrawn impurity-free hydrogen vapor, cooling said compressed impurity-free vapor by heat exchange, converting to liquid at least a portion of said compressed, cooled impurity-free hydrogen vapor by expansion, and delivering said impurity-free liquid hydrogen portion to replenish the said body of liquid hydrogen containing precipitated impurities therein.

12. The method of liquefying and purifying a hydrogen stream in accordance with claim 11 in which said entire impure stream is expanded in a work-expansion step from which the impurities are obtained as finely divided, solid particles in a substantially gaseous exhaust.

13. The method of liquefying and purifying a hydrogen stream in accordance with claim 11 in which another portion of said compressed, cooled impurity-free hydrogen vapor is converted to liquid by condensation in a coil surrounded by a refrigerant, said last-named portion of liquefied hydrogen being delivered to separate storage means containing another body of liquid hydrogen substantially free of said impurities.

14. The method in accordance with claim 13 wherein said body of liquid hydrogen containing precipitated impurities is utilized as the said refrigerant for the condensation of said impurity-free hydrogen vapor prior to delivery to said separate storage means.

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