

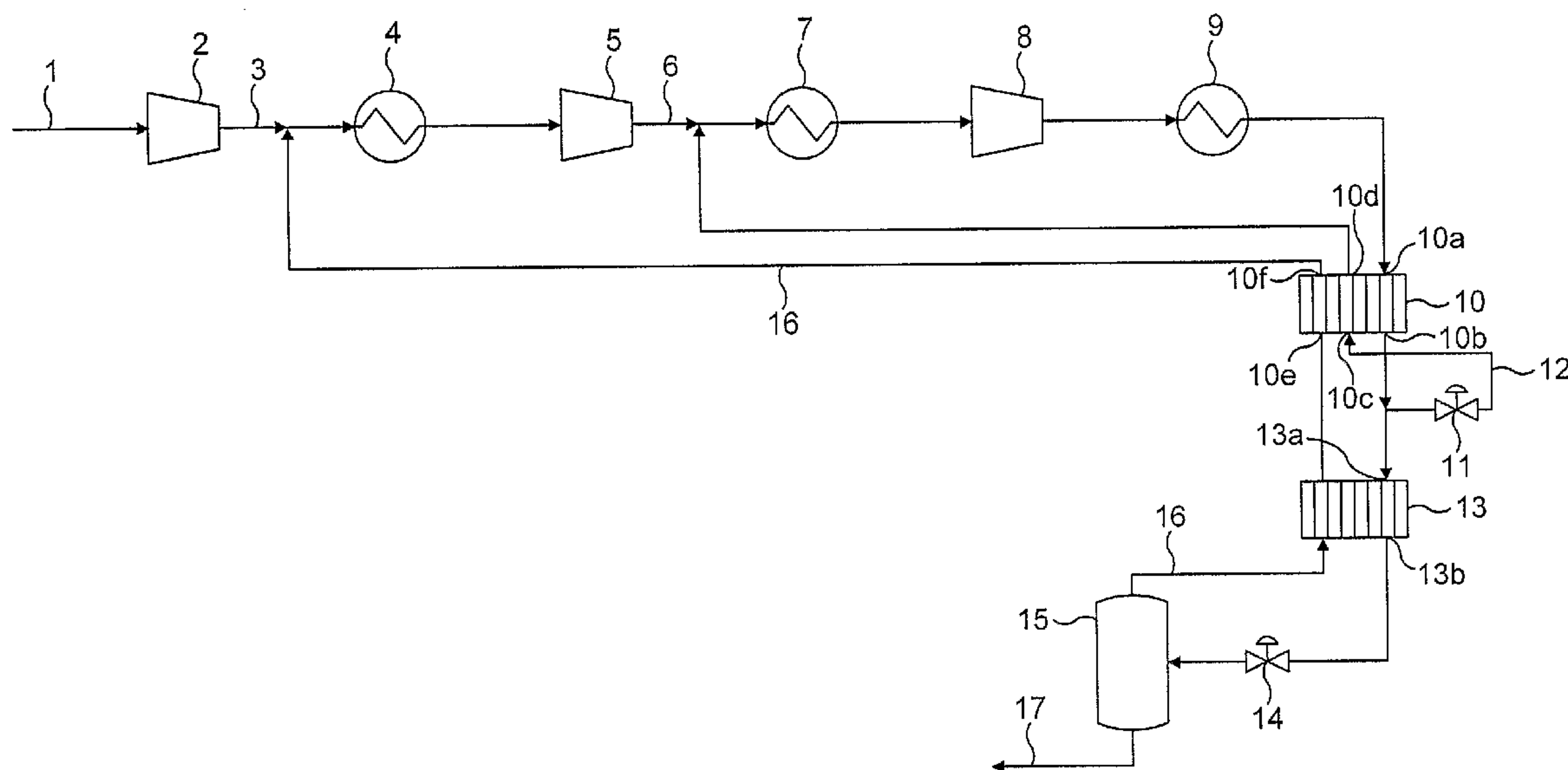
US 20080156035A1

(19) **United States**(12) **Patent Application Publication**
Aspelund et al.(10) **Pub. No.: US 2008/0156035 A1**(43) **Pub. Date: Jul. 3, 2008**(54) **PROCESS AND APPARATUS FOR THE
LIQUEFACTION OF CARBON DIOXIDE**(75) Inventors: **Audun Aspelund**, Trondheim
(NO); **Henrik Krogstad**, Heimdal
(NO); **Tor Erling Sandvik**,
Trondheim (NO)Correspondence Address:
BACON & THOMAS, PLLC
625 SLATERS LANE, FOURTH FLOOR
ALEXANDRIA, VA 22314(73) Assignees: **STATOIL ASA**, Stavanger (NO);
SINVENT AS, Trondheim (NO);
ORKLA ENGINEERING,
Orkanger (NO); **TEEKAY**
NORWAY AS, Stavanger (NO)(21) Appl. No.: **11/632,492**(22) PCT Filed: **Jul. 14, 2005**(86) PCT No.: **PCT/GB05/02777**§ 371 (c)(1),
(2), (4) Date: **Nov. 6, 2007**(30) **Foreign Application Priority Data**

Jul. 16, 2004 (GB) 0416001.6

Publication Classification(51) **Int. Cl.**
F25J 1/00 (2006.01)
F25J 5/00 (2006.01)(52) **U.S. Cl.** **62/606; 62/902**(57) **ABSTRACT**

Apparatus for carbon dioxide liquefaction comprising a flow channel for carbon dioxide passage from an inlet port to an outlet port. The channel comprises a plurality of compressors (2, 5, 8) and coolers (4, 7, 9, 10, 13) arranged in series with an expansion chamber (14, 15) in said flow channel downstream of the final compressor (8) and cooler (9, 10, 13). The apparatus also comprises a recirculation channel (16) arranged to return gaseous carbon dioxide from said expansion chamber (15) into said flow channel (3) upstream of said final compressor (8) and cooler (9, 10, 13).



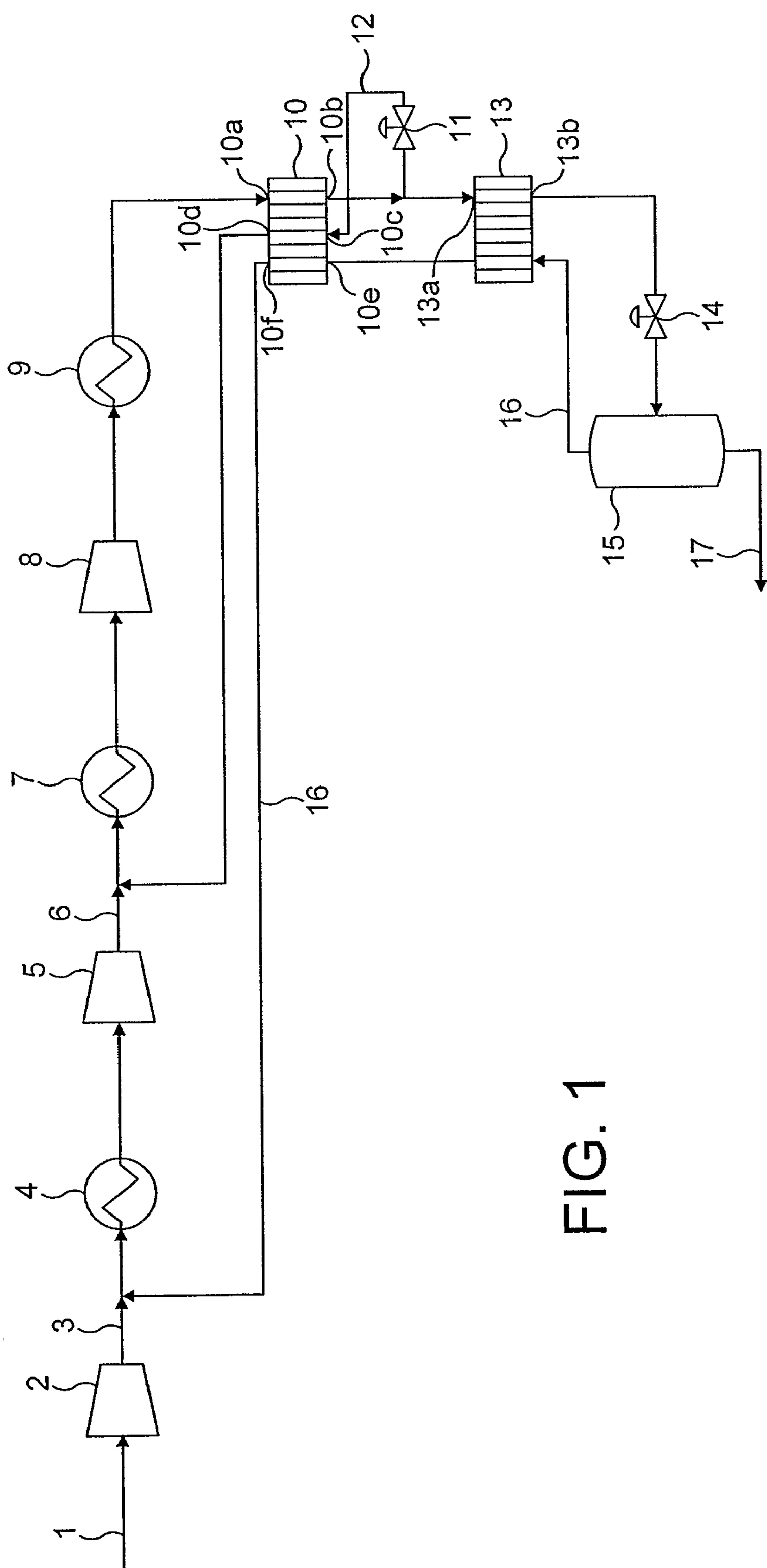


FIG. 1

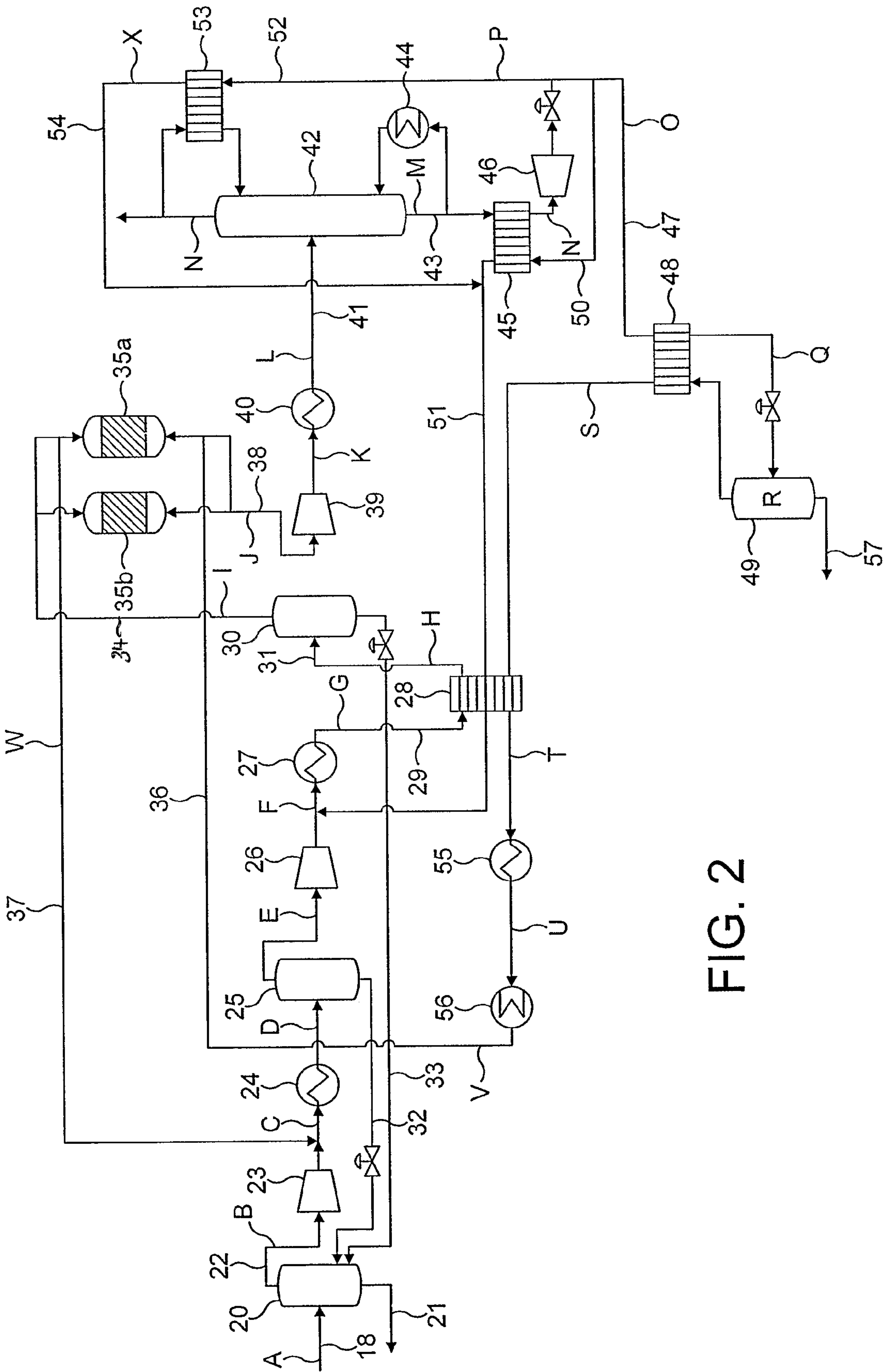


FIG. 2

PROCESS AND APPARATUS FOR THE LIQUEFACTION OF CARBON DIOXIDE

[0001] The present invention relates to a process for the production of liquid carbon dioxide and apparatus for use in said process.

[0002] Carbon dioxide (CO₂) is a gas produced as a by-product in large quantities in certain industrial operations, e.g. the manufacture of ammonia, or power generation by coal or gas power plants. Release of this by-product into the atmosphere is undesirable environmentally as it is a greenhouse gas. Much effort has thus been made towards the development of techniques for the disposal of CO₂ in a way other than simple release to the atmosphere. One technique of particular interest is to pump the CO₂ into porous sub-surface strata (i.e. rock), e.g. down an injector well in an oil field.

[0003] Subsurface disposal can be simply into porous strata or beneficial advantage of the subsurface disposal can be realised if the stratum into which it is disposed is hydrocarbon-bearing as the injected CO₂ serves to drive hydrocarbon (e.g. oil or gas) in the stratum towards the producer wells (i.e. wells from which hydrocarbon is extracted). Injection of CO₂ is thus one standard technique in late stage reservoir management for achieving enhanced recovery of hydrocarbons.

[0004] The quantities of carbon dioxide involved when disposal is by subsurface injection are immense, generally of the order of millions of tonnes. This poses problems in terms of transporting the CO₂ from the site at which it is created to the site at which it is injected, especially where the injection site is offshore. Carbon dioxide at ambient temperatures and pressures is gaseous and, if transported batchwise, such voluminous containers are required that the process would be unfeasible. While transport by pipeline might in some circumstances be feasible, the required infrastructure is expensive. It is therefore desirable to transport the carbon dioxide, especially to offshore injection sites, batchwise in liquid form.

[0005] Transport of liquid carbon dioxide is however not a problem- or expense-free exercise. If the liquid CO₂ is not refrigerated, the pressures required to maintain it in the liquid state are high (60-80 bar A) making the required wall thicknesses of the pressurized containers high and making such containers for large scale unrefrigerated liquid CO₂ transportation immensely expensive. Transport of liquid CO₂ at sub-ambient temperatures reduces the required pressures and required container wall thicknesses but is expensive since refrigeration is required and, as carbon dioxide has a solid phase, there is a risk that solid carbon dioxide can form. Solid carbon dioxide formation makes CO₂ transfer by pumping problematic and, due to the risks of pipe or valve blockage, potentially dangerous.

[0006] Thus in balancing the economies of refrigeration and container cost and avoiding the risk of solid CO₂ formation, in any given circumstances there will generally be a temperature and pressure which is optimal for the liquid CO₂ in the containers, e.g. a temperature which is below ambient and a pressure which is above ambient but still sub-critical (the critical point of CO₂ is 73.8 bar A). Typically for large scale liquid CO₂ transport the optimum temperature is likely to be in the range -55 to -45° C. and the pressure is likely to be 5.5 to 7.5 bar A, i.e. corresponding to the position in the phase diagram for CO₂ which is just above the triple point in terms of temperature and pressure. The triple point for CO₂ is

5.2 bar A and -56.6° C. Lower temperatures and pressures raise the risk of dry ice formation; higher pressures require more expensive containers; and lower pressures raise the risk of gas or solid formation.

[0007] While small scale production (e.g. currently typically 0.1 tonne/year) of liquid carbon dioxide is relatively trivial, generally involving two, three or four cycles of compression and cooling/expansion, bulk production at the level of millions of tonnes is by no means trivial since, starting with a gas which is, or is majoratively, carbon dioxide at or near ambient temperature and pressure, transforming this starting material to liquid carbon dioxide at the temperatures and pressures that are desirable for bulk transport involves significant pressurization and energy removal.

[0008] We have now found that production of liquid carbon dioxide in bulk and at temperatures and pressures desirable for bulk transport may be effected in an environmentally friendly and efficient manner by producing liquid or dense fluid (i.e. super critical) carbon dioxide at temperatures and pressures above the desired values, expanding it to generate liquid carbon dioxide at the desired values and cold gaseous carbon dioxide which is recycled into the compression and cooling/expansion cycles bringing down the mean enthalpy of the CO₂ flow through those cycles. In this way no expensive coolant is required and CO₂ release into the atmosphere may be avoided.

[0009] Thus viewed from one aspect the invention provides a process for the production from a feed gas which comprises carbon dioxide of liquid carbon dioxide at a desired temperature and pressure which temperature is below ambient, above the triple point temperature for carbon dioxide and below the critical point temperature for carbon dioxide and which pressure is above ambient, above the triple point pressure for carbon dioxide and below the critical point pressure for carbon dioxide, said process comprising: feeding said feed gas into the entry port of a liquefaction apparatus having a flow path from said entry port to an exit port connected to an expansion chamber; flowing said gas as a fluid along the flow path through said apparatus and subjecting said fluid to a plurality of compression and cooling cycles whereby to generate liquid or super-critical carbon dioxide having a temperature and pressure above said desired temperature and pressure; passing said liquid or super-critical carbon dioxide through said exit port into said expansion chamber whereby to generate in said chamber gaseous carbon dioxide and liquid carbon dioxide at said desired temperature and pressure; and recycling said gaseous carbon dioxide into fluid flowing through a said compression and cooling cycle; and optionally withdrawing said liquid carbon dioxide at said desired temperature and pressure from said expansion chamber.

[0010] One or more of the compression and cooling cycles, preferably all such cycles, may additionally involve an expansion step which will of course further cool the fluid. It is especially preferred that the fluid flowing to each compression step is monophasic, i.e. gaseous or dense fluid (super-critical); however it is optional whether the product of the final compression and cooling step comprises liquid carbon dioxide or dense fluid carbon dioxide.

[0011] If desired the expansion chamber may be detachable from the liquefaction apparatus and may thus serve as the transport vessel for the liquid carbon dioxide. Preferably however the expansion chamber has a liquid removal port through which the liquid carbon dioxide may be withdrawn

into a transport vessel. The expansion chamber may be any component suitable for expansion, such as an expansion valve and the like.

[0012] The gaseous carbon dioxide which is recycled is preferably passed through one or more heat exchangers to draw energy from the fluid flow before being returned into the fluid flow at an upstream point.

[0013] Since the feed gas may contain impurities, e.g. water, nitrogen, etc., it is desirable that the fluid flow be subjected to one or more treatments to remove these. Depending on apparatus design, these removal steps may cause some consequential removal of carbon dioxide from the apparatus other than as liquid CO₂. Careful design however can result in only minimal such non-liquid carbon dioxide removal.

[0014] In general, at least two (e.g. 2 to 8, preferably 4) compression steps will be required to transform the fluid into liquid or super-critical carbon dioxide. It is preferred to effect water removal after at least one compression step and before the final compression step, e.g. between the second and third compression steps, typically after the cooling step following the prior compression step. It is especially preferred to effect water removal before each compressor step. Desirably the CO₂ gas is dried to ppm level by adsorption after the last separator.

[0015] Water should be removed to avoid hydrates, freezing of water, corrosion and droplets of water in the compressor feed. The solubility of water in CO₂ gas decreases with higher pressure and lower temperatures. Water can be removed in several ways, e.g. using separators or by passage through a water absorbent or adsorbent bed or filter. Preferably most of the water is removed in separators, after each compression and cooling step.

[0016] For water removal by condensation and separators, the CO₂ gas with liquid contaminants (e.g. water and also other liquids such as liquefied heavy hydrocarbons) enters a separator where the condensed liquids are drawn off from the base of the separator and the CO₂ leaves the top of the separator in gaseous form.

[0017] Desirably the dried gas leaving a separator or separators is led through an adsorption unit before passing to the next compression step. In order to permit continuous operation, it is desirable to have two or more such adsorption units arranged in parallel so that one may be regenerated (for example by passing hot gas through it) while another is in use. The gas used for regeneration will typically be gaseous carbon dioxide which is being recycled. The hot, moist carbon dioxide leaving the unit being regenerated may desirably be recycled into the fluid at an upstream point, e.g. between the first and second compression steps, preferably between a compression step and the subsequent cooling steps.

[0018] Especially preferably the last free water is removed in a separator before the last compressor step at a pressure between 20 and 40 bar and at a temperature close to the hydrate formation curve, that is, between 10° C. and 15° C. Desirably the CO₂ gas is dried to ppm level by adsorption after the last separator.

[0019] Where the feed gas contains further gases that, at ambient temperature, undergo a phase change to liquid phase at a temperature lower than that of carbon dioxide, e.g. gases such as nitrogen, oxygen, methane or ethane, these gases are desirably removed prior to the last expansion.

[0020] For such feed gases it is therefore desirable that the liquefaction process include a step in which such "volatiles" are removed. This preferably occurs following a compression

or cooling step which generates liquid CO₂, or more preferably a fluid, which consists of as much gas as is to be removed in the removal step and the rest in the liquid phase. If heat is rejected at pressures higher than the CP in the supercritical phase, the removal of volatiles will be done after the first expansion step, where the fluid is in the two phase region under the CP with a low gas fraction.

[0021] The removal of volatile components may be done in a separation column after heat rejection close to the dew point line. At transport pressures of 6-7 bar A only small fractions of volatiles, typically 0.2-0.5 mole % can be included in the product to ensure that dry ice is not formed. If more volatiles are present in the feed they should be removed. A separator tank could be used; however, a separator column is preferably used to avoid venting of large quantities of CO₂ to the atmosphere. The cooling in the condenser is provided by vaporisation of liquid CO₂ at intermediate pressure stages or from the product tank. As a rule of thumb the loss of CO₂ will be equal to the amount of volatiles in the feed.

[0022] To further enhance volatile removal, some or all of the liquid CO₂ withdrawn from the separator column may be warmed (e.g. in a reboiler) and returned into this separator column. The reboiler may alternatively be integrated in the separator column.

[0023] The cooling units arranged to cool the fluid flow may use recycled carbon dioxide as the cooling fluid. However the cooling units in at least the first compression and cooling steps conveniently use an externally sourced fluid, typically water, e.g. sea, river, or lake water or ambient air.

[0024] The apparatus used in the process of the invention preferably comprises gas tight conduits joining the various operating units, i.e. compressors, coolers, heaters, heat exchangers, etc. and provided with appropriate valves. Ideally the flow path has only one entrance port (for the feed gas) and only one exit port (for the liquid CO₂); however exit ports for water or volatiles removal will be present in certain embodiments.

[0025] The feed gas for the process of the invention is preferably majoritively carbon dioxide (on a molar basis), e.g. 55 to 100% mole CO₂ or 70 to 95% mole CO₂, especially at least 70% mole CO₂, more especially at least 90% mole CO₂, particularly up to 95% mole CO₂. More preferably the feed gas contains less than 0.5 mole % of volatile components and less than 0.1 mole % of water. Preferably the water content is not in excess of 50 ppm by weight. As mentioned earlier, the carbon dioxide produced as a by-product in ammonia production or the carbon dioxide captured from coal or gas power plants is particularly suitable.

[0026] Viewed from a further aspect the invention also provides apparatus for carbon dioxide liquefaction comprising a flow channel for carbon dioxide passage from an inlet port to an outlet port, said channel comprising a plurality of compressors and coolers arranged in series, with an expansion chamber in said flow channel downstream of the final compressor and cooler and with a recirculation channel arranged to return gaseous carbon dioxide from said expansion chamber into said flow channel upstream of said final compressor and cooler.

[0027] The apparatus of the invention is conveniently provided with the further structural components discussed above in connection with the process of the invention.

[0028] Embodiments of the invention will now be discussed further by way of illustration and with reference to the following non-limiting Examples and the accompanying drawings, in which:

[0029] FIG. 1 shows a schematic of one embodiment of the apparatus of the invention; and

[0030] FIG. 2 shows a schematic of a preferred embodiment of the apparatus of the invention.

[0031] FIG. 1 is a schematic of the main elements of the apparatus. Feed gas containing 100 mole % carbon dioxide is supplied from a source (not shown) to the input port of conduit 1. The gas is fed to a first compressor 2 and then to a first intermediate cooler 4 via conduit 3. Second stage compression and cooling is performed by second stage compressor 5 and cooler 7 (connected by conduit 6) and the final stage of compression is achieved using compressor 8 and cooler 9. Heat is extracted in each of the coolers 4, 7 and 9 using ambient air or water (conduits not shown) as the cooling medium.

[0032] The fluid output from the last compression stage is communicated to a first input 10a of heat exchanger 10. The first output 10b of heat exchanger 10 is connected to first input 13a of a second heat exchanger 13. In addition, the first output 10b is connected via conduit 12 and expansion valve 11 to the second input 10c of heat exchanger 10. The expansion valve 11 is arranged to expand and cool the first output 10b from heat exchanger 10. This acts to cool the fluid flowing between 10 and 10b. The recycled carbon dioxide gas flowing between the third input 10e and 10f will also cool the fluid flowing 10a to 10b. The second output 10d is connected to conduit 6 between compressor 5 and cooler 7 whereby to recycle the gas drawn off down conduit 12.

[0033] The first output 10b from heat exchanger 10 passes through a further heat exchanger 13 and to expansion valve 14. The fluid is then expanded to the transport pressure by expansion valve 14 and fed into the separator 15. The gas phase (or flash gas) is returned via conduit 16 and heat exchangers 13 and 10 respectively to the conduit 3 arranged between the first compressor 2 and first cooler 4. The arrangement of the two heat exchangers 10 and 13 acts to cool the flow of fluid passing between 10a, 10b, 13a and 13b because the flash gas in conduit 16 and the expanded supply gas in conduit 12 will be at a lower temperature. This increases the efficiency of the process.

[0034] The liquid phase separated in separator 15 is output via output 17 to a storage or transport vessel (not shown).

[0035] Expansion of pressurised fluids as mentioned above may conveniently involve use of a Joule-Thompson valve. Alternatively, an expansion turbine may be used for expansion of the pressurised fluids as mentioned above. This will increase the energy efficiency of the process.

[0036] Referring to FIG. 2, feed gas is delivered into the inlet port of conduit 18 in the apparatus and thence into separator 20 which serves to condense water which is removed through conduit 21. The gas then passes, via conduit 22, to the first stage compressor 23 and to first stage intermediate cooler 24. This first stage of water removal, compression and intermediate cooling is repeated as shown in FIG. 2 by separator 25, second compressor 26 and second cooler 27. The output of the second intermediate cooler 27 is passed through a heat exchanger 28 via conduit 29 where the temperature of the feed gas is further reduced by heat exchange with gaseous carbon dioxide recycled from downstream in the apparatus.

[0037] Intermediate coolers 24 and 27 reject heat to sea water.

[0038] The feed gas flows from heat exchanger 28 to separator 30 via conduit 31. Water removed in separators 25 and 30 is returned to the first separator 20 via conduits 32 and 33.

[0039] Water is removed from the feed gas by means of the three separators 20, 25 and 30 by condensation. It is highly desirable to remove water from the feed gas to avoid hydrate formation and corrosion which can occur if significantly more than 50 ppm (wt.) water is present. Removal of water also increases the efficiency of the process.

[0040] Feed gas is then fed from the third separator 30 via conduit 34 to one of two water adsorption units 35a and 35b where the water content is reduced still further to approximately 50 ppm.

[0041] At any one stage, one water adsorption unit is in use while the other is being regenerated (dried) by hot carbon dioxide gas from conduit 36. The moist carbon dioxide from the unit being regenerated is recycled into the conduit after the first compressor 23 through conduit 37.

[0042] Feed gas, with a water content of approximately 50 ppm or less is fed via conduit 38 to the final stage compressor 39 and cooler 40. The feed gas leaves compressor 39 at the maximum pressure of the process (39 being the final compression stage) and is cooled by cooler 40 which rejects heat to sea water.

[0043] The liquid CO₂ then passes via conduit 41 to the removal of volatiles column where the volatiles are removed by distillation. The volatiles are removed in the top of the column leaving the bulk of the CO₂ in the liquid phase. Liquid carbon dioxide is drawn off through conduit 43. In order to enhance the removal of volatiles a re-boiler 44 is attached at the bottom of the column. The re-boiler provides heat in the bottom of the column to boil off volatiles, and thereby enhance the separation of volatiles from the CO₂. To enhance the recovery of CO₂ in the volatile rich gas stream at the top of the column a condenser is placed in the top of the column. The required cooling duty for the condenser is provided by vaporisation of liquid CO₂ at intermediate or product pressure.

[0044] The remaining liquid carbon dioxide passes through heat exchanger 45 to expansion unit 46 which generates cold carbon dioxide gas and carbon dioxide liquid. The liquid is directed via conduit 47 and heat exchanger 48 into the final expansion tank 49 in which it is the desired temperature and pressure. The gas is split, part flowing via conduit 50 back through heat exchanger 45 and thence via conduit 51 to heat exchanger 28 and part via conduit 52 through heat exchanger 53 and thence via conduits 54 and 51 to heat exchanger 28. Heat exchange 53 serves as a condenser for column 42.

[0045] The gas formed in the final expansion tank 49 is fed via heat exchangers 48, 28 and 55 to a heater 56 at which it is heated to a temperature sufficient to regenerate the water absorption units 35a and 35b.

[0046] The liquid carbon dioxide in expansion tank 49 may be drawn off via conduit 57 to a transport vessel.

[0047] In the embodiment shown in FIG. 1, the pressure and temperature before and after compressor 2 are preferably 5 bar A/25° C. and 11 bar A/25° C. The pressure and temperature in expansion tank 15 is preferably 6.5 bar A/-50° C.

[0048] In the embodiment shown in FIG. 2, the pressures and temperatures at the sites marked A, B, C, D, etc. are preferably as set out in Table 1 below:

TABLE 1

Flow location	Pressure (bar A)	Temperature (° C.)
A	1.1	25
B	1.1	25
C	5	140
D	4.5	20
E	4.5	20
F	20	140
G	19.5	20
H	19.5	10
I	19.5	10
J	19.5	10
K	60	180
L	60	20
M	60	18
N	60	-15
O	21	-20
P	21	-20
Q	21	-22
R	6.5	-50
S	6.3	-27
T	6.1	-5
U	5.9	200
V	5.7	400
W	5.5	200
X	20.5	-22

[0049] The following three Examples refer to alternative ways in which the process can be operated with respect to heat rejection above or below the critical point of the feed gas.

EXAMPLE 1

Heat Rejection to Sea Water/Atmosphere below the Critical Point

[0050] The carbon dioxide is compressed from the supply pressure of 1 bar to a maximum pressure of approximately 60 bar in 3 compression stages. Between each compression stage the feed gas is cooled using sea water or atmospheric air. The fully pressurised feed gas, i.e. the output from the final compressor, is condensed with a heat exchanger again using sea water. The condensed feed gas is expanded to the transport pressure using an expansion valve and communicated to the flash tank or separator. In the separator the liquid phase is removed and forwarded to a transport or storage vessel and the gas phase is returned to the compression stage.

EXAMPLE 2

Heat Rejection to an External Cooling Circuit below the Critical Point

[0051] The feed gas is compressed from the supply pressure of 1 bar to a maximum pressure of approximately 25 bar in 2 compression stages. The intermediate cooling (between compression stages) is achieved using sea water or atmospheric air. The pressurised feed gas is then condensed using a heat exchanger connected to an external cooling circuit. The condensed feed gas is then expanded using an expansion valve to the transport pressure and communicated to a flash tank or separator. In the separator the liquid phase is removed and forwarded to a transport or storage vessel and the gas phase is returned to the compression stage.

EXAMPLE 3

Heat Rejection to Sea Water/Atmosphere above Critical Point

[0052] The feed gas is compressed from the supply pressure of 1 bar to a maximum pressure of approximately 85 bar (i.e. above the critical pressure of 73.8 bar) in 4 compression stages. The intermediate cooling (between compression stages) is effected using sea water or atmospheric air. The pressurised feed gas is then cooled in the super-critical phase using sea water or atmospheric air. The pressurised fluid is then expanded from the supercritical phase into the two-phase region to the transport pressure using an expansion means and communicated to a flash tank or separator. In the separator the liquid phase is removed and forwarded to a transport or storage vessel and the gas phase is returned to the compression stage.

1. A process for the production from a feed gas which comprises carbon dioxide of liquid carbon dioxide at a desired temperature and pressure which temperature is below ambient, above the triple point temperature for carbon dioxide and below the critical point temperature for carbon dioxide and which pressure is above ambient, above the triple point pressure for carbon dioxide and below the critical point pressure for carbon dioxide, said process comprising: feeding said feed gas into the entry port of a liquefaction apparatus having a flow path from said entry port to an exit port connected to an expansion chamber; flowing said gas as a fluid along the flow path through said apparatus and subjecting said fluid to a plurality of compression and cooling cycles whereby to generate liquid or super-critical carbon dioxide having a temperature and pressure above said desired temperature and pressure; passing said liquid or super-critical carbon dioxide through said exit port into said expansion chamber whereby to generate in said chamber gaseous carbon dioxide and liquid carbon dioxide at said desired temperature and pressure; and recycling said gaseous carbon dioxide into fluid flowing through a said compression and cooling cycle; and optionally withdrawing said liquid carbon dioxide at said desired temperature and pressure from said expansion chamber.

2. A process as claimed in claim 1, wherein one or more of the compression cycles additionally involves an expansion step.

3. A process as claimed in claim 1, wherein the fluid flowing to each compression cycle is monophasic.

4. A process as claimed in claim 1, wherein the expansion chamber is provided with a liquid removal port through which liquid carbon dioxide is withdrawn.

5. A process as claimed in claim 1, wherein the recycled carbon dioxide passes through one or more heat exchangers.

6. A process as claimed in claim 1, wherein the recycled carbon dioxide is returned to the fluid flow at an upstream point.

7. A process as claimed in claim 1, comprising 4 compression cycles.

8. A process as claimed in claim 1, wherein water is removed after at least one compression cycle and before the final compression cycle.

9. Apparatus for carbon dioxide liquefaction comprising a flow channel for carbon dioxide passage from an inlet port to an outlet port, said channel comprising a plurality of compressors and coolers arranged in series, with an expansion

chamber in said flow channel downstream of the final compressor and cooler and with a recirculation channel arranged to return gaseous carbon dioxide from said expansion chamber into said flow channel upstream of said final compressor and cooler.

10. Apparatus as claimed in claim 9, wherein the expansion chamber is provided with a liquid removal port such that liquid carbon dioxide can be withdrawn.

* * * * *