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COMBINING PURE LIQUID AND VAPOR NITROGEN STREAMS FROM AIR SEPARATION FOR CRUDE HYDROGEN GAS WASHING

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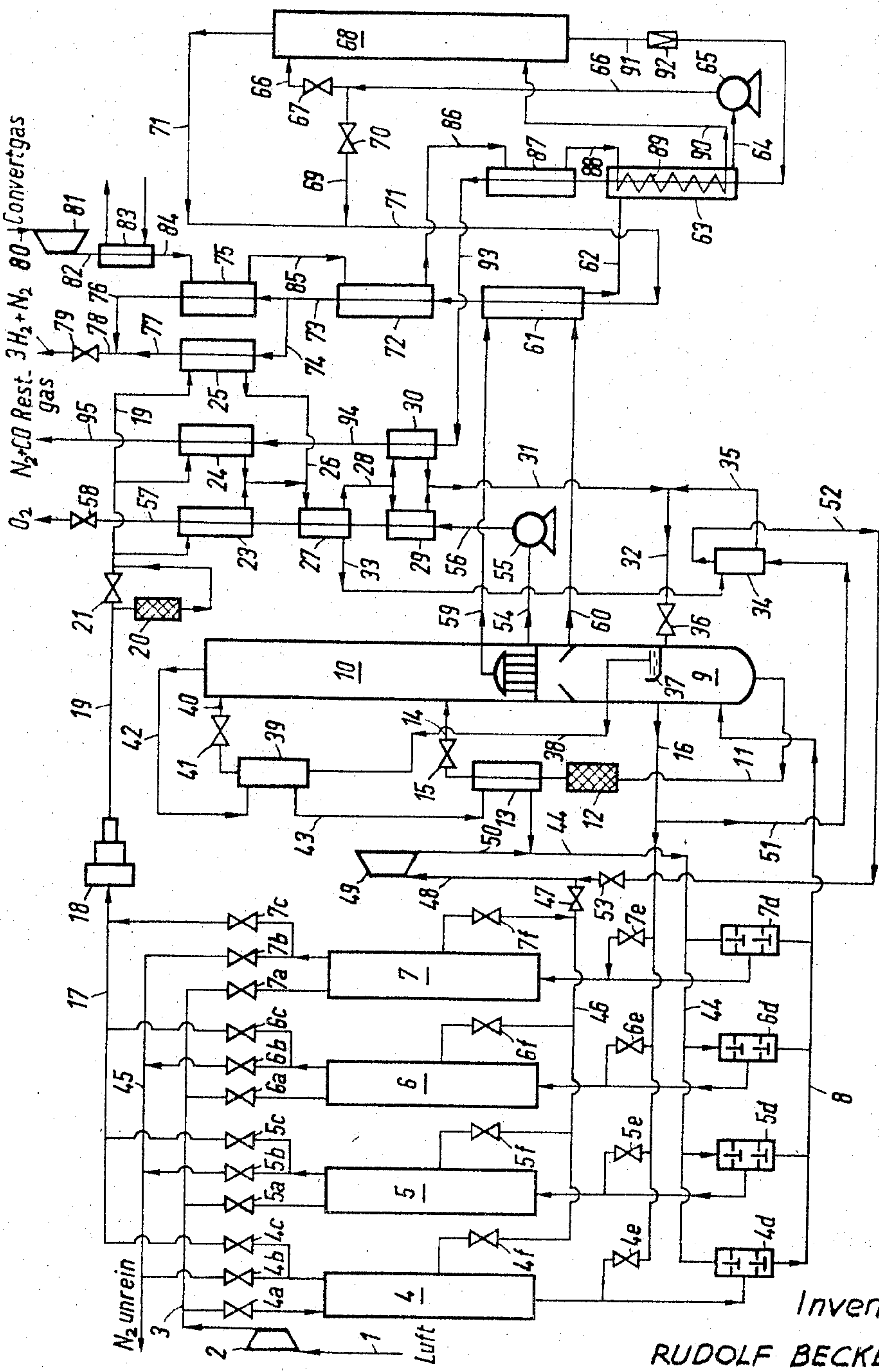

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COMBINING PURE LIQUID AND VAPOR NITROGEN STREAMS FROM AIR SEPARATION FOR CRUDE HYDROGEN GAS WASHING

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U.S. Cl. 62—13 21 Claims

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ABSTRACT OF THE DISCLOSURE

Air is separated in an air separation plant employing a double rectification column. An impure nitrogen stream from the high pressure column is recompressed and then cooled by vaporizing oxygen from the low pressure column as well as exiting ammonia synthesis gas and scrubber liquid streams from a crude hydrogen scrubber before returning to the high pressure column. Separate streams of pure nitrogen liquid and vapor are removed from the high pressure column which streams are combined and completely liquefied with part of the liquid nitrogen being used to wash a crude hydrogen gas while another part of the pure liquefied nitrogen is added to the washed hydrogen to form a gas stream for ammonia synthesis.

This is a continuation-in-part of copending U.S. patent application Ser. No. 373,418, filed June 8, 1964, now abandoned.

This invention relates to a process for air fractionation and is particularly concerned with the use of a highly compressed gas in cold circulation for pressure vaporization of liquid oxygen, and with the use of a group of periodically transposable regenerators for heat exchange between the air to be fractionated and the oxygen.

Besides the production of oxygen, the invention is also concerned with the separation of pure nitrogen, especially for the production of synthetic ammonia.

The invention is carried out in a very simple and economical manner by taking from the rectification column an impure fraction of circulating nitrogen, warming it to the temperature of the surroundings by passage through a regenerator which has been cleansed by scavenging with nitrogen during at least one preceding stage, liquefying the impure fraction by heat exchange after high compression and, preferably, after cleansing in an adsorber, and then, after passage through an expansion device, returning the impure nitrogen to the rectification column at a point near the place from which it was taken, whereby pure nitrogen is obtained from the head section of the column, preferably for independent use.

The impure nitrogen is preferably removed from the middle section of the pressure column and, after being at least partly liquefied, is returned to the same place.

For the production of the required additional cold, a portion of the impure nitrogen fraction that was taken from the middle section of the pressure column, after a preliminary warming, is expanded while doing work and is then used as a scavenging gas for the aforementioned scavenging step for the regenerators. The gas to be expanded can be taken, after sufficient prewarming, from a suitable place on the regenerator through which circulating nitrogen is passed, and/or if it bypasses this regenerator, is prewarmed by passage through a heat exchanger with circulating nitrogen before being returned to the pressure column.

Another feature of this invention is that the pure nitrogen is taken from the head of the pressure column.

If the pure nitrogen is to be used for the synthesis of ammonia, it is advantageous to take the pure nitrogen from the head of the column in a partly liquid and partly gaseous state, in preferred proportions of 1 part liquid to 6–20 parts gas, the most preferred proportion being 1 part liquid to 10 parts gas; and after complete liquefaction with further cooling under the same pressure if necessary, it is subjected to heat exchange with possibly expanded products of a synthetic ammonia plant, is then compressed to the pressure of the washing column of that plant, and is used as a washing fluid for hydrogen gas and as a component of the ammonia synthesis gas. In this manner the necessity of compressing the gaseous nitrogen to the normally higher pressure of the washing column of the synthetic ammonia plant is avoided, and the pump for compressing the liquefied nitrogen uses much less energy.

The process of this invention will now be described more in detail with reference to the schematic drawing illustrating the process and apparatus of the invention.

The air to be fractionated enters by conduit **1**, is passed through compressor **2** to compress it to about 6 atmospheres, and arrives by conduit **3** at regenerator **4**, which is one of the series of transposable regenerators **4** to **7**, through valve **4***a*, which is one of the series of valves **4***a* to **7***a* that control communication between conduit **3** and the regenerators. The deeply cooled air passes through a transposable valve or part of double check valve **4***d*, which is one of the series of such valves **4***d* to **7***d* for delivery through conduit **8** to the lower part of pressure column **9** which, in conjunction with the low pressure column **10**, forms a double rectifier tower arrangement.

The liquid in the sump of the pressure column, which is under a pressure of about 5.6 atm., is delivered from the bottom of the column by conduit **11** to adsorber **12**, thence to heat exchanger **13** from where it passes through conduit **14** and expansion valve **15** to the middle portion of the low pressure column **10** in which the pressure is about 1.4 atm.

From the middle portion of the pressure column **9** an impure nitrogen fraction is removed by conduit **16** and is passed through the transposable valve **7***e*, which is one of the series of valves **4***e* to **7***e*, for delivery to regenerator **7** of the series **4** to **7**. The greater portion of this fraction passes through transposable valve **7***c*, which is one of the series of valves **4***c* to **7***c*, and then through conduit **17** to the compressor **18** for compression to about 120 atm.

The compressed gas leaves the compressor via conduit **19**, and preferably passes through an adsorber **20** having a bypass valve **21**, to a group of heat exchangers **23**, **24** and **25** and from there passes through the collecting conduit **26** to heat exchanger **27**.

From heat exchanger **27**, the circulating nitrogen passes on the one side through conduit **28** and through heat exchangers **29** and **30** and through conduit **31** to the collecting conduit **32**, while on the other side it passes through conduit **33**, heat exchanger **34** and conduit **35** to the same collecting conduit **32**.

In the conduit **32** there is a throttle valve **36** through which the nitrogen, which is now at least partly liquefied, passes for return to the same portion of the pressure column **9**.

Above the place of entry of the conduit **32** in column **9** there is mounted a liquid-collecting basin **37** from which the conduit **38** leads to the outside, delivering liquid nitrogen through the heat exchanger **39**, conduit **40** and expansion valve **41** to the head of the low pressure column **10**.

From the head of the low pressure column **10** nitrogen is withdrawn through conduit **42** and through heat exchanger **39**, conduit **43**, heat exchanger **13** and conduit **44** and through the two valves *5d* and *6d* of the series *4d* to *7d*, and passes as scavenging gas through two transposable regenerators **5** and **6** of the series **4** to **7** in which it is warmed to the temperature of the surroundings. The scavenging gas then passes through the two valves *5b* and *6b* of the series *4b* to *7b* and makes its exit through conduit **45** as impure nitrogen gas.

The periodic reversal of the regenerators **4** to **7** is performed in such a manner that each regenerator in a first phase of operation is traversed in a downward direction by air to be cooled therein to a low temperature in preparation for its fractionation, in a second and third phase in an upward direction by scavenging gas which is to be warmed therein while effecting sublimation of the CO_2 and of ice formations, and in a fourth phase in an upward direction by circulating nitrogen that is to be warmed.

A portion of the circulating nitrogen fraction is advantageously diverted from the lower half of the corresponding regenerators through valve *7f* of the series of valves *4f* to *7f* and is delivered through conduit **46** having valve **47** therein and through conduit **48** to the expansion turbine **49**. The expanded gas then passes through conduit **50** to the collection conduit **44** for scavenging gas. Additionally, or alternatively, a portion of the impure nitrogen can be diverted from the circulation conduit **16** by way of conduit **51** for passage through heat exchanger **34** and conduit **52** having therein valve **53** and then through conduit **48** to the expansion turbine **49**. The regulation is determined by the temperature equilibrium which must be maintained during the process.

From the sump of the low pressure column **10** liquid oxygen is removed by conduit **54**, is compressed to about 41 atm. by pump **55**, and is delivered by conduit **56** to a series of heat exchangers **29**, **27** and **23** in which the liquid oxygen is brought to about the temperature of the surroundings for delivery under about 40 atm. by conduit **57** having therein valve **58** to its destination.

From the head of the pressure column **9** pure gaseous nitrogen is removed by conduit **59** while liquid nitrogen is removed by conduit **60** under a pressure of about 5.5 atm., both of these conduits delivering their nitrogen to the heat exchanger **61** in which most of the remaining gaseous nitrogen is liquefied. The largely liquefied nitrogen is then delivered by conduit **62** to heat exchanger **63** where it is further cooled and is delivered by conduit **64** to pump **65**. Pump **65** then delivers the liquid nitrogen through conduit **66** having therein valve **67** to the head of the washing column **68** under a pressure of about 25 atm.

A portion of the liquid nitrogen is diverted from conduit **66** by conduit **69** with valve **70** directly to conduit **71** which draws gas from the head of the washing column **68** to produce a stoichiometric mixture for ammonia synthesis. The conduit **71** then delivers the hydrogen-nitrogen mixture through heat exchangers **61** and **72**, conduits **73** and **74**, heat exchangers **75** and **25**, and then through conduits **76** and **77** to the collecting conduit **78** having therein valve **79** for delivery of the hydrogen-nitrogen mixture to an ammonia synthesis plant under a pressure of about 24 atm.

A hydrogen rich gas such as converter gas is delivered by conduit **80** to compressor **81**, and thence by conduit **82** and heat exchanger **83**, which can be water-cooled, and by conduit **84** to heat exchanger **75**, then through conduit **85** to heat exchanger **72**, and from there through conduit **86** to heat exchanger **87**. From heat exchanger **87** the gas is delivered by conduit **88** to the cooling coil **89** in heat exchanger **63** and from there by conduit **90** to the lower portion of the washing column **68**.

The liquid nitrogen with impurities consisting mainly of CO is taken from the sump of the washing column **68** by conduit **91** with expansion valve **92** therein for passage through heat exchangers **63** and **87**, conduit **93**, heat exchanger **30**, conduit **94**, heat exchanger **24**, and then to conduit **95** for delivery to the outside.

Referring to the drawing, the following table is illustrative of quantities found in the various conduits:

Conduit	Fluid description	Quantity
1	Air	Ca. 80,000 Nm.^{3}/h.
19	Impure N_2	Ca. 30,000 Nm.^{3}/h.
57	O_2	Ca. 12,500 Nm.^{3}/h.
82	Conversion gas	Ca. 35,000 Nm.^{3}/h.
78	$3H_2+N_2$	Ca. 42,000 Nm.^{3}/h.
59	N_2, gas	Ca. 10,000 Nm.^{3}/h.
60	N_2, liquid	Ca. 1,000 Nm.^{3}/h.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Consequently, such changes and modifications are properly, equitably, and intended to be, within the full range of equivalence of the following claims.

What is claimed is:

1. In a process of fractionating air and producing ammonia synthesis gas by washing raw hydrogen containing carbon monoxide with pure liquid nitrogen wherein said air is fractionated in a double column having a high pressure section and a low pressure section to produce said pure liquid nitrogen, the improvement which comprises withdrawing pure nitrogen fluid from the top zone of the high pressure section of the double column in two separate streams, one being substantially completely in the liquid phase, and the other being substantially completely in the vapor phase in proportions of 6–20 parts vapor to 1 part liquid, combining and completely liquefying said combined fluid streams by heat exchange with one or more streams from the ammonia synthesis gas production, said streams being (1) pure ammonia synthesis gas, (2) crude hydrogen, and (3) a mixture of nitrogen and carbon monoxide.

2. A process as defined by claim **1** wherein streams (1), (2), and (3) are heat exchanged with the pure nitrogen fluid.

3. In a process of fractionating air and producing ammonia synthesis gas by washing raw hydrogen containing carbon monoxide with pure liquid nitrogen wherein said air is fractionated in a double column having a high pressure section and a low pressure section to produce said pure liquid nitrogen, the improvement which comprises withdrawing pure nitrogen fluid from the top zone of the high pressure section of the double column in two separate streams, one being substantially completely in the liquid phase, and the other being substantially completely in the vapor phase in a proportion of 10 parts vapor to 1 part liquid, combining and completely liquefying said combined fluid streams by heat exchange with one or more streams from the ammonia synthesis gas production, said streams being (1) pure ammonia synthesis gas, (2) crude hydrogen, and (3) a mixture of nitrogen and carbon monoxide.

4. In a process of fractionating air and producing ammonia synthesis gas by washing raw hydrogen with liquid nitrogen wherein said air is fractionated in a double column having a high pressure section and a low pressure section, the improvement which comprises withdrawing impure nitrogen from the high pressure section, heating said impure nitrogen by indirectly transferring heat between said impure nitrogen and raw air, compressing resultant heated impure nitrogen, cooling resultant compressed impure nitrogen in indirect heat exchange with one or more streams from the ammonia synthesis gas production, said streams comprising (a) a mixture of nitrogen and carbon monoxide, and (b) pure ammonia synthesis gas; and recycling resultant cooled impure nitrogen to the double column.

5. A process as defined by claim **4** wherein said impure nitrogen is withdrawn from a middle section of said high pressure section.

6. A process as defined by claim **4** wherein said indirect heat exchange of compressed impure nitrogen is conducted with streams (a) and (b).

7. A process as defined by claim **4** wherein said indirect heat exchange of compressed impure nitrogen is conducted with streams (a) and (b).

8. A process as defined by claim **4**, further comprising withdrawing pure nitrogen fluid from the high pressure section of the double column, partly in the vapor and partly in the liquid state, and completely liquefying said fluid by heat exchange with one or more streams from the ammonia synthesis gas production, said streams being (1) pure ammonia synthesis gas, (2) crude hydrogen, and (3) a mixture of nitrogen and carbon monoxide.

9. A process as defined by claim **8** wherein streams (1), (2), and (3) are heat exchanged with the pure nitrogen fluid.

10. A method of fractionating air comprising: compressing air and passing the compressed air in one direction through a first regenerator means to the high pressure part of a double rectifying column near the bottom thereof, withdrawing liquid from the bottom of said high pressure column and delivering it to an intermediate point in the low pressure part of said double rectifying column, withdrawing nitrogen from the top of said low pressure column and passing said nitrogen through at least a second regenerator means to be scavenged in the direction opposite to said one direction, withdrawing impure nitrogen from a middle section of said high pressure column at a point wherein said impure nitrogen is not of sufficient purity for ammonia synthesis, and passing the impure nitrogen through a further regenerator means in the direction opposite to said one direction, compressing at least a part of the impure nitrogen after passing the same through said further regenerator means, drawing liquid oxygen from the bottom of said low pressure column compressing said liquid oxygen and exchanging heat between the evaporating compressed oxygen and the compressed impure nitrogen, the latter being thereby at least partly liquefied, and returning the at least partly liquefied impure nitrogen to said high pressure column near the point of withdrawal of the impure nitrogen from the column, and withdrawing pure gaseous nitrogen from the top of a condenser-reboiler in the high pressure column, the purity of said pure gaseous nitrogen being sufficient for ammonia synthesis gas.

11. A process as defined by claim **10**, further comprising withdrawing liquid nitrogen of sufficient purity for ammonia synthesis from the top zone of the high pressure column, said withdrawing being at a point above the point for said withdrawing of impure nitrogen.

12. A method as defined by claim **10** further comprising the steps of withdrawing pure condensed liquid nitrogen from the top zone of the high pressure column, and combining said liquid with said pure gaseous nitrogen for flow to ammonia synthesis.

13. A process as defined by claim **12**, wherein both said pure gaseous nitrogen and said pure condensed liquid are of sufficient purity for ammonia synthesis gas, the point of withdrawing said pure condensed liquid being above the point of withdrawing said impure nitrogen, said pure gaseous fraction and said pure liquid fraction being passed to the ammonia synthesis plant without any further rectification.

14. A method of fractionating air comprising: compressing air and passing the compressed air in one direction through a first regenerator means to the high pressure part of a double rectifying column near the bottom thereof, withdrawing liquid from the bottom of said high pressure column and delivering it to an intermediate point in the low pressure part of said double rectifying column, withdrawing nitrogen from the top of said low pressure column and passing said nitrogen through at least a second regenerator means to be scavenged in the direction opposite to said one direction, withdrawing impure nitrogen from a middle section of said high pressure column and passing the impure nitrogen through a further regenerator means in the direction opposite to said one direction, compressing at least a part of the impure nitrogen after passing the same through said further regenerator means, drawing liquid from the bottom of said low pressure column, compressing said liquid oxygen and exchanging heat between evaporating compressed oxygen and the compressed impure nitrogen thereby at least partly liquefied, and returning the impure nitrogen to said high pressure column near the point of withdrawal of the impure nitrogen from the column, withdrawing pure nitrogen from the head of said high pressure column partly as a liquid and partly as a gas, completely liquefying the withdrawn pure nitrogen by heat exchange with one or more streams from an ammonia synthesis gas plant, said streams being (1) pure pure ammonia synthesis gas, (2) crude hydrogen, and (3) a mixture of nitrogen and carbon monoxide. pumping the resultant liquefied nitrogen to an increased pressure, washing said hydrogen gas with a part of the nitrogen, and adding another part of the nitrogen to the washed gaseous hydrogen to produce ammonia synthesis gas.

15. A process as defined by claim **14**, further comprising exchanging heat between said compressed impure nitrogen and one or more streams from a plant for producing ammonia synthesis gas by scrubbing crude hydrogen with liquid nitrogen, said streams comprising (a) a mixture of nitrogen and carbon monoxide, and (b) pure ammonia synthesis gas.

16. A process as defined by claim **15** wherein both streams (a) and (b) are heat exchanged with said compressed impure nitrogen.

17. A process as defined by claim **16** wherein streams (1), (2), and (3) are heat exchanged with pure nitrogen.

18. A process as defined by claim **14** wherein streams (1), (2), and (3) are heat exchanged with pure nitrogen.

19. A method of fractionating air comprising: compressing air and passing the compressed air in one direction through a first regenerator means to the high pressure part of a double rectifying column near the bottom thereof, withdrawing liquid from the bottom of said high pressure column and delivering it to an intermediate point in the low pressure part of said double rectifying column, withdrawing nitrogen from the top of said low pressure column and passing said nitrogen through at least a second regenerator means to be scavenged in the direction opposite to said one direction, withdrawing impure nitrogen from a middle section of said high pressure column and passing the impure nitrogen through a further regenerator means in the direction opposite to said one direction, compressing at least a part of the impure nitrogen after passing the same through said further regenerator means, exchanging heat between said compressed impure nitrogen and one or more streams from a plant for producing ammonia synthesis gas by scrubbing crude hydrogen with liquid nitrogen, said streams comprising (a) a mixture of nitrogen and carbon monoxide, and (b) pure ammonia synthesis gas, drawing liquid oxygen from the bottom of said low pressure column compressing said liquid oxygen and exchanging heat between the evaporating compressed oxygen and said compressed impure nitrogen thereby at least partly liquefied, and returning the latter impure nitrogen to said high pressure column near the point of withdrawal of the impure nitrogen from the column, withdrawing pure nitrogen from the top zone of the high pressure column for separate use.

20. A process as defined by claim **19** wherein both streams (a) and (b) are heat exchanged with said compressed impure nitrogen.

21. The combination, in an apparatus for fractionating air; first regenerator means, means to compress air and pass it through said first regenerator means to chill the air, a double rectification column with a high pressure and a low pressure portion connected near the bottom of the high pressure portion to said first regenerator means to receive the chilled air therefrom, at least a second regenerator means, means for withdrawing nitrogen from the head of said low pressure column and for passing said nitrogen through said at least second regenerator means to scavenge said regenerator means, means for withdrawing impure nitrogen from a middle section of said high pressure rectifying column and for passing said impure nitrogen through a further regenerator means to be warmed, means for compressing the warmed impure nitrogen employed for cooling the further regenerator means, means for at least partly liquefying the compressed nitrogen, and means including a throttle valve for returning the at least partly liquefied nitrogen to said column near the point thereof from which it was withdrawn from the column, conduit means leading from the head of the high pressure portion of said column for drawing pure nitrogen therefrom, said conduit means comprising two separate pipes, one for withdrawing liquid-phase pure nitrogen, and the other for withdrawing vapor-phase pure nitrogen, heat exchanger means to which said conduit means lead operable for effecting complete liquefication of said nitrogen, pump means connected to the heat exchanger means to raise the pressure of said nitrogen, a washing column, means for supplying hydrogen to be washed to said washing column, means for supplying a part of the liquid nitrogen from said pump to said washing column to wash said hydrogen, and means for combining washed hydrogen from the washing column with nitrogen from said pump to form an intermediate product for ammonia synthesis.

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