

Aug. 13, 1957

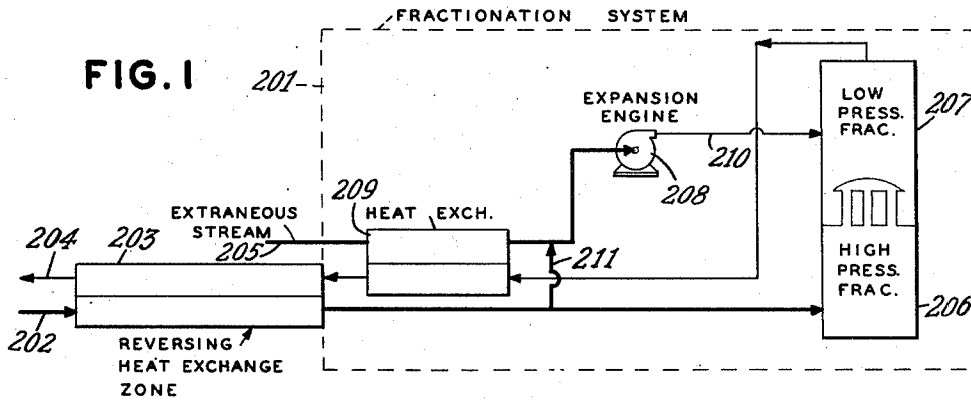
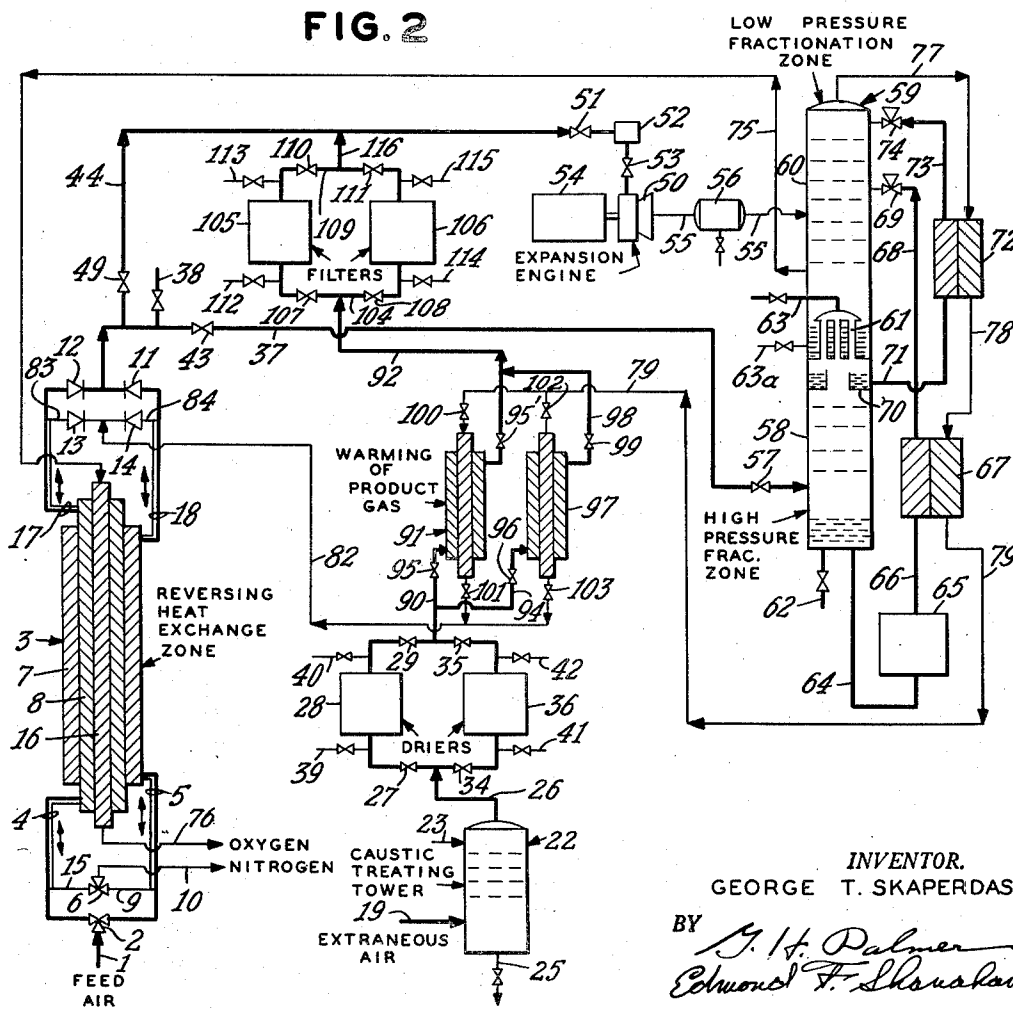
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2,802,349

REMOVING IMPURITIES FROM A GAS LIQUEFACTION SYSTEM
WITH AID OF EXTRANEEOUS GAS STREAM

Filed Aug. 25, 1951

2 Sheets-Sheet 1



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FIG. 3

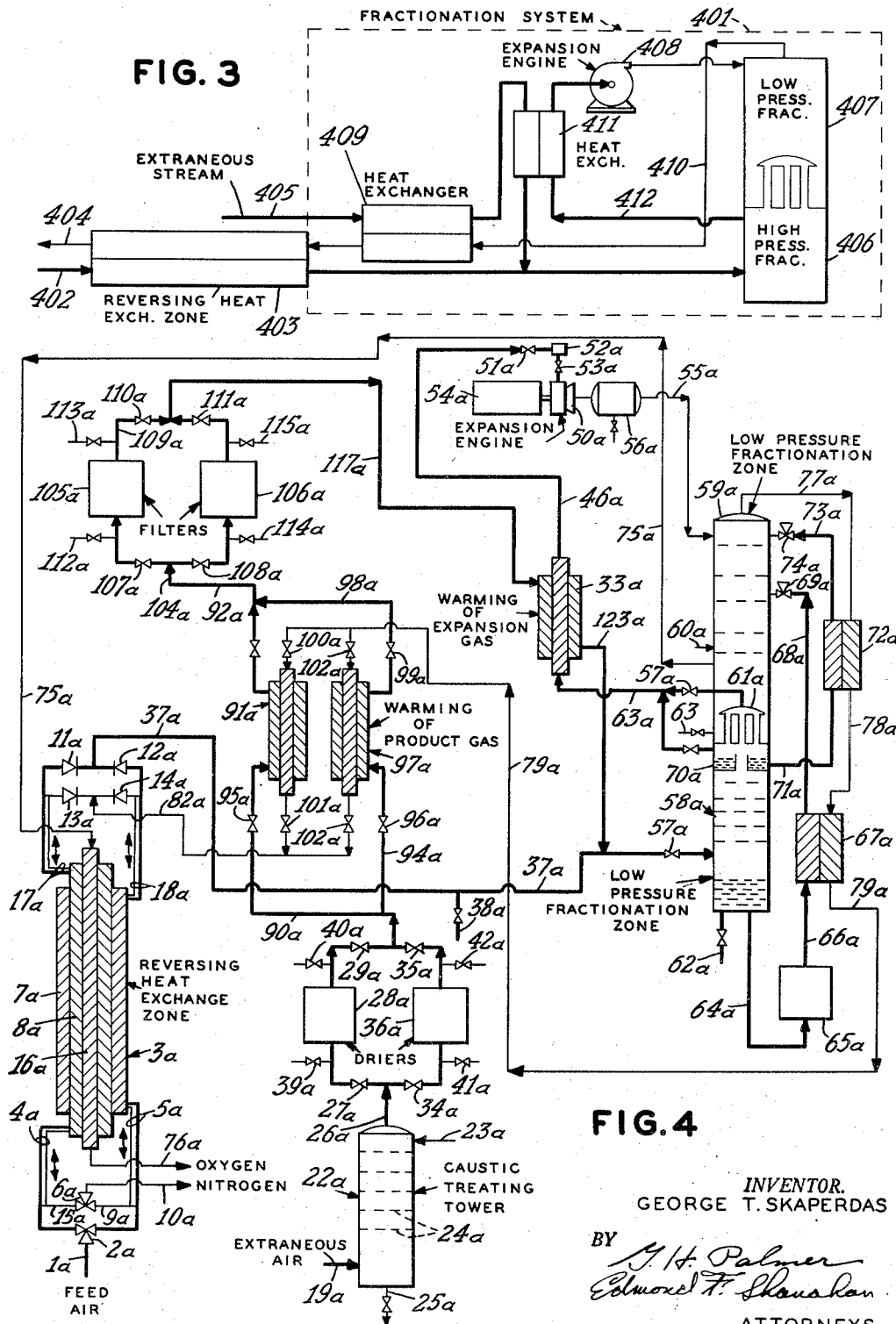


FIG. 4

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REMOVING IMPURITIES FROM A GAS LIQUEFACTION SYSTEM WITH AID OF EXTRANEEOUS GAS STREAM

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5 Claims. (Cl. 62—175.5)

This application is a continuation-in-part of my co-pending applications Serial No. 734,445, abandoned August 22, 1952 filed March 13, 1947, and Serial No. 693,799, filed August 29, 1946, abandoned April 16, 1953.

The present invention relates generally to processes for fractionating a compressed gaseous mixture in a low-temperature expansion and fractionating system, wherein an inflowing charge stream of said compressed gaseous mixture enters an expansion and fractionating system at a pre-expansion pressure from a reversing heat exchange zone in which said inflowing stream is cooled, and in a cold part of which high-boiling impurities are precipitated, and wherein an outflowing product stream leaves said system at a post-expansion pressure through said reversing heat exchange zone, absorbing heat and scavenging said precipitated high-boiling impurities by revaporization, said inflowing and outflowing streams being flowed countercurrently and alternately with each other through periodically reversing paths in an indirect heat exchange relation in said reversing heat exchange zone. More particularly, the invention relates to a method for preventing an excessive accumulation of a precipitated impurity in said cold part of the paths of said reversing heat exchange zone during several cycles of operation by introducing into said expansion and fractionating system an extraneous stream of relatively warm gas which enters said fractionating system under pre-expansion pressure without passing through said reversing heat exchange zone, but which after it leaves said fractionating system, does pass through said reversing heat exchange zone, thus increasing the scavenging capacity of said outflowing product stream. It is necessary that the mass flow rate of the extraneous stream be great enough so that the total of the mass flow rates of cold stream or streams outflowing through the reversing heat exchange zone exceed the mass flow rate of inflowing compressed gaseous mixture. Furthermore, the outflowing product stream is slightly warmed by indirect heat exchange with the extraneous stream, in order to avoid lowering the temperature of the reversing heat exchange zone to such a point that some of the inflowing compressed gaseous mixture might condense to liquid within the reversing heat exchange zone itself; such condensation is undesirable in systems not designed especially for it.

Subsequently, the extraneous stream is introduced into the fractionating system at a point under pre-expansion pressure, preferably into the inlet of an expansion engine. It is customary to expand at least a part of the gas flowing within a fractionating system under pre-expansion pressure to post-expansion pressure in an expansion engine; it is important that the gas introduced into the expansion engine be at a temperature sufficiently high so that no part of it will condense into liquid droplets in the expansion engine. Condensation within the expansion engine greatly reduces its efficiency of operation.

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The extraneous stream is warm relative to other streams within the fractionating system at pre-expansion pressure. Ordinarily, it is then mixed with a colder stream at pre-expansion pressure to produce a stream at a temperature suitable for expansion in the expansion engine. However, in rare cases probably with gas mixtures other than air, the extraneous stream may comprise all the gas expanded in the expansion engine.

The extraneous stream is ordinarily of the same composition as the inflowing stream of compressed gaseous mixture. However, if other gases of suitable physical properties are available, they may be used. Moreover, the extraneous stream may be introduced into the fractionating system at almost any point from which all or part of said stream can find its way out through the reversing heat exchange zone, thus increasing the mass flow rate of the outflowing cold product stream. It will be understood that applicant's invention is concerned with the mass flow rate and temperature of the outflowing cold product stream. It is of no importance, so far as applicant's invention is concerned, whether the "product" content of the outflowing stream is actually increased or not, as long as the total mass flow rate of the stream designated as the "outflowing cold product stream" is increased. For example, if the outflowing stream is nitrogen fractionation product applicant will refer to the "outflowing cold product stream" as being increased by the addition of the extraneous stream even if the extraneous stream contains no nitrogen at all. The term "cold product stream" as used herein, is used to designate a particular stream and not to limit the applicant as to chemical composition since that is quite irrelevant to his process as long as the physical properties of a satisfactory scavenging gas for the system are present.

Gaseous mixtures containing high-boiling impurities, for example air containing water vapor and carbon dioxide, have been separated in expansion and fractionating systems at low temperatures by compressing inflowing feed mixture and supplying it to the system through a reversing countercurrent heat exchange zone to precool the mixture by heat exchange with outflowing cold product under lower pressure. A gaseous stream is obtained from a point within the system, for example, by being separated from the precooled mixture subsequent to the heat exchange zone or from a product of a preliminary separation of the mixture in its compressed condition, and expanded with performance of external work to produce refrigeration to obtain the low temperatures required for liquefaction and fractionation. The expanded stream and at least one other stream from the preliminary separation are introduced into a low pressure zone of fractionation and subjected to fractionation under relatively moderate superatmospheric pressure conditions to produce the desired products of separation. At least one of the separated products of the low pressure fractionation is employed as the outflowing cold product to precool inflowing compressed feed gas in the reversing heat exchange zone. During the precooling of the feed gas, the high-boiling impurities precipitate and are deposited in the reversing paths of the heat exchange zone. The precipitate is re-evaporated and scavenged from the heat exchange zone by the stream of outflowing cold product which is precooling the compressed feed gas in the reversing paths. Inasmuch as precipitation of high-boiling impurity occurs after the inflowing compressed mixture has passed beyond the warm end of the heat exchange zone, any portion of the zone in which alternate precipitation and evaporation takes place is conveniently desig-

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nated as a "cold part," or "colder portion." Continued complete removal of the deposits by the evaporating and scavenging of the cold product in a reversing path will be effected only when there is a proper relationship between the rates of mass flow, the temperatures and the pressures of the precipitating and the evaporating gases. A variation of anyone of the factors necessarily must be compensated for by a suitable change in another of the factors to readjust the relationship to a proper one which provides for complete removal of deposited precipitate in that period. For instance, continued operation of a reversing heat exchange zone without plugging of its reversing passageways requires, for any particular pressure difference between the heat exchanging streams in the reversing paths, control of the differences between the temperatures of the gas precipitating and the gas evaporating a high-boiling impurity in the cold portion to keep these differences below a critical "maximum allowable difference" effective for evaporating the deposited impurity. One method by which such temperature control can be effected is by adjusting the relationship of rates of mass flow of the gases through the reversing paths of the heat exchange zone.

It is an object of the invention to supply an inflowing charge stream of a compressed gaseous mixture to an expansion and fractionating system through a reversing countercurrent heat exchange zone and to cool the inflowing stream in a cold part of the zone to a subatmospheric temperature sufficiently low to substantially completely precipitate a high-boiling impurity therefrom without liquefaction of the predominant components.

It is a further object of the invention to prevent excessive accumulation of a precipitated impurity from the feed gas in a cold part of the reversing paths of the heat exchange zone by introducing into the expansion and fractionating system an extraneous stream of relatively warm gas which enters the system under pre-expansion pressure without passing through the reversing heat exchange zone but which increases the mass of the stream or streams outflowing through the reversing exchange zone, so that their mass flow rate exceeds that of the inflowing stream, and so that the difference in temperature between the counterflowing streams is small enough to make possible effective scavenging by an outflowing scavenging stream of lower pressure.

It is a further object of the invention to warm an outflowing cooling and scavenging product stream from an expansion and fractionating system with heat of a relatively warm extraneous stream to avoid lowering the minimum temperature level in a reversing heat exchange zone where through said cooling and scavenging stream flows to a degree that some of an inflowing compressed gaseous mixture is condensed to liquid within the reversing heat exchange zone.

It is still a further object to employ heat of an extraneous relatively warm stream to warm an expansion feed gas under pre-expansion pressure to a temperature sufficiently high that no part of the expansion gas condenses into liquid droplets when expanded to a post-expansion pressure with the production of external work.

Other objects will be apparent from the following more detailed description of the invention.

The invention, with reference to air is illustrative of a gaseous mixture, involves cooling a compressed stream of air supplied to an expansion and fractionating system at a pre-expansion pressure to a relatively low subatmospheric temperature which is below a minimum temperature for effecting vapor phase expansion of the air in a work engine. The air is cooled in a reversing heat exchange zone, by passing through paths therein for alternate periods, to a subatmospheric temperature which is sufficiently low to effect substantially complete precipitation and deposition of a high-boiling component of the air, such as water vapor and/or carbon dioxide. A cooling and scavenging gaseous stream, for example, a

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nitrogen-rich stream, is obtained from the system under a post-expansion pressure and passed alternately through paths of the reversing heat exchange zone previously traversed by compressed air to cool the air by indirect heat exchange and to scavenge precipitated deposits from the paths. An extraneous stream of gaseous material, for example, air under a pre-expansion pressure and at a relatively warm temperature, such as atmospheric, is utilized in such manner as to augment the quantity of the cooling and scavenging stream. The extraneous stream is chemically purified and dehydrated and cooled. In effecting the cooling, the heat content of the extraneous stream in part is transferred to the cooling and scavenging stream before this latter stream is passed to the reversing heat exchange zone to warm it to a temperature sufficient to avoid condensation of inflowing compressed air in the reversing heat exchange zone. That part of the heat content of the extraneous stream which is not transferred to the outflowing cooling and scavenging stream is utilized to adjust temperature of the expansion gas under pre-expansion pressure to a temperature sufficiently high so that no part of that gas will condense into liquid droplets when its pressure is reduced to a post-expansion pressure with production of external work. The extraneous stream may effect this latter heat transfer either directly by having the stream comprise a part (or in an exceptional case, all) of the expansion gas or indirectly by a heat exchange relationship with expansion gas. In the first event the extraneous stream is introduced into the system through an expansion engine; in the second event it is introduced after indirect heat exchange with expansion gas into a high pressure stream in the fractionating system, such as a stream passing to the fractionation zone.

Introduction of the extraneous stream into the expansion and fractionating system without passing through the reversing heat exchange zone increases the amount of total product and thus modifies the rate of mass flow relationship between the inflowing compressed air and outflowing cold product in the reversing heat exchange zone. By controlling the mass quantity of the extraneous stream introduced, the rate of mass flow relationship is controlled, and the difference between the temperatures of the counterflowing streams of compressed air and cooling and scavenging product in the cold portion of the reversing heat exchange zone can be made less than the maximum allowable temperature difference to any desired degree.

In accomplishing such control of temperature difference it is to be understood that it is necessary to have the sum of the rates of mass flow of total cold gaseous products passing through the reversing heat exchange zone exceed the rate of mass flow of compressed air. If one of the products of fractionation should be recovered as a liquid or without exchanging heat with the compressed air in the reversing heat exchange zone, then more extraneous stream will be required than is necessary when all products of separation exchange heat with the compressed air. When such conditions are provided, carbon dioxide precipitated in a period between successive alternations of flow in the cold portion of the reversing heat exchange zone is substantially completely evaporated during the following period.

In the following detailed description of the invention, reference will be made to atmospheric air as illustrative of a gaseous mixture in the separation of which the present invention is applicable. It is to be understood, however, that the invention is applicable to the separation of other gaseous mixtures containing an undesirable high-boiling component as, for example, a mixture of low molecular weight hydrocarbons, or a raw hydrogen gas containing carbon monoxide and other impurities. Further explanation of the present invention will be made with reference to the accompanying figures of the drawing. It is to be understood that reference to the figures

is by way of example only and is not restricted to the physical limitations of the apparatus illustrated therein.

Two embodiments of applicant's invention are shown in the accompanying figures, in which:

Fig. 1 is a simple diagrammatic representation of a fractionation system in which a compressed extraneous stream is introduced to warm outflowing product by indirect heat exchange and is then passed through an expansion engine;

Fig. 2 is a flow diagram showing a system like that of Fig. 1, but in much greater detail;

Fig. 3 is a simple diagrammatic representation of an embodiment in applicant's invention in which the compressed extraneous stream is used to warm the outflowing product stream by indirect heat exchange and is then combined with cold inflowing compressed gaseous mixture; and

Fig. 4 is a flow diagram of a system like that of Fig. 3 but in much greater detail.

Figs. 1 and 3 have been simplified for purposes of explanation by the elimination of all details well-known to those familiar with the art of separating gaseous mixtures. For example, all the paraphernalia for reversing stream flows, preliminary purification of the extraneous stream, auxiliary heat exchange of various streams within the fractionating system, etc., are deliberately omitted from the simple representations of Figs. 1 and 3 in order to make it easier to understand. Also, no control or expansion valves are shown in these two figures.

In all the figures, streams flowing under relatively high pressure are shown as heavy lines, and streams flowing under relatively low pressure are shown as light lines.

In Fig. 1 the entire low-temperature fractionating system is represented by the dashed line rectangle indicated by the numeral 201. An inflowing charge stream 202 enters the fractionating system 201 by way of a reversing heat exchange zone 203, which is cooled and scavenged by an outflowing product stream 204, under substantially lower pressure. The fractionating system 201 also receives an extraneous stream of gas 205, ordinarily very small in quantity in relation to the main inflowing stream 202. Of course, there will be various outflowing streams of liquid and gaseous products in addition to the main outflowing stream 204, but these are not shown since they may be withdrawn in a variety of ways well-known to those skilled in the art, as shown in the typical examples of Figs. 2 and 4.

Within the fractionating system 201 the inflowing compressed gaseous mixture 202 is partially condensed to a liquid. At least part of the mixture must be condensed to a liquid at input pressure but in almost all cases part must remain vaporous and be expanded to a lower pressure; in systems of this type the condensing input vapors must transfer heat by indirect heat exchange to low pressure liquid to boil the latter and effect fractionation. For convenience, the pressures within fractionating system 201 or in reversing heat exchange zone 203 can be referred to as either pre-expansion or post-expansion pressures. The pre-expansion pressures are ordinarily about 90 pounds per square inch gage and the post-expansion pressures less than 15 pounds per square inch gage. The pre-expansion pressures will be in a range of a few pounds required for pressure drop from a point at which the inflowing stream enters to a point at which it is expanded to a post-expansion pressure. Post-expansion pressures will vary within a very small range required to overcome the pressure drop of fluids flowing in the system subsequent to expansion. When it is stated that the extraneous stream is introduced at a "pre-expansion pressure" it is meant that the extraneous stream is introduced at a pressure sufficient to cause it to enter a high-pressure part of the fractionating system and flow in the desired direction. The pre-expansion pressures are never more than a few atmospheres,

since the system to which applicant's method applies does not rely on the Joule-Thompson effect on the charge gas for obtaining refrigeration. This effect can be relied upon for substantial cooling if charge gas is introduced at pressures of 1000 pounds or more per square inch; but at pressures less than two hundred or three hundred pounds per square inch no significant refrigeration is obtained. Because of the advantages of operating in the lower pressure ranges, however, applicant's system deals entirely with processes involving pressures not more than two hundred or three hundred pounds per square inch. Of course, applicant's invention may be applied to systems of the cascade type in which auxiliary refrigerants assist in cooling the system, with or without Joule-Thompson effect in the auxiliary refrigerants. When applicant introduces his extraneous stream at pre-expansion pressure, he means a pressure about the same as the pressure of his compressed gaseous mixture, i. e., less than 300 pounds per square inch, and only about 90 pounds per square in a typical design.

In most systems for fractionating gaseous mixtures, a vertically extended fractionating tower, separated into a lower high-pressure fractionation zone 206 and an upper low-pressure fractionation zone 207 is employed. There is usually heat exchange between the two zones 206 and 207. Each is provided with a series of fractionation trays, and there is a countercurrent contacting of upflowing gases and downflowing liquids, with various sidestreams and product streams entering or leaving each of the fractionation zones.

The expansion of inflowing compressed gaseous mixture, the compressed extraneous stream, or other streams in a system under pre-expansion pressure, to post-expansion pressure, usually takes place mostly through expansion valves. But it is preferred by applicant, as it is generally in the design of systems of separating gaseous mixtures, to expand at least part of the gas in an expansion engine, an expansion engine being any device by means of which the expansion of the gas produces work, thus effecting marked cooling of the gas. An expansion engine 208 is shown in fractionating system 201. Extraneous stream 205 is passed through expansion engine 208, after being cooled by indirect heat exchange with outflowing cold product 204 in heat exchanger 209, and being blended with a portion of the inflowing compressed gaseous mixture through line 211. In some rare cases, blending of these two streams may not be necessary. The expanded stream leaving engine 208, now much colder, is introduced into low-pressure fractionation zone 207. It is the outstanding feature of applicant's invention that the compressed extraneous stream 205 warms the outflowing stream 204 in heat exchanger 209 sufficiently to avoid excessively low temperatures within reversing heat exchange zone 203, and thus to avoid the condensation of any part of inflowing compressed gaseous mixture 202 within said zone.

It is a second important feature of the embodiment of Fig. 1 that the extraneous stream is cooled in exchanger 209 so that the resulting blended stream entering engine 208 is at temperatures near the temperatures prevailing throughout fractionation system 201, but not so low as to condense droplets within expansion engine 208 as a result of expansion therein.

The term "fractionating system" is not limited to the high or low pressure fractionation zones, the heat exchangers other than the reversing heat exchange zone, the expansion engine, or other equipment; the term is all inclusive for the entire system except the reversing heat exchange zone itself, and includes all the streams flowing to and from the cold end of reversing heat exchange zone 203, but the term does not include the extraneous stream prior to cooling or mixing, or any liquid product streams withdrawn from the system without traversing the reversing heat exchange zone 203. Fig. 1 does not show any non-reversing product stream oxy-

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gen, for example, outflowing through the reversing heat exchange zone, but these are frequently present and they are included in the fractionating system up to the point at which they begin heat exchange with the reversing streams and are thereafter part of "the outflowing products."

The fractionation system is not limited to those which have both high and low pressure fractionating zones. It includes systems which have only one fractionating zone, which have no bubble trays or rectification, and systems in which the object is primarily liquefaction, and the product stream differs only slightly in composition from the inflowing compressed gaseous mixture.

Fig. 2 of the drawing is a diagrammatical representation of a process flow arrangement for the liquefaction and fractionation of air under relatively moderate super-atmospheric pressure. This figure illustrates a specific application of the embodiment of the invention shown in the simplified Fig. 1, wherein an extraneous stream of air under a pre-expansion pressure is chemically purified, dehydrated, utilized to warm a product gas and thereafter is introduced into a fractionation zone through an expansion engine. The extraneous air is commingled at a desired temperature with sufficient process air for expansion to produce an average temperature of the commingled gases above the maximum inlet temperature at which condensation can occur within the pressure reduction range to which the commingled gases are subjected when expanded with the production of external work.

Referring to Fig. 2, a stream of atmospheric air for separation in the process is introduced under a relatively moderate pre-expansion pressure and at a relatively warm temperature through line 1. The pre-expansion pressures for the expansion and fractionation system of the present invention are not more than a few atmospheres; within the ranges described heretofore. For the purpose of the present description, the feed air may be considered compressed to a pressure in the order of magnitude of about 100 pounds per square inch absolute and "after cooled" to a temperature relatively near atmospheric, for example, about 90° F., before it is introduced into line 1. Before compression of the atmospheric feed air, or at least before the stream of air is drawn in line 1, it is desirable to treat the air to remove impurities such as dust or entrained oil. As a further purifying treatment it may be desirable to chemically eliminate acetylene impurity which is usually associated with atmospheric air. Such chemical treatment may be accomplished in any desired manner. The treatment may be carried out conveniently by subjecting the feed air directly after compression but before cooling to atmospheric temperature to the catalytic action of a suitable catalyst, for example, a catalyst containing a mixture of copper and magnesium oxide.

A reversing heat exchange zone which is shown in Fig. 2 as being a heat exchanger 3 but which may, if desired, be a regenerator type of heat exchange, provides for precooling the compressed feed air by countercurrent heat exchange with outflowing cold product of the process. The reversing heat exchange zone serves also as a zone of purification since high-boiling impurities, for example, water, vapor and carbon dioxide, are precipitated from compressed air stream at the low subatmospheric temperatures to which air is precooling in the reversing heat exchanger.

Heat exchanger 3 is a multi-stream arrangement for effecting heat exchange between inflowing feed air under pre-expansion pressure and outflowing cold product under post-expansion pressure. In Fig. 2, heat exchanger 3 is shown as comprising three passageways for carrying air and oxygen-rich and nitrogen-rich products. It is understood, however, that a plurality of such passageways may be incorporated into the heat exchange zone if it is expedient to do so for handling large quantities. Also, the oxygen passageway may be omitted in the event that

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oxygen is recovered directly from the fractionation zone. Two of the passageways, identified by the numerals 7 and 8, are similar in flow resistance and are "reversing" passageways that alternately carry the inflowing air and the outflowing nitrogen-rich product. Each passageway is constructed to be thermally connected with all the others throughout the effective length of the exchanger.

Exchanger 3 is illustrated in Fig. 2 to diagrammatically represent a sectional elevation of a multi-annular vessel surrounding a central tubular passageway. This particular construction of the exchanger is not essential to its performance and other forms of construction may be suitably used. It is preferable to pack the passageways with a suitable metallic material to form extended heat transfer surfaces. The metallic material conveniently may consist of a coil of edge wound metallic ribbon, metal pins, longitudinally placed strips of metal or the like. Since it is important to provide for an efficient path of thermal flow between all the passageways, the metal packing material preferably is joined to the walls of the passageways with a suitable metal-to-metal bonding material, for example, solder and when necessary likewise the bonding material is employed to bond passageways together.

The compressed feed air is passed alternately through passageways 7 and 8 for relatively short periodic intervals, for example, of about 2 to 5 minutes' duration. To direct the flow of air through the passageways in this manner line 1 is connected through a reversing valve 2 and lines 4 and 5 to passageways 7 and 8, respectively. Valve 2 has a single inlet opening to the flow of the incoming air in line 1 and two outlet openings, one leading into line 4 and the other into line 5. The valve is constructed to direct inflowing air into either one of the connecting lines. Preferably, valve 2 is operated periodically by an automatic timing device not shown in the figure so that the valve settings are automatically timed and changed to divert the feed air alternately into line 4 or line 5 at predetermined intervals. Backward-returning nitrogen-rich product also passes alternately through passageways 7 and 8, flowing in one of the passageways at the time compressed air passes through the other. Lines 9 and 15 connect lines 5 and 4 to a reversing valve 6 to permit outflowing nitrogen-rich product to pass alternately from passageways 7 and 8 through lines 5 and 4 and empty into a product removal line 10.

The cold end of passageway 7 connects with line 18 which in turn connects through check valves 11 and 14 with lines 37 and 82 respectively. Similarly, the cold end of passageway 8 connects with line 17 which in turn connects through check valves 12 and 13 with lines 37 and 82, respectively. Line 82 is the source of the nitrogen-rich product stream which flows to reversing heat exchanger 3 from the fractionating system in a manner to be described. Line 37 is provided to transmit to the fractionating system the cold compressed feed air emerging from the cold end of the reversing heat exchanger 3. Check valves 13 and 14 are arranged to be held closed by air pressure from line 18 or line 17, while check valves 11 and 12 are arranged to be held open by such pressures. The nitrogen pressure from line 82 opens whichever of valves 13 and 14 is not subjected to air pressure.

The cold compressed air from heat exchanger 3 flows into line 37 in the manner described. A line 44 connects line 37 with expansion engine 50. Normally, the air is distributed between lines 37 and 44 in proportions which depend upon the capacity of the plant and operating conditions. As for example, for a plant of moderate capacity about 80 weight percent of the air is taken through line 37, having a valve 57 positioned therein into a high pressure fractionation zone 58 of fractionator 59. In this fractionation zone the air is subjected to a preliminary fractionation under a pressure of the order of

86 p. s. i. a. to remove a part of its nitrogen content and thereby produce an oxygen-enriched liquid air. The liquid air fractionation product contains approximately 40% oxygen.

The process is arranged to pass vaporous nitrogen into a calandria 61 located at the top of zone 58. This calandria protrudes into the bottom of a low pressure fractionation zone 60 and is arranged to be submerged in a pool of liquid oxygen-rich product at the bottom of the interior of the low pressure fractionation zone. Nitrogen vapors pass to the interior of condensing tubes in calandria 61. These vapors are a little warmer than the liquid oxygen in the pool so that their heat exchange with the liquid oxygen reboils the latter as required by the fractionation treatment in the low pressure fractionation zone and cools the nitrogen vapors, for example, to about -285°F. , whereby condensation of the nitrogen is substantially completed in calandria 61.

Liquefied oxygen-enriched air is withdrawn continuously from the bottom of the high pressure fractionation zone 58 through line 64. A drain line 62 is provided to permit separate draining of liquid air from the bottom of zone 58. A vent line 63 is also provided to permit removal of uncondensed vapors from the top of calandria 61. Line 64 connects fractionating zone 58 with a filter 65. In filter 65, the liquefied air passes through a body of granular filtering material to remove any solid particles such as carbon dioxide, or hydrocarbons such as acetylene which may be present in the liquefied air. Filtered air passes from filter 65 through a line 66 to a subcooler 67 in which the liquefied air is further cooled by heat exchange with cold nitrogen-rich product obtained from the top of fractionator 59 to about -285°F. The further cooled liquid air flows from subcooler 67 through a line 68 which connects with the upper portion of fractionator 59 through a pressure reduction valve 69. The air is expanded on passing through valve 69 to a pressure of the order of about 24.7 pounds per square inch absolute, and subcooling is provided at 67 to reduce the temperature of the liquid air to a level at which it does not vaporize extensively when the pressure is reduced at valve 69.

Liquefied nitrogen from the condensing tubes of calandria 61 is collected on a trap-out tray 70 in the upper portion of the high pressure fractionation zone 58. This liquefied nitrogen is withdrawn continuously from trap-out tray 70 through a line 71. Line 71 connects with a subcooler 72 in which the liquefied nitrogen is further cooled by heat exchange with cold nitrogen-rich product from the top of fractionator 59 to about -306°F. The cooled liquefied nitrogen flows from subcooler 72 through a line 73 which connects with the upper portion of low pressure fractionation zone 60 through a pressure reduction valve 74. The liquefied nitrogen is expanded on passing valve 74 also to about 24.7 pounds per square inch absolute and the subcooling is provided at 72, not only to reduce the temperature of the liquefied nitrogen to a level at which it does not vaporize extensively, but to produce the lowest temperature for fractionation when the pressure is reduced at valve 74.

Returning now to the air in line 37, the remainder of the cooled compressed feed air is passed through a valve 49 and a line 44, which is provided with a strainer 52 and valves 51 and 53, to the inlet of an expansion engine 50. In accordance with the process arrangement of the present example, air flowing through line 44 to expander 50 would amount to about 16% of the compressed feed air. It should be understood that the discrepancy in percentage quantities of air in the example is caused by normal operating losses usually experienced in these reversing heat exchange type of plants. The air passes through expander 50 and is expanded with the performance of external work to an exit pressure of approximately 24.7 pounds per square inch absolute. This expansion with the performance of external work lowers the tem-

perature of the air to approximately -304°F. Under these conditions of temperature and pressure the expanded air flows from the exit of expander 50 through a line 55. A surge and trap-out drum 56 may be interposed in line 55 to minimize pressure surges in this line if the expansion engine 54 is of the reciprocating type, and to remove solid carbon dioxide which may appear in the expanded air during starting-up periods.

In section 60 of fractionator 59 the air is fractionated under a pressure of approximately 24.7 p. s. i. a. and temperature conditions effective to separate an oxygen-rich product in the lower portion of the low pressure fractionation zone 60 and a nitrogen-rich vapor product at the top of this zone. The low temperature necessary in the top of the low pressure fractionation zone is provided by the liquefied subcooled air and nitrogen and the expanded air from line 55. The liquid bottom product, being substantially pure oxygen, accumulates at about -289°F. in the pool around calandria 61. Reboiling in the bottom of the low pressure fractionation zone 60 is provided by calandria 61 in the manner described. The fractionator 59 is provided with gas liquid contact means which may be bubble cap trays, or similar means, for assisting fractionation of the air into oxygen-rich and nitrogen-rich products.

The oxygen-rich product is withdrawn in the vapor phase from the low pressure fractionation zone at about -289°F. through a line 75 which connects with this zone at a point above, but near, the pool of liquid oxygen in the base thereof. Oxygen-rich vapors pass through line 75 into the passageway 16 of reversing heat exchanger 3. Passageway 16 is a non-reversing passageway through which the oxygen product stream passes continuously in countercurrent heat exchange with incoming compressed feed air flowing through either of passageways 7 or 8. After passing through passageway 16 of the heat exchanger, the oxygen-rich product is discharged from the system through a product removal line 76 at about 83°F. and substantially atmospheric pressure.

Referring again to reversing heat exchanger 3, as the air is cooled, water, ice and carbon dioxide are precipitated and deposited in the exchanger. Were the flow of air and nitrogen not interchanged between passageways 7 and 8, the accumulation of ice and carbon dioxide eventually would plug the passageways. However, reversing valves 2 and 6 are periodically actuated to cause the incoming air to be directed into the alternate passageway which has been carrying the nitrogen product. This change of flow causes check valves 11, 12, 13 and 14 to respond automatically so that the nitrogen product is changed immediately from the passageway which has been carrying it into the passageway which has just been carrying air. The streams in both reversing passageways are interchanged, or switched, periodically by the action of the reversing valves but the flow of each stream through the exchanger is always in the same direction. Since the two reversing streams flow countercurrently to each other, the direction of flow relative to the high-boiling components deposited in the passageways is reversed by the action of valves 2 and 6. It is because of this fact that exchanger 3 is referred to as a "reversing exchanger" and passageways 7 and 8 are designated "reversing passageways." The time interval following a change of the reversing valves until the next consecutive change is designated a half cycle. Two consecutive half cycles complete a cycle. For example, air flows through passageway 7 for a half cycle and then through passageway 8 for a half cycle. Then when the air is again caused to flow in passageway 7, a reversing cycle has been completed.

Inasmuch as the nitrogen-rich product, serving as a cooling and scavenging stream in the reversing passageways, is at a post-expansion pressure, its capacity to hold water or carbon dioxide in the vapor state is larger than the capacity in the air stream to do this at the same tem-

perature. Therefore, as the scavenging stream passes over the deposited ice and carbon dioxide, which the air left in the passageway during its cooling flow, such deposit is evaporated and carried out of the system. Such a precipitating and evaporating cycle could keep each passageway clear indefinitely if the material precipitated in one half of a cycle were completely evaporated in the succeeding half cycle. To obtain complete evaporation, however, actual operating conditions of the exchanger must be such as will ensure complete evaporation.

For a more specific exemplification, the deposition and evaporation of carbon dioxide is described specifically, since carbon dioxide deposition is a most serious cause of plugging reversing exchangers in air fractionation processes. The explanation may be made more readily with respect to a sectional length of a cold portion of a passageway which includes the cold end of the passageway. This is because the description may be based conveniently upon conditions under which air is cooled to a sufficiently low subatmospheric temperature that only a negligible quantity of carbon dioxide can leave the passageway in the outflowing cooled air stream. Under such conditions the amount of carbon dioxide brought into and deposited in the section is determined from the flow rate, the pressure and the temperature of the air entering the section. In order for carbon dioxide not to accumulate in the section, the same quantity of carbon dioxide must be contained in the vapor phase in the outflowing nitrogen-rich stream leaving the section during the scavenging period. Since the flow rate of the nitrogen-rich stream is known, the actual concentration of carbon dioxide in it may readily be determined for the condition that ensures complete evaporation.

It is known that for any given concentration of a gaseous component in a gas, and for any given pressure of that gas, there exists a saturation temperature below which the gas cannot contain the given concentration of the gaseous component. This is true with respect to any given concentration of evaporated carbon dioxide held in the vapor phase by the nitrogen-rich product stream as it passes as the scavenging stream through the above-mentioned section. Therefore, if the nitrogen-rich stream leaving the section is colder than the saturation temperature corresponding to the concentration of carbon dioxide determined for the complete evaporation of this component, the nitrogen-rich product stream will not completely evaporate all of the carbon dioxide deposited by the air in the section during the next preceding half cycle of reversal. The nitrogen product stream, therefore, must have a temperature equal to or greater than the saturation temperature established in this manner if it is to completely evaporate deposited carbon dioxide in each half cycle of the reversing periods.

The difference between the temperature of the compressed air stream entering the section of the exchanger under consideration and the saturation temperature of the scavenging stream leaving this section is of critical value since it is the maximum value for complete evaporation of carbon dioxide. Any operating difference between the temperatures of these streams in excess of this critical value indicates that the scavenging stream is too cold to evaporate the deposit of carbon dioxide completely and, therefore, indicates also that there will be an accumulation of carbon dioxide. Temperature differences below this critical value indicate a scavenging stream which is at a temperature warmer than the saturation temperature and which can, therefore, evaporate the carbon dioxide deposit completely. It is understood that in order to allow for factors which affect the actual operation of the exchanger, such as incomplete saturation of the scavenging stream during its passage through the exchanger, it is desirable to operate at temperature differences somewhat smaller than the critical value. This critical value is defined as "maximum allowable temperature difference" and in the present explanation is appli-

cable to the point where the compressed air stream enters the section of the exchanger selected for the exemplification, and to the temperature condition at that point. For other sectional lengths, similar maximum allowable temperature differences may be established corresponding to other temperature conditions. In air separating plants, the maximum allowable temperature difference decreases in the direction toward the colder parts of the exchanger.

Because the quantity of carbon dioxide that the scavenging stream can evaporate decreases with temperature but increases with decrease in pressure, there are two competing influences involved in the operation of exchanger 3—the difference between the pressures of the counter-flowing streams which aids evaporation and the difference between their temperatures which hinders evaporation, the resultant effect of which determines the actual evaporation. In process arrangements, such as is exemplified by Fig. 2, the difference between the pressure of the compressed air and the pressure of the products is determined and fixed by the distillation and refrigeration requirements decided upon and established within fixed limits at the time the process is designed. With one of the competing influences involved in the operation of exchanger 3 thus fixed, it becomes necessary to operate the reversing streams in heat exchange at temperatures such that the difference between these temperatures is less than the maximum allowable temperature difference to continuously and completely evaporate and remove carbon dioxide deposit left in a passageway during the preceding half cycle period of the reversing cycle. It is to be understood, that while the foregoing explanation is related to the removal of carbon dioxide only, the principles involved are equally applicable to the precipitation and evaporation of water vapor or other high-boiling condensible components present in a gaseous mixture.

The maximum allowable temperature difference establishes the conditions within which the actual operation of reversing heat exchangers are capable of continued precipitation and evaporation. Such condition is not necessarily always obtainable in gas separating plants as, in the separation of air by the process arrangement shown in Fig. 2. When exchanger 3 is operated in "balanced flow" the differences between the temperatures of the compressed air and the nitrogen-rich product streams do not remain less than the maximum allowable temperature difference at successive points over the whole length of the exchanger. This is because the specific heat of air under a pressure of about 100 pounds per square inch absolute is somewhat larger than the specific heat of air, or of its components at atmospheric pressure. The difference is somewhat smaller at the temperature of the atmosphere and increases more and more rapidly as the temperature drops. When exchanger 3 is operating in "balanced flow" the rate of mass flow, that is, the flow expressed in terms of weight per unit time, of the compressed air is equal to the sum of the rates of mass flow of the products of the separation. In such balanced flow heat exchange, the change in temperature of the stream of higher specific heat is smaller than that of the streams of lower specific heat. As a result, because of the compressed air has the higher specific heat in exchanger 3, the difference between the temperatures of the reversing streams increase toward the cold end of the exchanger. In consequence of the progressively larger difference in specific heats as the temperature decreases, the differences between the temperatures of the reversing streams progressively increase in degree toward the cold end of the exchanger. This progressive change in temperature difference relationship is of fundamental importance in the operation of the exchanger's reversing passageways 7 and 8 because the difference between the temperature of the streams at the warm end of the exchanger is less than the maximum allowable temperature difference for the evaporation of water and ice by the nitrogen-rich product stream. There-

fore, the water vapor which has been precipitated during the cooling of the air, either as a liquid or ice, readily can be completely evaporated during the next succeeding half cycle period of reversal. Toward the cold end of exchanger 3, however, the differences between the temperatures of the compressed air and the nitrogen-rich product streams increase to values greater than the critical value required for the complete evaporation of both the carbon dioxide and water in the half cycle time interval between reversal of valves 2 and 6 and, therefore, the exchanger will eventually become plugged with solid precipitate. In this manner, the change in specific heat causes the difference between the temperatures of the compressed air and nitrogen-rich product streams to increase progressively toward the cold end of the exchanger to values that make the exchanger eventually inoperable when it is operating with balanced flow conditions. Inoperability is wholly independent of the difference between the temperatures of the heat exchanging streams at the warm end of exchanger 3 because, even if this difference were negligible, the difference between the temperatures at the cold end of the exchanger still would be in excess of the maximum allowable temperature difference.

According to the present invention, the difference between the temperatures of the compressed air and the nitrogen-rich product streams in exchanger 3 is controlled to values less than the maximum allowable temperature difference by employing an extraneous stream of air and introducing this extraneous air at a suitable temperature and under a pre-expansion pressure into the expansion and fractionation system without passing through exchanger 3. Part of the extraneous air finds its way out of the system in the nitrogen-rich product stream and part leaves the system in the oxygen-rich product stream. This augments the mass of the product streams having lower specific heats in the reversing heat exchanger. Then, as a consequence of the larger mass of cold material in countercurrent heat exchange relation with inflowing compressed air, the temperature change of the product streams is smaller for a given temperature change of the compressed air, which, it is noted, is the opposite of the effect resulting from the lower specific heats of the product streams. The difference between the temperatures of the reversing streams, i. e., the compressed air and the nitrogen-rich product streams, toward the cold end of the exchanger is decreased. The temperature differential between these streams may be adjusted to any suitable desired difference by controlling the quantity of the extraneous air stream introduced into the expansion and fractionation system.

According to the process arrangement exemplified in the modification of the invention shown by Fig. 1, exchanger 3 may be operated so that the compressed air leaving the exchanger will have an exit temperature relatively near but above the liquefaction temperature of air, which at the pressure is about -266° F. to provide for the substantially complete precipitation of its carbon dioxide constituent in the exchanger. The temperature of the nitrogen-rich product stream passing to exchanger 3 must be adjusted to be within a few degrees of the air temperature, or approximately -271° F. in order that the difference between the temperatures of these counterflowing streams will be less than the maximum allowable temperature difference at the cold end of the exchanger under these operating conditions. To obtain such conditions, atmospheric air, amounting to approximately 3 to 5 weight percent of the air passing through line 1, is introduced under a pressure of about that of the feed air entering through line 1 and at a temperature of about 90° F. into line 19. The amount of air required to be drawn into line 19 is not a fixed quantity but is dependent upon the actual temperature differences required between the reversing streams in exchanger 3. The quantity also must be modified to meet changes in the amount of feed air charged, and refrigeration losses

through the insulation; the greater such losses, the greater must be the weight percent of extraneous air taken into line 19, and vice versa.

From line 19 the extraneous air passes into the bottom of a tower 22. It is the function of tower 22 to chemically remove the carbon dioxide impurity contained in the extraneous air stream. For this purpose, a caustic solution, which conveniently may consist of a 10% solution of potassium or sodium hydroxide, is introduced into the top of tower 22 through a line 23. The caustic solution from line 23 is caused to pass downwardly through the tower over vapor-liquid contacting means which may comprise a plurality of bubble cap trays 24, or suitable tower packing material. Spent caustic solution is drawn from the bottom of tower 22 through a draw-off line 25.

The treated air passes overhead from tower 22 and is taken by way of a line 26 through a valve 27 into a dryer 28 wherein it is brought into contact with a granular adsorbent material, such as silica gel or activated alumina, and dehydrated.

At infrequent intervals of time, when dryer 28 requires regeneration, valves 27 and 29 are closed and valves 34 and 35 are opened to divert the passage of the air from line 26 into dryer 36. For the regeneration a suitable drying medium is used, which conveniently, may be a portion of effluent from exchanger 3. This portion is removed from line 37 through the valved line 38 whereafter it may be warmed by any suitable means. This warmed portion of the purified air from line 37 is passed in a single pass flow arrangement into and out of dryer 28 by way of the valved lines 39 and 40 until the bed of granular material is regenerated sufficiently to again serve as a dehydrating adsorbent. The spent drying medium from line 40 is vented from the system. Dryer 36 similarly may be regenerated by passing the warmed effluent from line 37 into and out of this dryer by way of the valved lines 41 and 42, when valves 34 and 35 are closed and valves 27 and 29 are opened, respectively.

Dried, purified air is taken from dryer 28 through a valve 29 and is passed by way of a line 90, having a valve 95 therein opened, to heat exchanger 91. In passing through heat exchanger 91 the extraneous air warms a stream of nitrogen-rich product from line 79, as will be hereinafter described. In giving up heat in exchanger 91 the extraneous air stream is cooled to about -137° F. and the cooled air is taken from exchanger 91 through a line 92 which connects with a filter 105 through a branch line 104 having an open valve 107.

In the event that exchanger 91 becomes fouled, the extraneous air is diverted from line 90 into a line 94 by simultaneously closing valves 95 and 95' and opening a valve 96 in line 94 and a valve 99 in line 98. This takes exchanger 91 off the line and directs the inflowing extraneous air through an alternate exchanger 97. A line 98 connects the cold end of exchanger 97 with line 92 so that the extraneous air after passing through exchanger 97 may be returned to its former course of flow through line 92. After its removal from the line of flow of the extraneous air, exchanger 91 may be suitably cleared and again used by merely reversing the manipulation of the above-mentioned valves in a manner to take exchanger 97 from the line and switch over to exchanger 91.

Exchangers 91 and 97 are shown in Fig. 2 diagrammatically to represent an annular type extended surface heat exchanger constructed so as to have a concentric annular passageway surrounding a central tube. This particular construction of the exchanger is not essential, as other forms of construction are equally suitable for satisfactory performance of the described heat exchange relation. Exchangers 91 and 97 may be packed with a metallic packing material, metal bonded to the walls of the passageways in the manner as heretofore described in connection with exchanger 3.

From line 92 the extraneous air stream is passed either into filter 105 or a switch filter 106 by properly opening

or closing valves 107 and 108 in branch line 104 and valves 110 and 111 in a branch line 109 connecting filters 105 and 106 to an exit line 116. The filters are packed with a granular adsorbent material such as silica gel or activated carbon, the purpose of which is to remove from the extraneous air any impurity, such as acetylene or residual carbon dioxide which may have penetrated thus far into the system. The filtered air leaves either of the filters through branch line 109 into a transfer line 116. The two filters likewise may be revived, in a manner essentially as heretofore described in connection with dryers 28 and 36, by taking one filter at a time from the line and then passing through it a revivifying medium of the character as heretofore mentioned. For this purpose, the valved lines 112 and 113 have been provided as inlet and outlet flowline for the material used in revivifying filter 105 and lines 114 and 115 similarly have been provided for such use when revivifying filter 106.

Referring to the stream of cooled compressed feed air in line 37, it has been stated heretofore that about 16 weight percent of the material in this line was utilized for expansion in the engine to provide for the refrigeration requirements of the present illustrative process flow arrangement. In the present modification an extraneous stream of air is introduced through line 19 and the intervening apparatus to line 116 in an amount equivalent to approximately 3 to 4 weight percent of the air in line 37. Since refrigeration requirements of the process are not changed by the modified arrangement over what was needed in the normal arrangement, now it is necessary to remove only about 13 weight percent of the air in line 37 from that line through valve 49 and pass it to expansion engine 50 through line 44. The 3 to 4 weight percent of extraneous air is taken from line 116 and commingled with the 13 weight percent of air flowing through line 44 from line 37. Again, the total commingled air passing to the expansion engine totals to about 16 weight percent of the compressed feed air.

The portion of the main stream of cooled compressed air from line 37 for expansion enters line 44 at about -266°F . The extraneous air enters line 44 from line 116 at a temperature of about -137°F . The quantity of the extraneous air stream is determined by the rate of mass flow requirements for achieving the necessary temperature difference relationship in exchanger 3. The expansion air in line 44 is determined by the difference between the quantity needed to meet the refrigeration requirement and the quantity of the extraneous air brought into the stream. The temperature of the extraneous air is adjusted in exchanger 91 to accomplish two purposes. First, the extraneous air stream is used to warm the nitrogen-rich product gas stream to a predetermined temperature to avoid liquid condensation in exchanger 3. Second, the extraneous air stream is caused to retain sufficient heat content so that, when it becomes commingled with the air flowing in line 44 from line 37, the resultant average temperature of the commingled stream will be warm enough to pass through pressure reduction in the expansion engine without formation of liquid droplets therein. According to the present example, the average temperature of the commingled streams passing to the inlet of the expansion engine is approximately -235°F . This procedure, therefore, obviates the formation of liquid during expansion and provides for the proper temperature condition of the stream of vaporous air passing from expansion engine 50 through a line 55 into the low pressure section 60 of fractionator 59 to meet the distillation requirements of vapor feed to this section.

A portion of the oxygen content of the extraneous air stream introduced into the system by way of line 19 necessarily becomes separated in the fractionator 59 and is withdrawn therefrom as a part of the oxygen-rich product stream outwardly flowing through line 75, but a portion of the extraneous air stream passes overhead from fractionator 59 as a component part of the nitrogen-

rich product stream flowing from the fractionator through a line 77. The additional material in lines 77 and 75 which was derived from the extraneous air stream augments the otherwise normal amount of backward-returning cold products in reversing exchanger 3, to provide unbalanced flow. As has been heretofore described this expedient maintains the difference between the temperatures of the reversing streams in the cold portion of exchanger 3 to a value which is less than the critical maximum allowable temperature difference required to permit a passageway of exchanger 3 to clear itself of solid deposits in a half cycle which was precipitated in that passageway during the next preceding half cycle of reversal.

To reach reversing exchanger 3, the augmented nitrogen-rich product vapors are withdrawn overhead from fractionator 59 through a line 77 at a temperature of about -309°F . and under pressure of approximately 24.7 pounds per square inch absolute. These vapors are then brought into heat exchange in subcooler 72 with the liquefied nitrogen taken from tray 70 through line 71. In cooling the liquefied nitrogen from about -288°F . to about -306°F . the nitrogen-rich vapors become warmed to about -292°F . At this latter temperature they are taken through a line 78 to subcooler 67, wherein they are further warmed to about -280°F . by absorbing heat from the oxygen-rich liquid entering subcooler 67 from line 66 to subcool the oxygen-rich liquid from about -279°F . to about -286°F . From subcooler 67 the partially warm nitrogen-rich vapors are taken through a line 79 and through a valve 100 to exchanger 91. In passing through exchanger 91 the nitrogen-rich vapors are warmed again to about -271°F . by heat derived from the extraneous air stream as hereinbefore described. This warming step is sufficient to avoid any possibility of condensation of some of the compressed feed air in exchanger 3 when it is cooled therein by the backward-returning cold product vapors. In the event that exchanger 97 is being utilized as the heat exchange apparatus in the warming step, valves 100 and 101 are closed at the inlet and outlet ends of exchanger 91 and valves 102 and 103 are opened to direct the flow of the nitrogen-rich vapors from line 79 through exchanger 97 and into line 82 for transfer therethrough to either check valves 13 or 84 at the cold end of exchanger 3.

The modification of the invention shown by Fig. 2 has been described for that event where the oxygen-rich product passes through reversing heat exchanger 3. It is to be understood, however, that this modification is equally applicable to an arrangement in which the oxygen-rich product is removed without passing through exchanger 3. In the latter event the quantity of the extraneous stream and other conditions such as the amount of air expanded, may readily be adjusted in a suitable manner well-known to those skilled in the art.

In Fig. 3, the parts and streams identified by the numerals 401 to 409 correspond to the similar parts and streams 201 to 209 in Fig. 1. However, the compressed extraneous stream 405, after passing through heat exchanger 409 in indirect heat exchange with outflowing product stream 404, is passed through a second heat exchanger 411 and then combined with inflowing compressed gaseous mixture 402, instead of being passed directly to expansion engine 408. Instead, a gaseous fraction under pre-expansion pressure, is withdrawn from the high pressure fractionation zone 406, passed through heat exchanger 411 in indirect heat exchange with the compressed extraneous stream 405, expanded in expansion engine 408, and introduced into low pressure fractionation zone 407 by means of line 413. In this case, the heat content of the extraneous stream 405 is used to avoid condensation in expansion engine 408 by the employment of indirect heat exchange in the heat exchanger 411, instead of by mixing the extraneous stream directly with a stream destined for expansion engine 408 as shown in

Fig. 1, or by introducing the extraneous stream itself directly into the expansion engine 408.

Fig. 4 of the drawing illustrates a specific application of the embodiment of the invention shown in a simplified form by Fig. 3. According to this embodiment an extraneous stream of air under a pre-expansion pressure is chemically purified, dehydrated, utilized to warm backward-returning nitrogen product and expansion feed gas and then is combined with inflowing compressed air to the fractionator. In this modification, a gaseous fraction under preexpansion pressure is obtained from the fractionation zone, warmed by indirect heat exchange with the extraneous stream and expanded in an expansion engine. The extraneous stream is used to avoid condensation in the expansion engine by warming the expansion gas by indirect heat exchange. The principal apparatus is the same as that described in connection with Fig. 2 and the function of the several process steps and process conditions therein are the same. Those parts common to both Fig. 2 and Fig. 4 are shown with the same reference numerals but bearing the subscript "a" in Fig. 4.

In the modification of Fig. 4, a stream of compressed feed air is introduced by way of line 1a, cooled in the reversing passageways 7a and 8a of reversing heat exchanger 3a to a temperature of about -266°F . During the cooling the compressed air stream is purified in exchanger 3 as heretofore described in connection with Fig. 2 of the drawing. The same condition of incomplete evaporation of the carbon dioxide impurities again is present in the present modification, since the processing conditions for separating air have not changed. The difference between the temperatures of the compressed air stream and the nitrogen-rich product stream in the cold part of reversing heat exchanger 3a is made less than the maximum allowable temperature difference by an extraneous stream of air. In the present instance, however, the total cooled and purified compressed air is withdrawn from exchanger 3a and passed through line 37a directly into high-pressure section 58a of fractionator 59a wherein the compressed air is separated into a liquefied oxygen-enriched air fraction, a liquid nitrogen fraction, and a vaporous nitrogen fraction. The vaporous nitrogen fraction is removed from calandria 61a through a line 63a which connects to a heat exchanger 33a. The nitrogen vapors enter line 63a at a temperature of the order of about -286°F . and under a pressure of approximately 86 pounds per square inch absolute. The quantity of these nitrogen vapors is equivalent to about 19 weight percent of the main stream of compressed feed air entering the system through line 1a and are expanded in an expansion engine 50a to supply the refrigeration requirement of the system. The temperature of -286°F . for nitrogen is very close to the dew point of the vapors under about 86 pounds pressure. Hence, these nitrogen vapors cannot be expanded to the pressure of the low-pressure fractionating section 60a without formation of liquid droplets. The nitrogen vapors are warmed, therefore, to about -250°F . in exchanger 33a by heat from the extraneous stream of warm air from line 117a, as shall hereinafter be described. A line 46a connects the warm end of exchanger 33a to expansion engine 50a and the warmed nitrogen vapors are conducted through line 46a to the expansion step. The nitrogen vapors are expanded in the expansion engine to lower pressure of about 24.7 p. s. i. a. completely in the vapor phase with the production of external work and are resultantly cooled to about -312°F . The cooled expanded nitrogen vapors are conducted through a connecting line 55a from the outlet of the expansion engine to the top of fractionation section 60a wherefrom they pass into line 77a to permit recovery of refrigeration.

Referring now to the extraneous stream of air, this stream, which is about 3 to 5 percent of the compressed air, in line 1a, is taken through inlet line 19a and passed through a caustic treating step in tower 22a and through

a drying step in one of the dryers 28a or 36a in the manner and for the purpose as heretofore described in connection with Fig. 2. The stream then is conducted through a line 90a to a heat exchange step in exchanger 91a or 97a with cold backward-returning nitrogen-rich product from line 79a in the manner and for the purpose as heretofore described in connection with the description of Fig. 2. The temperature of the extraneous air after heat exchange is about -40°F . to about -100°F . and at this temperature it is then taken by way of line 92a to one of a pair of filters 105a and 106a for removal of any impurity, such as acetylene or carbon dioxide which may have penetrated thus far into the system. Filtering is carried out in the manner as described in connection with the performance of filters 105 and 106 in the description of Fig. 2. The filtered air passes from either of the filters through a branch line 109a which connects with a transfer line 117a which, in turn, connects with the warm end of exchanger 33a.

In passing through exchanger 33a from line 117a the extraneous stream of air warms the nitrogen vapors from line 63a by indirect heat exchange and in so doing is cooled to substantially the temperature of the cooled compressed air flowing through line 37a. A line 123a connects the cold end of exchanger 33a with line 37a at a point intermediate between heat exchanger 3a and high-pressure fractionation zone 58a. The now cooled extraneous air stream is conducted through line 123a and introduced into line 37a and becomes commingled with the main stream of feed air flowing through line 37a. If the additional cooling experienced by the extraneous stream in passing through heat exchanger 33a causes precipitation of further high boiling impurities, filters 105a and 106a may be shifted from the position shown to a place in line 123a, i. e., downstream instead of upstream relative to heat exchanger 33a. In this case, it is also desirable to provide a duplicate of exchanger 33a which can be periodically switched into the system as an alternate so that impurities can be evaporated from one unit while the other is in operation after the manner of exchangers 91a and 97a.

The commingled streams are introduced into high-pressure fractionation zone 58a through a control valve 57a. The extraneous air is separated into components as part of the main feed air and the separated components comprise portions of the outflowing products of the separation, thereby increasing the rate of mass flow of the product streams leaving the expansion and fractionation system. Thus, the rate of mass flow of the nitrogen-rich product stream is augmented by a portion of the extraneous stream when it flows through line 77a from the top of fractionator 59a. The augmented nitrogen stream passes through subcoolers 72a and 67a as heretofore described in connection with Fig. 2 after which it is taken through line 79a to one of the heat exchangers 91a or 97a, wherein it is warmed by heat from the extraneous air stream to a temperature sufficiently high to avoid its cooling the compressed air in exchanger 3a so low as to cause any condensation. The separation products are augmented in this manner for the purpose as described in connection with Fig. 2 and are employed in heat exchanger 3a to maintain the difference between the temperatures of the reversing streams in the cold end of exchanger 3a less than the maximum allowable temperature difference.

I claim:

1. The method of separating the constituents of a compressed gaseous mixture by liquefaction and fractionation into product fractions which comprises the steps of cooling a major part of the compressed mixture to a temperature slightly above its liquefaction temperature in a path of a reversing heat exchange zone by heat exchange with at least a cold product fraction of the separation passing in another path through said zone countercurrently to the direction of flow of the gaseous mixture

therethrough to precipitate an impurity from said mixture and deposit the precipitate in said zone, periodically interchanging the paths of flow of the mixture and cold product, adding a partially cooled minor part of the compressed mixture to the purified major part, subjecting the added parts of said mixture to fractionation, warming a vaporous product of said fractionation by heat exchange relation with said minor part immediately prior to the addition of the latter to said purified major part whereby said minor part attains said partially cooled condition, expanding said warmed vaporous product of the fractionation step to lower pressure, combining the expanded vaporous fraction with other products of said fractionation, fractionating said expanded fraction and liquid products of said fractionation under said lower pressure to provide the cold product fractions of the separation, warming one of said cold product fractions by heat exchange relation with said minor part of the compressed mixture to partially cool said minor part and passing the thus warmed cold product fraction through said reversing heat exchange zone whereby said product fraction passes over the precipitate and thereby causes the evaporation and removal thereof.

2. The method of separating a gaseous mixture into output products by liquefaction and fractionation which comprises, cooling a major part of the gaseous mixture in a compressed condition by the refrigerating effect obtained by countercurrent heat exchange in a reversing heat exchange zone with cold output product material of the separation to eliminate impurities therefrom, further cooling the purified mixture to produce vaporous and liquefied fractions, warming a vaporous fraction of the further cooled gaseous mixture by countercurrent heat exchange relation with a minor part of the gaseous mixture in a compressed condition, then combining the minor part of the gaseous mixture with the major part thereof about to be subjected to said further cooling, expanding the warmed vaporous fraction of the purified further cooled gaseous mixture, and then fractionating the expanded vaporous fraction with a liquid fraction of the further cooled gaseous mixture to provide the cold output products of the separation.

3. In a process for fractionating a compressed gaseous mixture in a low-temperature expansion and fractionating system, wherein an inflowing charge stream of said compressed gaseous mixture enters said system at a pre-expansion pressure from a reversing heat exchange zone in which said inflowing stream is cooled and in a cold part of which high-boiling impurities are precipitated, and wherein an outflowing product stream leaves said system at a post-expansion pressure through said reversing heat exchange zone, absorbing heat and scavenging said precipitated high-boiling impurity by re-vaporization, said inflowing and outflowing streams being flowed countercurrently and alternately with each other through periodically reversing paths in a heat exchange relation in said reversing heat exchange zone, and wherein some gas is fractionated and liquified in a fractionating zone under pre-expansion pressure and some gas is fractionated and liquified in a fractionating zone under post-expansion pressure, and wherein at least a portion of the gas flowing within said fractionating system under a pre-expansion pressure is expanded to a post-expansion pressure in an expansion engine, a method for preventing the excessive accumulation of said precipitated impurity in said cold part of the paths of said reversing heat exchange zone, which method includes the steps of: introducing a major part of said compressed gaseous mixture into said fractionating system through said reversing heat exchange zone, whereby said major part is chilled and purified; introducing a minor part of said compressed gaseous mixture into said fractionating system through a non-reversing passage and eliminating said high-boiling impurities therefrom subsequent to said non-reversing passage; at least partially cooling said minor part by indirect heat

exchange with outflowing product stream to prevent condensation in said reversing heat exchange zone; subsequently mixing said minor part with at least a part of the purified major part of the compressed gaseous mixture; subsequently introducing said added parts into said pre-expansion fractionating zone to effect an augmentation of said outflowing product stream.

4. In a process for fractionating a compressed gaseous mixture in a low-temperature expansion and fractionating system, wherein an inflowing charge stream of said compressed gaseous mixture enters said system at a pre-expansion pressure through a reversing heat exchange zone in which said inflowing stream is cooled and in a cold part of which high-boiling impurities are precipitated, and wherein at least one outflowing product stream leaves said system at a post-expansion pressure through said reversing heat exchange zone, absorbing heat and scavenging said precipitated high-boiling impurity by re-vaporization, said inflowing and outflowing streams being flowed countercurrently and alternately with each other through periodically reversing paths in a heat exchange relation in said reversing heat exchange zone, a method for preventing the excessive accumulation of said precipitated impurity in said cold part of paths of said reversing heat exchange zone, which method includes the steps of: introducing a major part of said compressed gaseous mixture into said fractionating system through said reversing heat exchange zone; removing at least part of said high boiling impurities from a minor part of said compressed gaseous mixture by chemical treatment; introducing said minor part into said fractionating system through a non-reversing passage; flowing said minor part in indirect heat exchange with said outflowing product stream to warm the latter sufficiently to prevent condensation of said inflowing compressed gaseous mixture within said reversing heat exchange zone; mixing said minor part with at least a part of said purified major part of the compressed gaseous mixture; subsequently fractionating a stream comprising said last formed mixture; and augmenting said product stream outflowing through said reversing heat exchange zone by products derived from said fractionation.

5. In a process for fractionating a compressed gaseous mixture in a low-temperature expansion and fractionating system, wherein an inflowing charge stream of said compressed gaseous mixture enters said system at a pre-expansion pressure through a reversing heat exchange zone in which said inflowing stream is cooled and in a cold part of which high-boiling impurities are precipitated, and wherein at least one outflowing product stream leaves said system at a post-expansion pressure through said reversing heat exchange zone, absorbing heat and scavenging said precipitated high-boiling impurity by re-vaporization, said inflowing and outflowing streams being flowed countercurrently and alternately with each other through periodically reversing paths in a heat exchange relation in said reversing heat exchange zone, a method for preventing the excessive accumulation of said precipitated impurity in said cold part of paths of said reversing heat exchange zone, which method includes the steps of: introducing a major part of said compressed gaseous mixture into said fractionating system through said reversing heat exchange zone; introducing a minor part of said compressed gaseous mixture into said fractionating system through a non-reversing passage; flowing said minor part in indirect heat exchange with said outflowing product stream to warm the latter sufficiently to prevent condensation of said inflowing compressed gaseous mixture within said reversing heat exchange zone; mixing said minor part with at least a part of said purified major part of the compressed gaseous mixture; subsequently fractionating a stream comprising said last formed mixture; augmenting said product stream outflowing through said reversing heat exchange zone by products derived from said fractionation; and filtering out high-boiling

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impurities precipitated from said minor part after at least partial cooling thereof but prior to said fractionation.

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