

July 31, 1951

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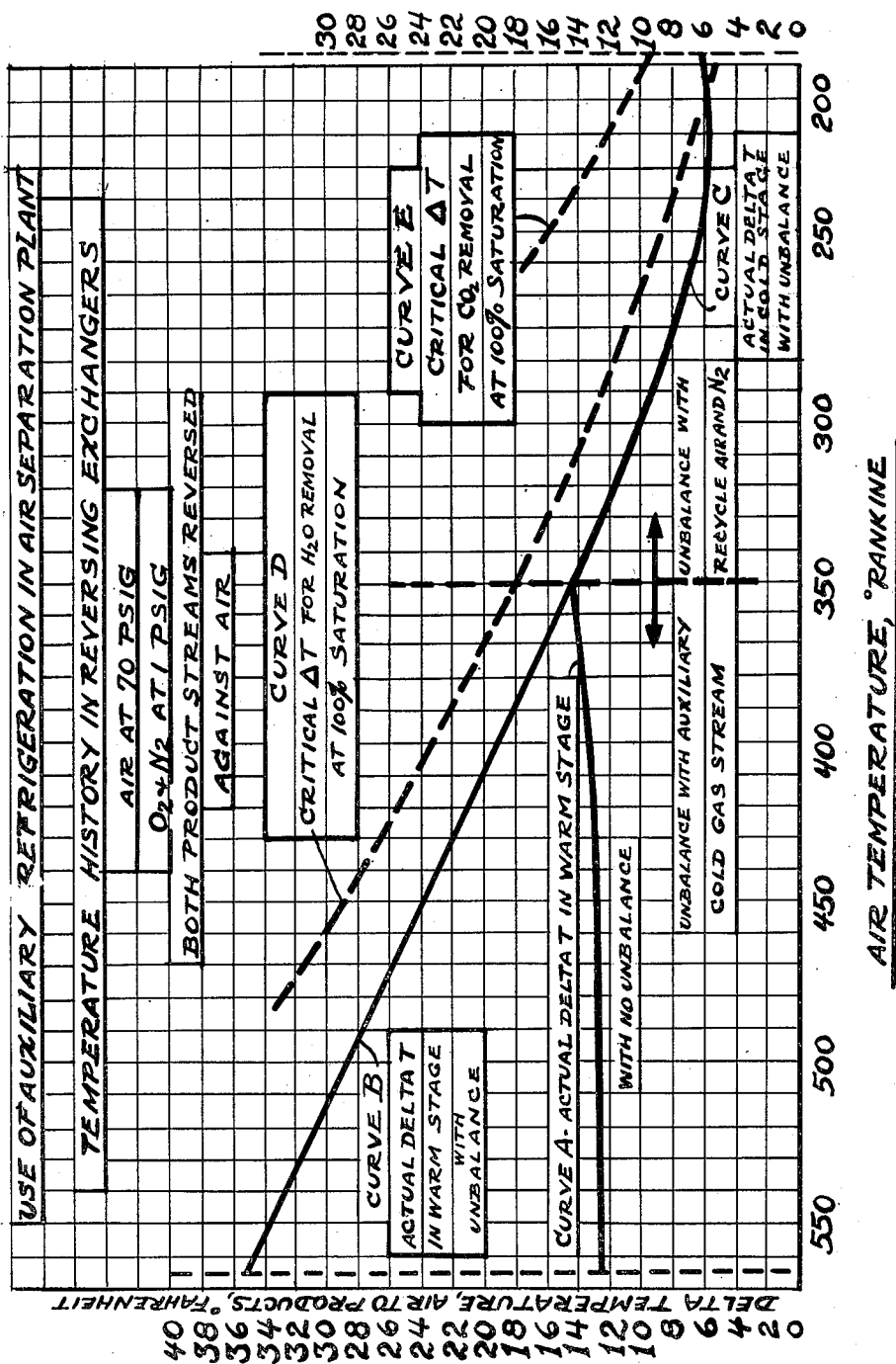
2,562,812

LIQUEFACTION OF AIR

Filed Aug. 9, 1947

2 Sheets-Sheet 1

FIG.-1



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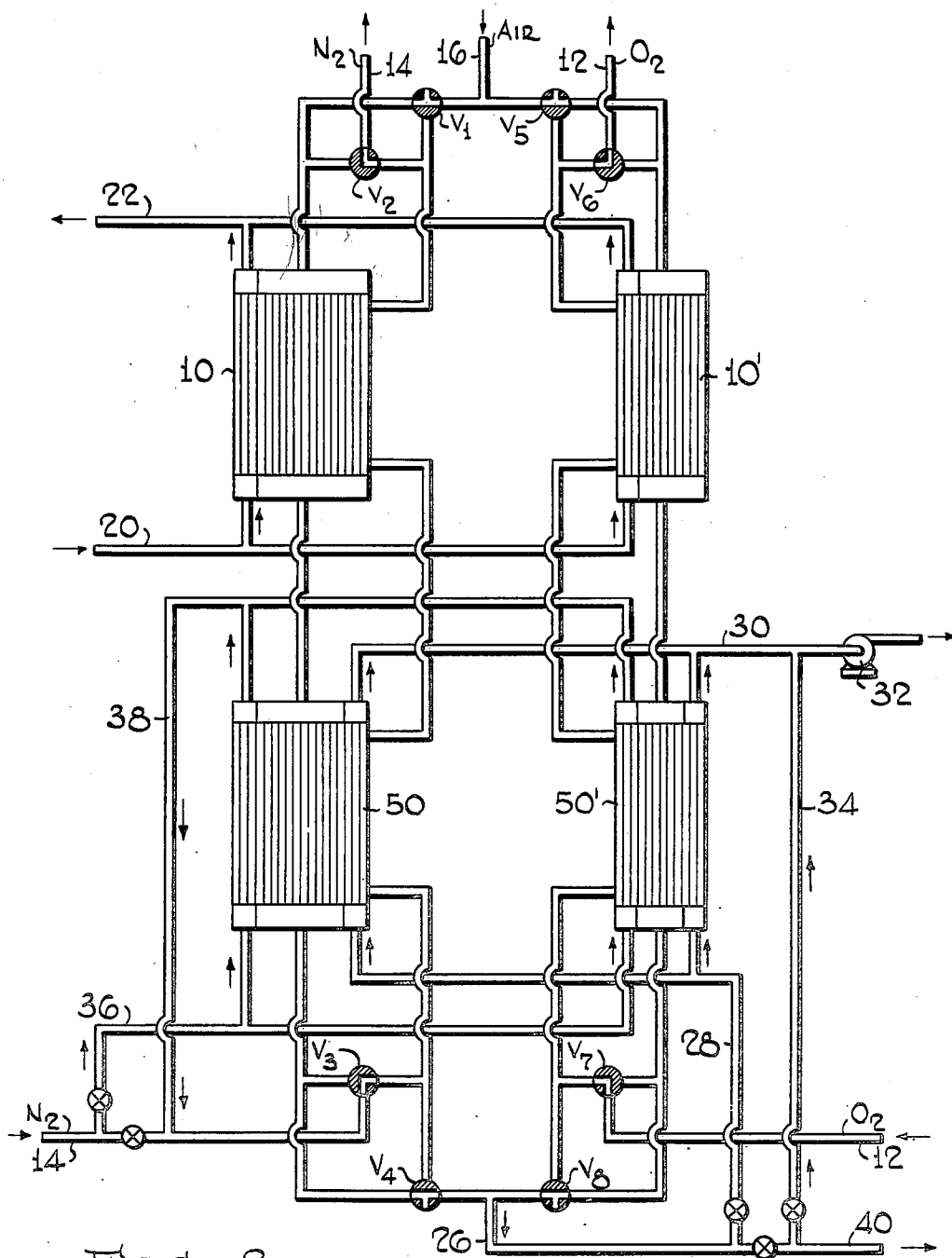


FIG. -2

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LIQUEFACTION OF AIR

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1 Claim. (Cl. 62—175.5)

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This invention relates to the preparation of oxygen from air by the liquefaction process and in particular, to the use of an external cooling fluid adapted to improve the process, all of which will be more fully described in the following specification, the accompanying drawings Figures 1 and 2, and in the claim.

In Figure 1 curves are given showing the temperature differential in an air cooling operation in which air under 70 p. s. i. g. pressure is cooled by heat exchange against separated products returning at atmospheric pressure. Figure 2 is a diagrammatic showing of a two stage tube and shell type reversing heat exchanger for the cooling of inlet air by separated products.

An important use of oxygen prepared on a large scale is in forming carbon monoxide and hydrogen to be used as a feed gas to a hydrocarbon synthesis process, the oxygen being used to convert normally gaseous hydrocarbons such as methane, or in conjunction with steam being employed to gasify solid carbonaceous fuels, to the said carbon monoxide and hydrogen. As is known in the hydrocarbon synthesis process, normally gaseous products are formed in addition to liquid and solid materials. In one modification of the invention the gaseous products, which are usually under relatively high pressure and are often referred to as tail gas are employed as the source of the external cooling fluid in the liquefaction of air.

It is a matter of record and commercial practice to produce oxygen by liquefying and thereafter to subject the liquefied air to fractional distillation. One of the most successful processes in this field has been the Linde-Frankel process in which air is purified of its content of water vapor and carbon dioxide by cooling in so-called "reversing accumulators." In these accumulators, a heat storage medium generally consisting of aluminum spirals is chilled by the passage of separated nitrogen or oxygen products returning in gaseous form and at substantially atmospheric pressure from the air fractionator. After a period of time, the returning product stream is switched to a similar refrigeration storing unit while air under moderate pressure of from 4 to 6 atmospheres absolute pressure is passed in the opposed direction through the first-mentioned accumulator vessel and is cooled by the chilled bodies therein contained.

In the process of being cooled, the vaporous impurities contained in the air stream, such as water and carbon dioxide, are condensed and deposited in solid form on the surface of the

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heat storing medium. At frequent and regular intervals of the order of about 2 to 3 minutes, the incoming air stream is switched to pass through the other heat storing body which has meanwhile been chilled by the cold product stream and the cold product stream is returned to the first-mentioned heat storing vessel. In its passage through this heat storing vessel, the cold product stream not only serves to chill the heat storing bodies therein contained but also serves to revaporize the impurities deposited on the surface of the heat storing material. By this procedure, the refrigeration contained in the products issuing from the air separation vessel is recovered to a very high degree and at the same time, the incoming air is freed of its content of water vapor and CO₂ without the necessity of chemical purification. It will be appreciated that if such purification were not carried out, the air separation apparatus and the heat exchange means associated therewith would be rapidly plugged with a deposit of the solidified impurities.

Subsequent to the successful operation of the Linde-Frankel process, the so-called "reversing heat exchanger" type of operation was developed. Generally, this process is one in which the transfer of heat between the returning oxygen and nitrogen streams and the incoming air is effected by maintaining the two product streams in direct thermal contact with the air. The product streams are passed countercurrently to incoming air through a heat exchange vessel through paths separated by heat conducting walls, instead of passing in alternation with the air through separate vessels in which the refrigeration content of the cold stream is transferred to a heat storing body and subsequently employed to cool the incoming air stream. Air purification, as in the Linde-Frankel units, is accomplished by alternating the flow paths of the two heat exchanging streams through the heat exchanging vessel. The form of the heat exchange vessel is not significant and may consist, for example, of a shell and tube arrangement or of a sandwich type arrangement, in which the flow of gaseous streams is through adjacent paths of rectangular cross section.

As used herein the term "reversing exchangers" has its conventional connotation. However, the process described and claimed herein is applicable to the Linde-Frankel type of operation in which so-called accumulators are employed in which air and oxygen or nitrogen are alternately contacted with metallic bodies

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for the purpose of cooling air subsequently to be subjected to low temperature fractionation to produce oxygen and nitrogen.

Certain considerations are of importance in insuring that the carrying capacity of the product streams for water and carbon dioxide is sufficient to accomplish complete revaporization of the impurities deposited on the heat exchange surface. It must be appreciated that in order for cooling of the air to be effectuated, the product streams must be at a lower temperature level than the incoming air. Also, for those colder streams to revaporize the deposited solid impurities they must represent a greater volume than the incoming air. Since in normal operation the quantity of the product streams returning is at least equal in mass to the quantity of air being cooled, while they are at lower pressure level, this requirement is readily met in practice. A readily calculable difference in temperature level between the two streams is allowable for any given differential in volume at each temperature level. This allowable differential temperature is less as the volume of product gas employed for purification is lowered relative to the volume of the incoming air stream.

One important point is that for established relative volumes of incoming air and product stream used for purification, the allowable temperature differential for complete sublimation of the deposited ice and solid carbon dioxide is reduced as the temperature level is lowered. It is unfortunately true, however, that in adiabatic heat exchange between the air and product streams of the same mass but of different volume resulting from a pressure differential, there is a tendency for the temperature differential between the streams to increase in progressing from the warm end to the cold end of the exchanger. This follows from the fact that the heat capacity of the air under pressure is slightly higher than that of the low pressure product streams. As a consequence, the allowable temperature difference for complete sublimation of the deposited carbon dioxide is exceeded at the cold end of the reversing exchanger and the purpose of the reversing exchanger is partially circumvented unless means for preventing this temperature difference from becoming excessively large are introduced.

Various means have been proposed to keep the temperature differential at the cold end of the exchanger within limits permitting complete revaporization of the carbon dioxide, as for example, recycling a portion of the nitrogen product stream from the warm end back to the cold end, or returning a portion of the cold purified air back through the exchanger, or cooling the air stream by refrigeration obtained from an external source, or adding to the relative mass of the returning products by means of a separately purified and cooled portion of the inlet air. All these means have as their purpose the decreasing of the effective heat capacity of the air being cooled relative to the streams being warmed to a level such that the progressive increase in temperature differential between the reversing streams, as the cold end of the exchanger is approached, may be kept within the limits permitting complete sublimation of the deposited carbon dioxide in the product streams on reversal.

It will be appreciated from this review of the prior art that when a stream of air at a higher pressure level is in continuous countercurrent

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heat exchange relationship with its separated components at a lower pressure level, that is, when the masses of the two streams are equal and the heat removed from the one is absorbed by the other, there is a progressive increase in temperature differential as the cold end of the heat exchange means is approached. An exchanger of this type wherein the nature of the gases is similar and the mass in the two streams is identical may be termed "a balanced exchanger." When however, the effective heat capacity of the stream being cooled is decreased relative to the effective heat capacity of the stream being warmed, as by artificially increasing the mass of the stream being warmed, or by applying refrigeration to the stream being cooled, or by various other means, the system is said to be thermally "unbalanced" and the mechanism by which this "unbalance" is effected is called the "unbalancing means."

As it has been known in the prior art, "unbalance" has had for its purpose the reduction of the temperature differential at the cold end of the reversing exchanger in order to permit complete revaporization of the deposited carbon dioxide on reversal. It has always resulted in decreasing the average temperature differential and, as a consequence, has been harmful to the heat transfer rates. Accordingly, the exchange of heat between the product streams and the incoming air is preferably accomplished in two stages of which the lower temperature stage is unbalanced and the higher temperature stage is not. The deposition of the carbon dioxide from the air stream occurs entirely in the lower temperature stage while the bulk of the water is deposited in the higher temperature stage.

At the warm end of the two stages of heat exchange, the temperature differential is determined by the amount of refrigeration available in excess of the heat leak into the air separation plant. In the latest designs of large scale oxygen plants, this refrigeration is provided by expansion of approximately 20% of the inlet air in a work engine. Under these conditions, a warm and differential temperature of the order of 12° to 13° F. is maintained. This temperature differential is about the maximum economically obtainable under normal large scale oxygen plant conditions, since added refrigeration from internal sources requires expansion of a larger proportion of the air and a loss in oxygen purity or oxygen recovery is experienced. The provision of refrigeration from an external source has been generally considered to be excessively expensive.

Figure 1 is a graphic showing illustrating the normal temperature differential in an air-cooling operation in which air under 70 p. s. i. g. pressure is cooled by countercurrent heat exchange with separated products at 1 p. s. i. g. pressure. Curve A shows the temperature differential in the warm stage of the exchanger in the absence of unbalance, while curve C illustrates the temperature differential in the cold stage of the exchanger with unbalance by internal means introduced to the degree necessary to permit complete vaporization of the deposited carbon dioxide. Curve B represents the differential temperature in the warm stage of the exchanger when introducing unbalance in this stage by external means according to the working of the present invention.

Figure 1 also shows in curves D and E the critical temperature differentials which must not

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be exceeded if complete revaporization of the deposited ice and solid carbon dioxide is to occur, for the case when both product streams are employed to revaporize these impurities. It will be noted that in the warm stage of the two stage exchanger, the allowable temperature differential for complete removal of deposited water is progressively higher as the temperature level is raised, that is, as the warm end is approached, and is substantially in excess of the normal differential temperature, indicated by curve A, over most of this heat exchange. In this connection, heat transfer rates could be increased and surface requirement decreased in proportion to any increase in temperature differential which could be achieved.

It is highly desirable, therefore, to supply added refrigeration from an external source to the oxygen plant and further to distribute this added refrigeration in such a manner as to increase progressively the temperature differential between the inlet air and the product streams as the warm end of the exchanger is approached. This desirable feature may be obtained if the refrigeration is supplied in the form of cold gas employed in countercurrent heat exchange with the inlet air. The processing of this invention is a means by which added refrigeration can be supplied to the oxygen plant in a manner particularly advantageous for achieving economy in the heat transfer equipment.

According to the present invention, a cold gas stream is employed as an "unbalance" stream in the warmer stage of a two-stage reversing exchanger, in which the air feed supply to an air fractionating tower is being cooled and purified. The cold stream is introduced into the heat exchange system at such a temperature level and in such quantity as to cause the temperature differential between the reversing gas streams—inlet air and returning oxygen and nitrogen products—to increase progressively toward the warm end of the exchanger in a manner roughly paralleling the progressive increase in allowable temperature differential for complete revaporization of deposited water. At all times, however, the margin between the allowable temperature differential for complete revaporization and the actual temperature differential is kept such that buildup of deposited ice is not allowed to occur to a harmful degree. Normally this means that the actual temperature differential will be somewhat less than that theoretically allowable for complete revaporization, as is illustrated by curve B in Figure 1. Where the quantity of deposited impurity is very small, as is the case with air which has had practically all of its water content already frozen out, the theoretical differential temperature may be exceeded without resulting in an excessively high rate of accumulation of the deposited impurity. In general, unbalance according to the method of the invention may be employed from atmospheric temperature down to about -200°F .

When the oxygen plant is operated in conjunction with a hydrocarbon synthesis unit operating at substantial pressure, a particularly attractive source of the cold gas stream required for unbalance, in the manner of the invention, is the tail gas leaving the absorber of the hydrocarbon synthesis unit. This tail gas may be cooled from the absorber temperature level to the temperature range desired for the oxygen plant unbalance stream by expansion through an engine, such as a Kapitza-type turbo-expander. The

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cold expanded tail gas may be used directly as the unbalance stream, or it may be used in an indirect manner, as by abstracting heat from a separate gas stream which is recycled through the warm-stage reversing exchanger of the oxygen plant and is thus the actual unbalance stream.

In order to employ the tail gas from a hydrocarbon synthesis unit most effectively as a source of the refrigeration required for the unbalance operation outlined, the moisture content of the tail gas stream must be reduced to a very low level, since otherwise ice deposition in the expander engine and possibly on the heat transfer surfaces will occur. Drying to a satisfactory degree can be accomplished by passing the tail gas under pressure over beds of silica gel or activated alumina. Similarly deposition of carbon dioxide snow is preferably prevented, and although very substantial contents of carbon dioxide, of the order of 25% by volume may be tolerated, it may in certain cases be desirable to adjust the carbon dioxide content before expansion, as by contacting with an easily regenerated amine solution.

In employing a cold gas stream in the manner advanced by the invention, the unbalance resulting in the reversing exchanger from this added source of cooling will permit the temperature differential to be increased at the warmer end and accordingly, will improve significantly the heat transfer rates. Furthermore, by varying the amount and temperature level of the unbalance refrigeration supplied, the temperature differential curve can be adjusted at will over a wide range. In this connection, reference is again made to Figure 1 in which the temperature differential is shown throughout the air cooling zone along with the permissible differential temperature for effective purification. The curves are drawn for conditions indicated to be optimum and representative of current design. Curve A represents the differential temperature in the absence of unbalance in the warm stage of heat exchange. From this curve, it will be seen that above -110°F . (350°R .), there is a progressively increasing departure from the permissible temperature differential. By the introduction of unbalance in the form of cold gas, the differential temperature is shifted to curve B which substantially matches the allowable differential on the design basis of 70% saturation of the product oxygen and nitrogen streams with regard to water vapor.

According to the invention, therefore, an auxiliary cold gas stream is utilized to provide refrigeration for air supplied to an air fractionation unit, over a range of temperature from inlet conditions to an intermediate temperature level. This auxiliary cold gas stream may in preferred operation represent dried tail gas from a hydrocarbon synthesis unit operated under pressure, which has been cooled by expansion through a work engine, or a closed circulating gas system to which the refrigeration capacity of such expanded tail gas transferred. The work engine produces available power which may be employed in driving compression equipment or other power consuming equipment necessary in the operation of the air fractionation unit, and hence contributes to the further efficiency of operation of the air fractionation equipment. The cold gas stream produced by expansion, or by interchange with the expanded stream, or supplied from some other external source, will

pass continuously through heat transfer passages in the first stage of the reversing exchanger of the air fractionation plant in order to obtain the desirable gradient in temperature differential. Due to the refrigeration unbalance provided by the cold gas, a warm end differential of about 35° F. or even higher can be employed, compared to the normal differential of from 5 to 15° F. when this auxiliary refrigeration is not supplied. In the second stage of the reversing exchanger the inlet air is further cooled to about -275° F. with the oxygen and nitrogen streams obtained from the air fractionation unit. The cold end differential temperature is reduced to about 6° F. as desired for effective resublimation of deposited solid carbon dioxide, by any of the known techniques for producing unbalance, as by recycling portions of the nitrogen stream or of the cold air stream. The present invention is concerned only with the cooling obtained in the first stage and mention is made of the second stage only for purposes of completeness.

In order that the invention may be more fully understood, the following description of an embodiment, in which the warm stage unbalance is provided directly by expanded hydrocarbon synthesis tail gas, is presented. In understanding this description, reference is also made to Figure 2 in which a diagrammatic showing is presented of a two-stage shell and tube type reversing exchanger for the cooling of the inlet air stream. A piping and valve arrangement is depicted in Figure 2 setting forth means for effecting the reversal of the air stream on the one hand and the oxygen and nitrogen streams on the other, through the heat exchangers 10 and 50 and 10' and 50', so that during alternate periods, the air passes through the tube side of the heat exchangers while the oxygen and nitrogen pass through the shell side, and after reversal the air passes through the shell side of the exchangers while the oxygen and nitrogen pass through the tube side.

In a hydrocarbon synthesis unit in which 50 mm. CFD of natural gas are burned with 31.4 mm. CFD of 95% oxygen to produce synthesis gas for the reaction step, approximately 29.4 mm. CFD of tail gas is discarded from the absorber plant at a pressure of 400 p. s. i. g. and 100° F. This gas has the following approximate composition: 34% N₂, 28% CO₂, 18% N₂, 12% CH₄, 4-5% heavier hydrocarbon, 0.25% H₂O and 3.25% CO. About 123 mm. CFD of air must be cooled, liquefied and separated to provide the necessary oxygen for the combustion of the natural gas. The cooling is effected as shown in the drawing in two pairs of reversing exchangers 10 and 10' and 50 and 50'. Passing through the exchangers 10 and 50 is shown the stream of nitrogen as indicated by the reference numeral 14 while the stream of oxygen indicated by 12, passes through exchangers 10' and 50'. Into the reversing exchangers 10 and 10' air is passed through line 16 at a pressure of 75 p. s. i. g. and 105° F. The air is removed from the exchanger 10 and 10' through line 18. Also passing into the heat exchangers 10 and 10' through line 20 is the expanded tail gas at a temperature in this embodiment of -125° F. The warmed tail gas is removed from the exchanger through line 22. The air removed from exchangers 10 and 10' is passed into exchangers 50 and 50' and is removed therefrom through line 26. A portion of the air removed through line 26 is recycled into heat exchanger 50 and 50' through line 28 and thence

through line 30 to an expansion engine 32. Also another portion of the air removed through line 26 may be passed directly through line 34 to the expansion engine 32. After passing through the expansion engine 32, the air stream is sent directly to the low pressure fractionation tower (not shown). The cooled and purified air leaving through line 40 at a pressure of 74 p. s. i. g. is sent to the high pressure fractionation tower (not shown). The nitrogen stream passed through line 14 may pass as a single stream through the exchanger 50 or as shown in the drawing, a portion may be diverted through line 36 into exchanger 50 and 50' and thence recycled through line 38. The N₂ and air streams passing through lines 28 and 36 represent possible forms of unbalance in the second stage of the reversing heat exchange, and are outside the scope of the present invention.

In the operation of the exchangers 10 and 50, the flow of the nitrogen is alternated between the interior and the exterior of the tubes in opposition to similar shifts in flow path of the air stream by suitable manipulation of valves V-1, V-2, V-3 and V-4, so that alternate deposition and vaporization of impurities occurs on any unit of surface. The flow of recycle N₂ through line 36, of recycle air through line 28, and of cold expanded absorber gas through line 20 is continuously through certain tubes reserved for this purpose, since these streams must be kept separate from the others and are not required to act as revaporization agents. It will be appreciated that where both oxygen and nitrogen are being reversed against air, the two products must be kept separate by passing them through separate though parallel exchanger units. Similarly, alternation of the flow paths of oxygen and air in exchangers 10' and 50' is obtained by simultaneous manipulation of valves V-5, V-6, V-7 and V-8. Alternatively, the oxygen may be passed continuously through certain of the tubes and only the nitrogen reversed, but this has the effect of reducing the allowable differential temperatures for complete revaporization of deposited impurities.

With air admitted through line 16 at a temperature of 105° F. and a pressure of 75 p. s. i. g. expanded tail gas admitted through line 20 at -125° F. and oxygen-nitrogen streams admitted to the reversing exchanger 10 at a temperature of -124.3° F., the air leaving the exchanger through line 18 is of a temperature of -110° F. The cooled air passing into the exchanger 50 through line 24 has a temperature of removal through line 26 of -275° F. and a pressure of 74 p. s. i. g. The temperature of about -124° F. for the product streams entering exchanger 10 is maintained by the passage into the exchanger 50 of oxygen and nitrogen streams through line 12 for the oxygen at a temperature of -281° F. and through line 14 for the nitrogen of -291° F. By control of the flow through lines 28, 30 and 34, the air passed to the expander 32 has a temperature of -234° F. and a pressure of 73 p. s. i. g., which are altered by the expansion to -306° F. and 3 p. s. i. g.

For the production of the required degree of unbalance in the oxygen plant, 16.5 mm. CFD of the absorber tail gas is required from a total of 29.4 mm. CFD. The remaining 12.9 mm. CFD is available for other uses. If desired it may be similarly expanded, making available about 2,000,000 B. t. u. hr. of additional refrigeration below 70° F. About 68 H. P. of by-product power

are produced for each 1 mm. CFD expanded, or a total of approximately 2000 H. P. from the total absorber tail gas stream.

Although the invention is particularly useful in the separation of air, it will be understood that it may be usefully used in conjunction with many other processes involving low temperature purification of gaseous streams, as for example in the separation of helium from natural gas, and in the drying of hydrocarbon gases prior to low temperature fractionation. In such cases the auxiliary refrigerant stream employed for unbalance is readily obtained by drying a small portion of the gas being processed and expanding it through a turbine in order to cool it to the desired degree. Also, although the invention has been particularly described and illustrated with regard to shell and tube reversing exchangers, it is to be understood that the invention is also applicable to any other type of heat exchange means employing regular alternation of the flow paths, such as Frankel type accumulators.

What is claimed is:

A process of pre-cooling air by heat transfer from the cool products of air distillation which comprises passing said air in heat transfer relationship and in countercurrent flow with product streams obtained by the distillation of air periodically causing the air to traverse the paths previously traversed by the product streams of the distillation process, but in the opposite di-

rection, and improving the efficiency of the cooling process by continuously passing, in the warmer stage of the system, an extraneous cooling fluid as a separate stream in heat exchange relationship with the said air and product streams and in the same direction as the said product streams, and introducing said extraneous cooling fluid in such quantity and at such a temperature level as to cause a progressive increase of temperature differential between the air streams and the product streams as the warmer end of the heat exchanging streams is approached, such said last named temperature differential being the maximum at the warm end of the streams that will still permit revaporization of the ice.

HENRY J. OGORZALY.

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