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Nov. 16, 1943. F. KOEHLER 2,334,632

RECOVERY OF NITROGEN AND OXYGEN

Filed Dec. 15, 1939 3 Sheets-Sheet 1

Fig. 1.

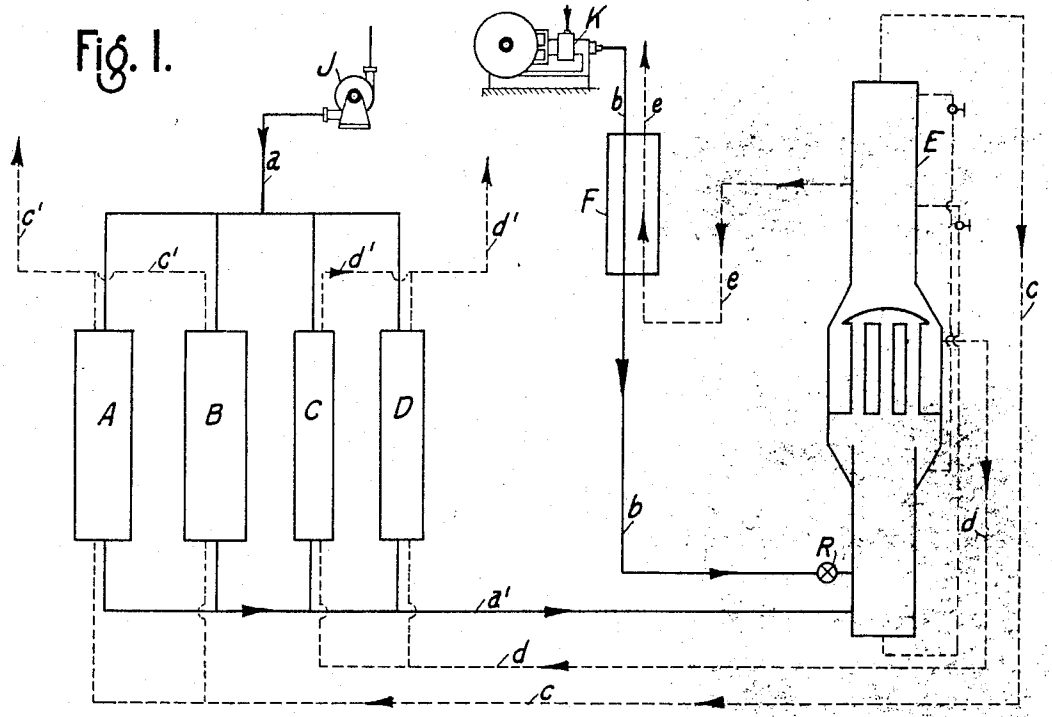
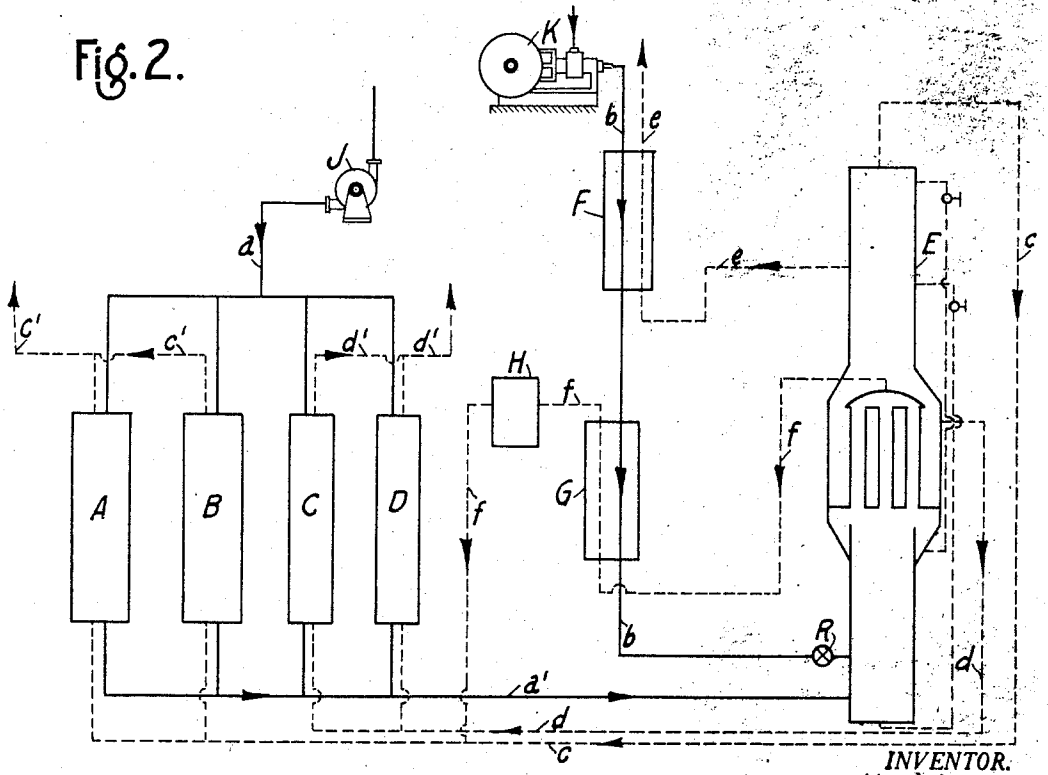


Fig. 2.



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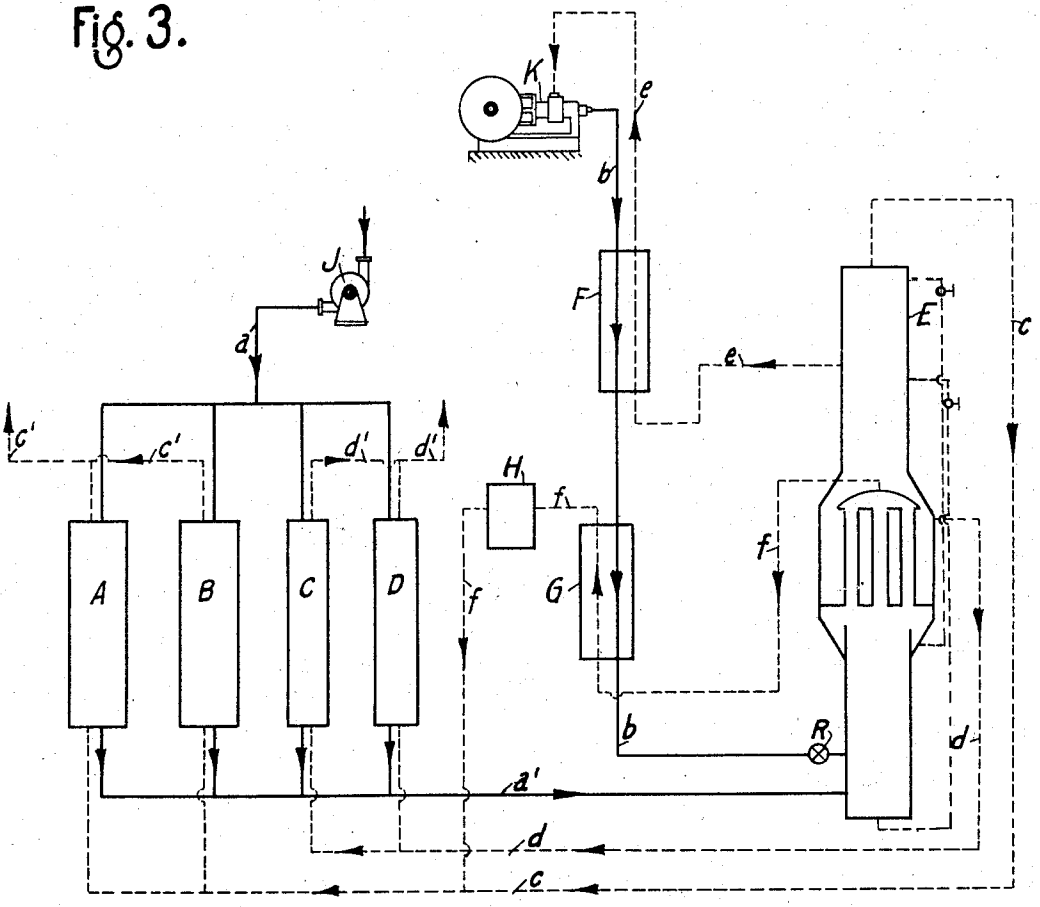
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RECOVERY OF NITROGEN AND OXYGEN

Filed Dec. 15, 1939 3 Sheets-Sheet 2

Fig. 3.



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RECOVERY OF NITROGEN AND OXYGEN

Filed Dec. 15, 1939 3 Sheets-Sheet 3

Fig. 4.

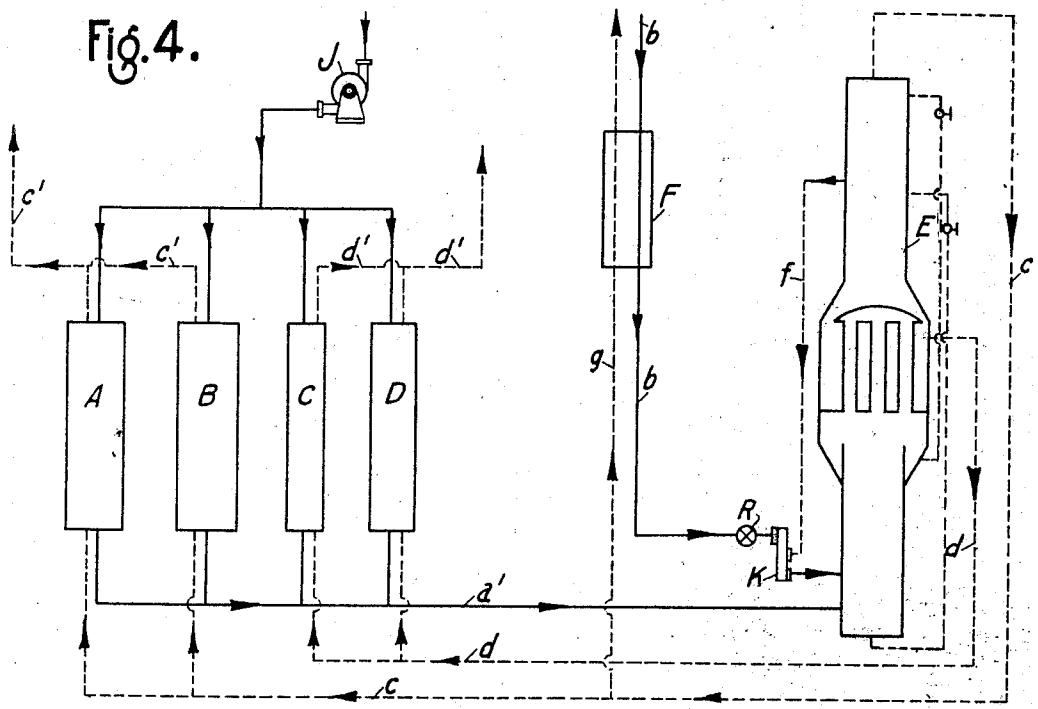
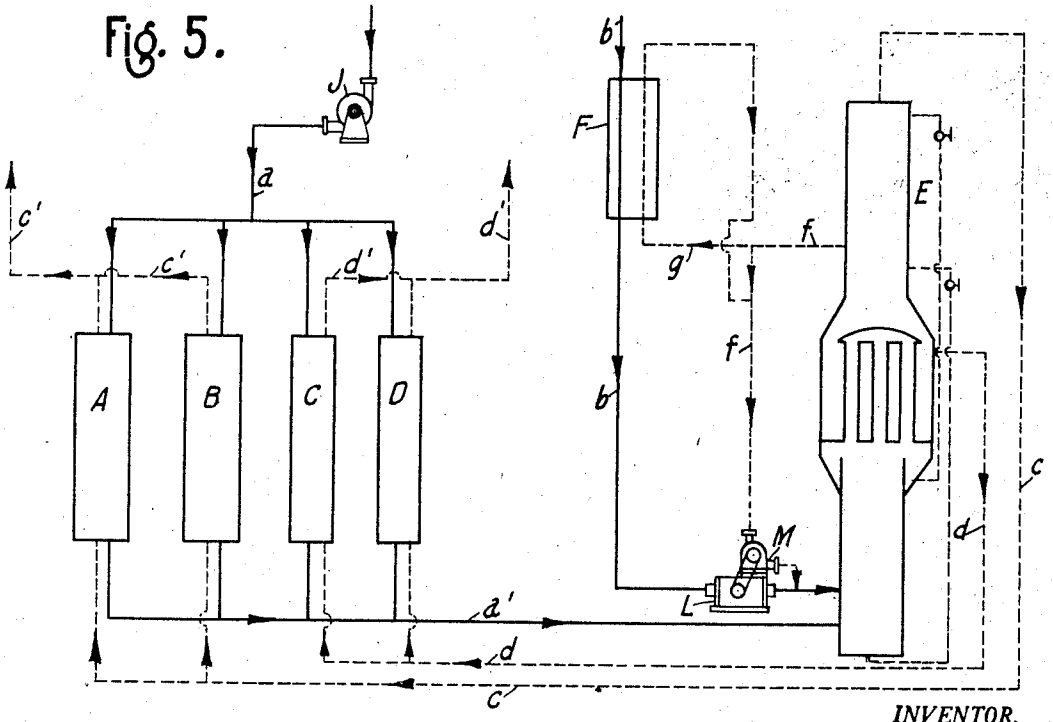


Fig. 5.



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UNITED STATES PATENT OFFICE

2,334,632

RECOVERY OF NITROGEN AND OXYGEN

Franz Koehler, Leuna, Germany; vested in the Alien Property Custodian

Application December 15, 1939, Serial No. 309,446
In Germany August 28, 1937

14 Claims. (Cl. 62—175.5)

The present invention relates to improvements in, and apparatus for, the recovery of nitrogen and oxygen.

It is already known that practically pure nitrogen and oxygen can be prepared by liquefaction of air at high pressure in counter-current tubular heat-exchangers and subsequent rectification of the liquefied mixture. This method has two considerable disadvantages, however, namely (1) that a great part of the air to be separated into its constituents must be brought to high pressure and (2) that all water and carbon dioxide must be removed from all the air before the liquefaction in order to avoid stoppages in the counter-current tubular heat-exchangers.

By reason of these disadvantages, another process has been in use for several years in which considerably lower pressures are used and in which it is unnecessary to separate the water vapor and carbon dioxide from all the air before the liquefaction. This method differs mainly from that already mentioned in that the heat-exchange is not effected by a counter-current flow of the gas to be cooled and the gas absorbing heat in tubular exchangers but in so-called regenerators or recuperators which are cooled periodically, whereby the cooling required to make up for the heat gained is produced by releasing from pressure a small amount (from about 4 to 10 per cent) of all the air compressed to high pressure (as for example 200 atmospheres) and if necessary by releasing from pressure one of the gases to be recovered in expansion engines. By reason of the advantages attending this method, it has acquired a great importance for the recovery of oxygen, although by the said method it is impossible to obtain pure nitrogen as well as the pure oxygen.

I have now found that by the last-mentioned method both nitrogen and oxygen of high purity can be prepared by withdrawing from the central part of the upper of the two columns used for rectification a small amount of a mixture of nitrogen and oxygen and using its low heat content within the system.

In other processes for separating air into its constituents in which a recuperator is not used, it has already been proposed to withdraw a mixture of nitrogen and oxygen at a central part of the fractionation column in order to obtain purer nitrogen and purer oxygen. It could not have been expected, however, that this step would be useful in a method using a recuperator in which any removal of a gas mixture from the system would be deemed injurious because considerable amounts of nitrogen and oxygen are necessary for the removal of the substances (carbon dioxide and water) separated in the recuperator from the gases which are not purified according to the said process.

In spite of this, however, pure nitrogen and oxygen are obtained according to this invention by the withdrawal of a certain amount of a mixture of nitrogen and oxygen at a central part of the upper column, when the amount of highly compressed, preleminarily purified air is increased as a substitute for the withdrawn gas mixture and as an additional source for the cooling. This additional highly compressed air provides the additional amount of nitrogen and oxygen necessary for the continuous removal of the impurities from the recuperator. Moreover, by releasing the pressure on the same, so much cooling is effected that all the nitrogen of the lower column can be used as a trickling liquid for the upper column. In this way it is possible to recover in the same apparatus not only very pure oxygen but also very pure nitrogen.

The production of the additional highly compressed and preliminarily purified air, according to this modification, requires extra energy and therefore involves extra expense. This may be avoided according to another modification of the invention by combining the steps usual in the low pressure process with the withdrawal of a small amount of a nitrogen-oxygen mixture from the central part of the upper of two columns used for rectification, i. e. by using expansion engines in which nitrogen withdrawn from the lower rectification column is released from pressure for the purpose of cooling economically. Contrary to expectation it has been found that in this modification of the invention, in spite of the relinquishment of a part of the trickling liquid by reason of the release from pressure of a part of the nitrogen of the lower column in expansion machines, only a relatively small amount of a mixture of nitrogen and oxygen need be withdrawn from the central part of the upper column. Additional large amounts of preliminarily purified, highly compressed air are not necessary.

The invention therefore has the advantage of requiring only a simple apparatus, a small expenditure of energy and the use of low pressures for the major portion of the air and of not requiring a preliminary purification of the major portion of the air.

The mixture of oxygen and nitrogen can be withdrawn from the rectification column at a point at which it contains from about 5 to 35, preferably from 15 to 25 per cent of oxygen. By withdrawing such a mixture there are produced in the rectification column such equilibrium relations that the amount of trickling liquid (nitrogen) present is sufficient for washing the mixture of nitrogen and oxygen even when a part of the nitrogen has been withdrawn from the lower column for the cooling in expansion engines.

The mixture of nitrogen and oxygen withdrawn from the upper rectification column serves in particular to precool the highly compressed air used for the additional refrigeration. This highly compressed air is released to the pressure prevailing in the rectification column and introduced into the upper or lower rectification column to absorb heat.

The highly compressed air, after the precooling by the mixture of nitrogen and oxygen withdrawn, may be further cooled by heat exchange with that part of the air or of the nitrogen which is withdrawn from the rectification column in the manner known in the low pressure process in order to be released from pressure in an expansion engine to about the temperature of liquid air.

A specially advantageous modification of the present invention consists in adding the mixture of nitrogen and oxygen withdrawn from the middle of the upper rectification column, after subjection to heat exchange, to the air to be separated into its constituents. Since this added mixture of nitrogen and oxygen is free from water and carbon dioxide, the content of water and carbon dioxide in the air to be separated into its constituents is reduced. It is then readily possible for these substances, which are deposited by the cooling of the air in the recuperators, to be further removed in the next working operation by the pure oxygen and the pure nitrogen without it being necessary to increase the amount of highly compressed air purified from water and carbon dioxide supplied for the further cooling of the mixture to be separated into its constituents in the rectification column, in order to render certain the sublimation of the deposited substances in the recuperators.

In some cases it may be advantageous to compress the gas mixture withdrawn from the central part of the upper rectification column to high pressure after the heat exchange and to use it instead of the highly compressed air serving for the cooling by releasing it from pressure, if desired in expansion engines. In this way the amount of air which must be freed from water and carbon dioxide before its cooling is still further reduced.

Another way in which the low heat content of the gas mixture withdrawn from the upper rectification column may be utilized consists in using the mixture for the cooling of one or more additional recuperators which are arranged parallel with the pair of recuperators through which the nitrogen and oxygen flow. It may also be used for the preliminary cooling of the initial air while it is under low pressure.

Another particularly advantageous modification of the present invention consists in introducing the gas mixture withdrawn from the upper column of the rectification vessel directly into the lower column, preferably with the aid of the energy produced when releasing the said highly compressed air from pressure. To this end the mixture is caused to be sucked by the highly compressed air supplied to the lower column through a spray nozzle behind the release valve, being thus compressed to the pressure of the lower column.

This measure lessens the amount of highly compressed air required to the amount required for the obtaining of pure oxygen alone, according to the known process, and yet to obtain pure oxygen and pure nitrogen simultaneously from air in an output of approximately 100 per cent.

Another modification of this process consists in compressing the mixture of nitrogen and oxygen to the pressure of the lower rectification column, for example, by means of a revolving compressor. The compressor may be driven by the energy released in an expansion engine by all or a part of the highly compressed air to be introduced into the lower column.

This method of returning a mixture of nitrogen and oxygen from the upper column into the lower one offers the combined advantage that any increase in the quantity of highly compressed air otherwise necessary is avoided and that a considerably larger amount of heat is withdrawn if the highly compressed air be released from pressure with the performance of external work than by the Thompson-Joule effect alone, so that the quantity of highly compressed air required to make up for the gains in heat may be decreased even more, unless they are compensated for in a known and inexpensive way by releasing low-pressure nitrogen from pressure in an expansion turbine. Thus the process makes it possible to simultaneously obtain pure nitrogen and pure oxygen from the air in an output of approximately 100 per cent with an extremely small expenditure of energy.

In the process according to the present invention there is no interchange of heat between the mixture of nitrogen and oxygen withdrawn from the upper column and the highly compressed air. Such interchange may be established, however, between part of the mixture and the highly compressed air, whereupon both fractions of the mixture are introduced in combination into the lower part of the rectification tower in the manner above referred to. Instead of the said mixture of nitrogen and oxygen, a small amount of pure nitrogen also may be withdrawn in front of the regenerators and used for cooling the highly compressed air.

Five embodiments of apparatus in accordance with this invention will now be described with reference to the accompanying drawings, but the invention is not restrcted to the particular embodiments shown.

In Fig. 1, A, B, C and D are recuperators which are operated alternately in known manner, E is a two-column apparatus for separating air into its constituents, F is a counter-current heat exchanger, J is a low pressure air turbo-compressor, R is a pressure release valve and K is a high pressure air compressor.

The air compressed by the compressor J to about 4.5 atmospheres is cooled in the recuperators A, B, C and D almost to the liquefaction temperature and introduced through a pipe *a'* into the lower column of the apparatus E for rectification. Furthermore a certain amount of air compressed to about 200 atmospheres and freed from water and carbon dioxide is led through a pipe *b* and the heat exchanger F and released from pressure through the pressure-release valve R into the lower rectification column. The cold constituents (oxygen and nitrogen) are led from

the upper column, in which a low pressure prevails, through pipes *c* (nitrogen) and *d* (oxygen) into recuperators A, B, C, D from which they escape through *c'* and *d'* after absorbing heat. From about the middle of the upper rectification column, there is withdrawn through *e* a small amount of a mixture of nitrogen and oxygen which is led through heat exchanger F in counter-current to the highly compressed air introduced at *b*.

The embodiment according to Figure 2 differs from that according to Figure 1 in that for the purpose of additional cooling, nitrogen under a pressure of about 4.5 atmospheres is withdrawn from the lower rectification column and supplied through a pipe *f* to a counter-current exchanger G in which it absorbs part of the heat of the highly compressed air precooled in F. This nitrogen is then released from pressure in the expansion engine H and led into the recuperators A and B together with the nitrogen escaping from the upper rectification column.

In Figure 3 the mixture of oxygen and nitrogen withdrawn through *e* from the middle part of the upper rectification column in this embodiment is compressed by the compressor K, after flowing through heat-exchanger F, and used instead of the highly compressed air serving for the cooling by releasing it from pressure with the aid of the pressure release valve R.

According to Figure 4, the air having been compressed to about 4.5 atmospheres by the compressor J is cooled down nearly to liquefaction temperature in the cooling tanks A, B, C and D and fed through line *a'* into the lower column of the separator E for rectification. Besides, a certain quantity of air free of water and carbon dioxide and compressed to about 200 atmospheres is released from pressure through line *b*, by way of the release valve R and the spray nozzle K, into the lower rectification column. The cold separation products oxygen and nitrogen flow through the lines *c* (nitrogen) and *d* (oxygen) into the recuperators A, B, C and D, whence they are led off through *c'* and *d'* after absorbing heat from the incoming air. Approximately from the middle of the upper rectification column a small quantity of the mixture of nitrogen and oxygen is withdrawn through *f* and introduced into the lower rectification column through the spray nozzle K. The highly compressed air, prior to being released from pressure, is cooled down in a heat exchanger F by means of a small amount of nitrogen branched off from line *c* and passed to F through line *g*.

In the embodiment according to Figure 5, in distinction from that according to Figure 4, the release from pressure of the highly compressed air is accomplished in an expansion apparatus L, which actuates a gas compressor M by which the mixture of nitrogen and oxygen withdrawn from the upper column through *f* is brought to the pressure of the lower column and then introduced into the latter. The highly compressed air is precooled in this case prior to being released from pressure, by a cold mixture of nitrogen and oxygen which is branched off from the line *f* and passed to F through line *g'*.

This application is a continuation-in-part of my co-pending application Ser. No. 226,597, filed August 24, 1938.

What I claim is:

1. Apparatus for rectifying air into substantially pure nitrogen and oxygen which comprises a plurality of recuperators, a two-column rectification vessel, means for forcing air through said recuperators and into said rectification vessel, means for forcing a comparatively small quantity of highly compressed air into the lower column of the rectification vessel, means for reducing the pressure of said highly compressed air during its introduction into the rectification vessel, means for separately removing substantially pure nitrogen and oxygen from the rectification vessel, means for conducting the same in heat-exchange relationship through the recuperators, means for withdrawing a mixture of nitrogen and oxygen from the upper column of the rectification vessel and means for recycling said mixture.

2. Apparatus according to claim 1 which comprises further means for precooling the said highly compressed air before introducing it into the rectification vessel by heat-exchange with the mixture of nitrogen and oxygen withdrawn from the upper column of the rectification vessel.

3. Apparatus according to claim 1 which comprises further means for introducing the gas mixture withdrawn from the upper column of the rectification vessel into the lower column of the rectification vessel with the aid of the energy produced when releasing from pressure the said highly compressed air.

4. Apparatus according to claim 1 which comprises further means for operating a compressor by which the gas mixture withdrawn from the upper column of the rectification vessel is introduced into the lower column of the rectification vessel with the aid of the energy produced when releasing from pressure the said highly compressed air.

5. Apparatus according to claim 1 which comprises further means for compressing the gas mixture withdrawn from the upper column of the rectification vessel and means for releasing the pressure thereon while introducing it into the rectification vessel.

6. Apparatus according to claim 1 which comprises further means for adding at least a portion of the gas mixture withdrawn from the upper column of the rectification vessel to the air to be rectified.

7. Apparatus according to claim 1 which comprises further means for withdrawing nitrogen from the lower column of the rectification vessel and for using it as cooling medium and a machine for releasing it from pressure.

8. Apparatus according to claim 1 which comprises further means for withdrawing nitrogen from the lower column of the rectification vessel and for using it as cooling medium for the said highly compressed air.

9. Apparatus according to claim 1 which comprises further means for cooling the said highly compressed air by heat-exchange with a part of the nitrogen withdrawn from the upper end of the rectification vessel.

10. Process of rectifying air into substantially pure nitrogen and oxygen which comprises refrigerating air at a slightly elevated pressure in recuperators periodically cooled to very low temperature, passing the refrigerated air into a two-column rectification vessel to thereby effect rectification of the air into its major constituents, separately withdrawing said constituents and using them as cooling medium for the said recuperators, withdrawing a relatively small amount of a mixture of nitrogen and oxygen from the upper column of the said rectification vessel compressing it to high pressure and introducing it

into the lower column of the rectification vessel while releasing it from pressure.

11. Process of rectifying air into substantially pure nitrogen and oxygen which comprises refrigerating air at a slightly elevated pressure in recuperators periodically cooled to very low temperature, passing the refrigerated air into a two-column rectification vessel to thereby effect rectification of the air into its major constituents, separately withdrawing said constituents and using them as cooling medium for the said recuperators, withdrawing a relatively small amount of a mixture of nitrogen and oxygen from the upper column of the said rectification vessel compressing it to high pressure after using it as cooling medium and introducing it into the lower column of the rectification vessel while releasing it from pressure.

12. Apparatus according to claim 1 which comprises further means for compressing the gas mixture withdrawn from the upper column of the rectification vessel with the aid of the energy produced when releasing from pressure the said highly compressed air and means for introducing it into the lower column of the rectification vessel.

13. Process of rectifying air into substantially pure nitrogen and oxygen which comprises refrigerating air without liquefaction at a slightly elevated pressure in recuperators periodically cooled to a very low temperature, passing the refrigerated air into a two-column rectification vessel, introducing a relatively small quantity of highly compressed air into the lower column of said vessel while releasing the pressure thereon to thereby effect rectification of the air into its major constituents, separately withdrawing said constituents and using them as cooling medium for the said recuperators, withdrawing a relatively small amount of a mixture of nitrogen and oxygen from the upper column of the said rectification vessel and utilizing its low heat content to cool said highly compressed air.

14. Apparatus for rectifying air into substantially pure nitrogen and oxygen which comprises a plurality of recuperators, a two-column rectification vessel, means for forcing air through said recuperators and into said rectification vessel, means for forcing a comparatively small quantity of highly compressed air into the lower column of the rectification vessel, means for reducing the pressure of said highly compressed air during its introduction into the rectification vessel, means for separately removing substantially pure nitrogen and oxygen from the rectification vessel, means for conducting the same in heat-exchange relationship through the recuperators, means for withdrawing a mixture of nitrogen and oxygen from the upper column of the rectification vessel and means for conducting said mixture in heat-exchange relationship with the highly compressed air.

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