United States Patent [19]

Frischbier

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[54] **CONCENTRATING KRYPTON AND XENON IN AIR SEPARATION BY LIQUID OXYGEN WASH**

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[30] **Foreign Application Priority Data**

Nov. 10, 1970 Germany ..... P 20 55 099.6

[52] **U.S. Cl.** **62/41,** 62/22, 62/29

[51] **Int. Cl.** **F25j 3/02,** F25j 3/03

[58] **Field of Search** 62/22, 23, 24, 27, 62/28, 29, 41

[56] **References Cited**

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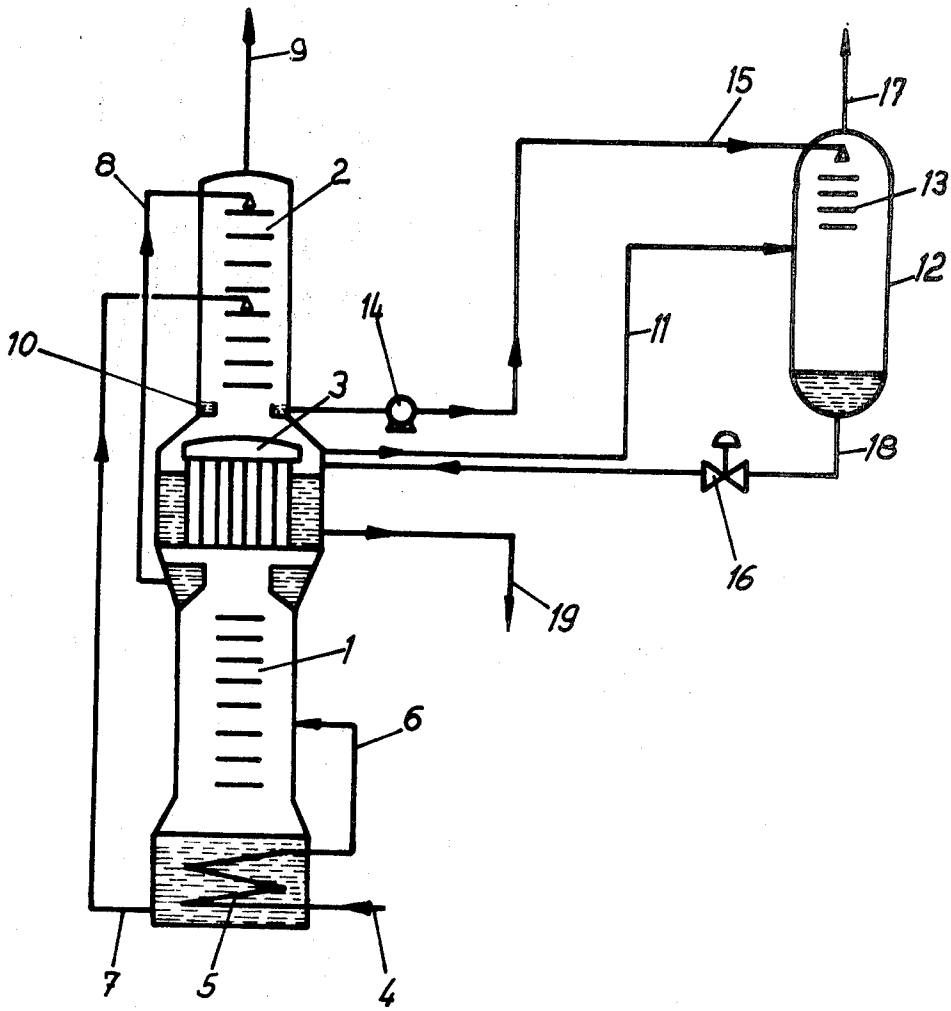
[57] **ABSTRACT**

In air separation, oxygen containing krypton, xenon and hydrocarbons is passed from the rectifying column to a separator where as a rising gas it is washed with a controlled downflow of liquid oxygen drawn from above the sump liquid in the column. The controlled washing permits gaseous oxygen and some methane to leave the separator top while krypton and xenon are trapped in the wash liquid which returns from the separator bottom to the column sump. Thus enriched sump liquid is withdrawn for further processing to recover krypton and xenon.

8 Claims, 2 Drawing Figures



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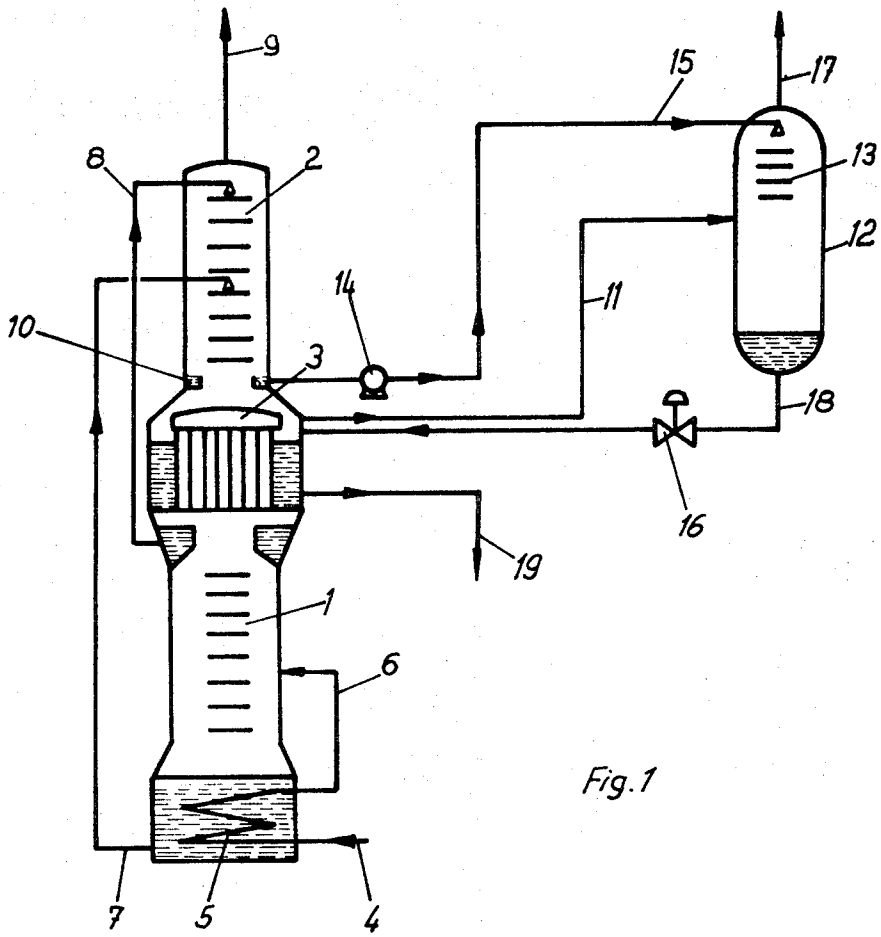

Fig. 1

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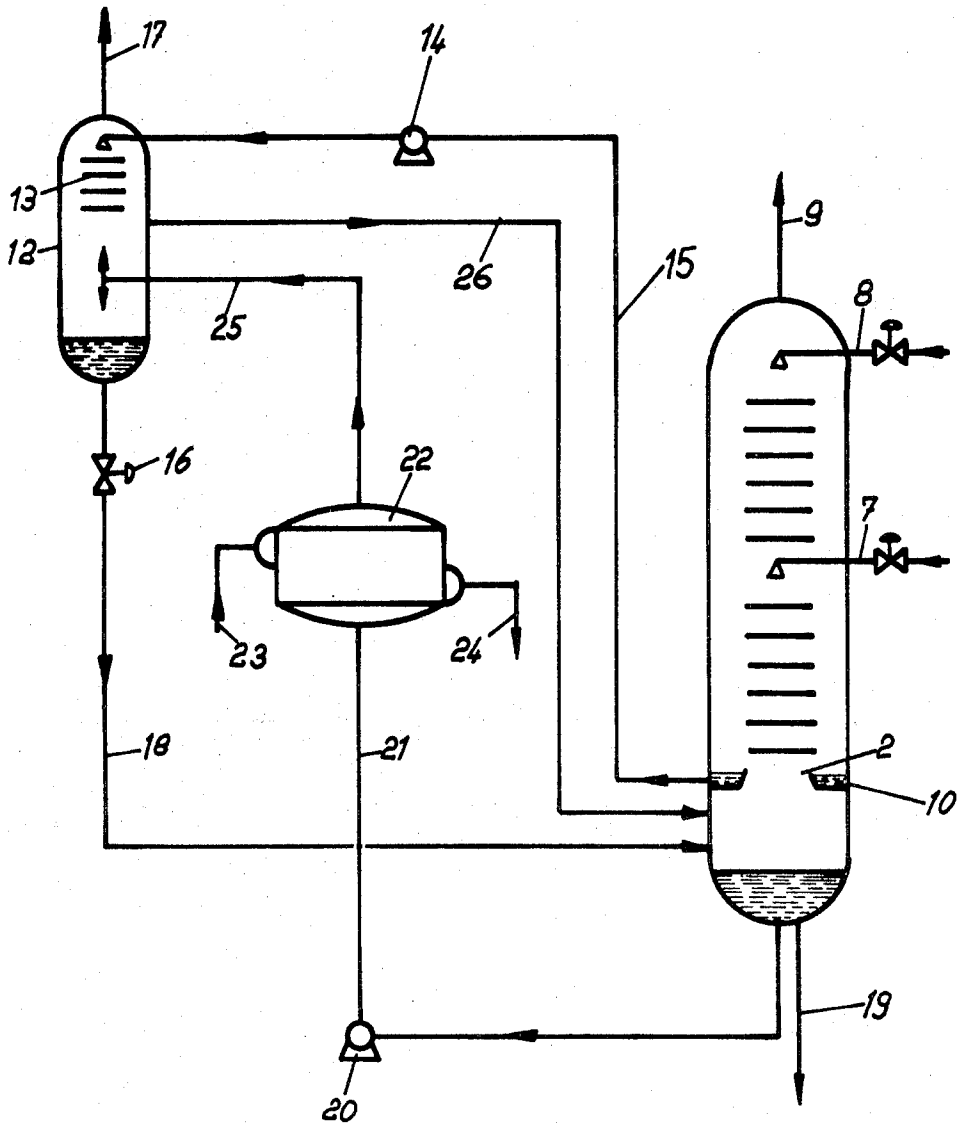

Fig. 2

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CONCENTRATING KRYPTON AND XENON IN AIR SEPARATION BY LIQUID OXYGEN WASH

BACKGROUND OF THE INVENTION

This invention relates to the concentration of krypton and xenon in air separation systems.

Very small traces of krypton and xenon are present in the air. The krypton content is about 1 ppm (part per million) by volume and the xenon content about 0.08 ppm by volume. Both rare gases are higher-boiling than oxygen (X 165°K; Kr 120°K; O_2 90°K). Therefore, in air separation plants, they end up in the liquid oxygen. The air contains such small proportions of these two rare gases that, first of all, a large volume of feed air is required in order to recover a measurable amount and, secondly, a process is required for concentrating these slight traces in the liquid oxygen. This concentration represents the first intermediate step toward complete separation of the krypton and xenon from the oxygen. This invention is particularly directed to this first intermediate step.

The recovery of krypton and xenon in commercial proportions is associated with large air separation plants. These operate in accordance with the known low-pressure process with air compression to about 5 atmospheres; cooling down in regenerators or reversing plate exchangers; fractionation into the two main components, oxygen and nitrogen, in a double rectifying column; recovery of the products in gaseous state at ambient temperature; generation of refrigeration by expansion of a part of the process air or nitrogen under pressure.

Normally, the oxygen product is withdrawn in gaseous form above the condenser-reboiler which connects the two rectifying columns. Since the liquid oxygen is vaporized completely, the krypton and xenon contained in the liquid oxygen escape with the gaseous oxygen product stream. Concentration of krypton and xenon in the liquid oxygen cannot be obtained in this manner.

In order to keep these rare gases trapped in the liquid oxygen and, preferably, to increase their concentration, it is necessary to make a change to the process. In German Pat. No. 1,099,564, it is suggested not to withdraw the oxygen product directly aobve the reboiler but only after passage through a number of rectifying trays of the low-pressure column above the reboiler. The idea is to wash out the rare gases contained in the rising gas on the two or three lowest trays by means of the downflowing oxygen-rich liquid and to return them to the oxygen sump. This is possible because the equilibrium constant "K" of these rare gases is considerably lower than that of oxygen. For krypton, $K = y/x$ is approximately 1/15. This means that the concentration of krypton in the liquid oxygen is about 15 times larger at equilibrium than in the vapor. The reflux ratio of liquid to vapor on the lowest trays of the oxygen section of an air separation plant is relatively high: 1.30 to 1.45. The liquid portion amounts to about 70 percent of the air volume. Consequently, the rare gas portion (Kr + X) therein is about 1.5 ppm. This liquid flows toward the lowermost "barrier" trays. By providing a sufficiently large number of rectifying trays in the "barrier zone," it is possible to achieve a nearly equilibrium condition between the vapor escaping from the barrier zone and the incoming liquid; i.e. with $K = 1/15$ and $x = 1.5$ ppm, $y = 0.1$ ppm. Since only 20 parts of gaseous oxygen are withdrawn laterally, it would be possible, by means of such a "barrier zone," to trap about 98 percent of the krypton and xenon in the liquid oxygen of the low-pressure column and to concentrate it therein to a considerable degree. However, the simultaneously occurring hydrocarbon concentration puts a limit on the krypton and xenon concentration.

In air separation plants, the danger stems mainly from the C_1 through C_4 hydrocarbons. Their solubility in liquid oxygen is relatively high, with the exception of acetylene. It exceeds 1000 ppm, compared to only 7 ppm for acetylene. If the air separator is provided with gas phase adsorbers, the acetylene is kept away from the columns. It may be disregarded in the subsequent considerations. As compared to the rare gases krypton and xenon, the equilibrium constants $K = y/x$ in the oxygen portion of the low-pressure column are higher by a factor of about 2 for methane, and lower by a factor of 10^{-1} and even smaller for the other hydrocarbons. That is to say, the "barrier effect" is almost the same for methane and considerably better for the other hydrocarbons, as compared to krypton and xenon.

One tries to eliminate the danger of too high a concentration of C_2 to C_4 hydrocarbons in the liquid oxygen by inserting an adsorber having an adsorption capacity that even increases as the inlet concentration rises. However, methane cannot be trapped that way.

On the other hand, due to the high liquid-to-vapor ratio, the methane is prevented from leaving the "barrier zone;" and of all things it is the methane which gets into the air separator at relatively the highest concentration together with the process air. This is shown, almost without exception, by all air analyses. The amount is often 10 to 20 times larger than that of all other hydrocarbons combined.

Although, of all the hydrocarbons, it is methane that has the highest solubility in oxygen, it is irresponsible for safety reasons to allow the methane volume retained within and below the "barrier zone" to exceed a certain kilo amount. The theoretically possible explosive power must be kept within limits.

The endeavour to trap krypton and xenon by means of the "barrier zone" and the safety requirements for limiting the methane content in liquid oxygen are opposed to each other. For all practical purposes, the methane content therefore limits the rare gas concentration.

Therefore, in the aforementioned patent, the basic idea was weakened by providing the possibility of withdrawing the oxygen product gas from below the "barrier zone" from time to time. This does serve to decrease and limit the methane level, but at the same time it creates an "escape hatch" for the rare gases, krypton and xenon, through which they escape together with the methane. The previously enforced concentration below the "barrier zone" is lost. In case of a high methane content, it may be necessary to open the "hatch" so frequently that the rare gas concentration is no longer acceptable. Another way of controlling the methane would be to keep the "hatch" open continuously, although throttled down. This, however, leads to a constantly lower yield.

It is the object of this invention to overcome the described dilemma.

SUMMARY OF THE INVENTION

A process has been found for concentrating krypton

and xenon during air separation by rectification wherein liquid oxygen containing krypton, xenon and hydrocarbons and drawn from the sump section of a rectifying column is vaporized, freed of krypton and xenon by rectification, and withdrawn as gaseous oxygen product.

The invention is characterized by the combination of the following features:

a. the liquid oxygen containing krypton, xenon and hydrocarbons and drawn from the sump section of the rectifying column is conducted into a vessel provided with several rectifying trays, entering below the rectifying trays,

b. the liquid oxygen drawn from the sump section of the rectifying column at about the level of the lowest rectifying tray is dumped as reflux on the rectifying trays of the foresaid vessel,

c. gaseous product oxygen, freed of krypton and xenon on the rectifying trays, is withdrawn at the head of the aforesaid vessel, and

d. the krypton and xenon-enriched wash liquid is withdrawn from the bottom of the aforesaid vessel and returned to the sump of the rectifying column while liquid oxygen enriched in krypton, xenon and some hydrocarbons is withdrawn from the sump of the rectifying column for further concentration.

According to this invention, therefore, the "barrier zone" for the gaseous product oxygen is removed from the rectifying column and installed separately.

Another essential feature of the invention is that it is possible, by means of the liquid oxygen drawn from the sump section of the rectifying column, to adjust the reflux ratio in the separate "barrier zone," i.e., on the rectifying trays of the separate vessel, to any desired value. Since the equilibrium constant K for methane is about twice as high as K for krypton, the reflux in the separate "barrier zone" can be adjusted so that methane can escape with the gaseous phase, while krypton and xenon are still being washed out of the gas stream.

As explained, the basic idea of the invention is to provide a "barrier" which, due to the reflux being variable within wide limits independently of the air separation plant, is a "barrier" in the true sense of the word for the rare gases, krypton and xenon, but represents a continuously open "hatch" for methane. As wash liquid for the separate "barrier," part of the liquid running off the loWest tray of the rectifying column is collected and withdrawn. This liquid has a lower rare gas content than that of the sump liquid in the rectifying column and is therefore most suitable as barrier liquid.

The low-pressure column of a double rectifying column serves as a suitable rectifying column. The vaporization of the sump liquid may take place in the known manner by condensing nitrogen from the medium-pressure column in a tube condenser located within the double column between the low-pressure and medium-pressure columns. However, it may also take place in a plate condenser of the type frequently used in modern plants. This plate condenser may be located outside the rectifying columns between the low-pressure and medium-pressure columns; therein, sump liquid from the low-pressure column is heated by condensing nitrogen vapor from the medium-pressure column. In such case, the sump liquid to be vaporized is pumped through the condenser in excess in order to prevent dry evaporation.

For a fuller understanding of the invention, two illustrative embodiments will now be explained in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS:

FIG. **1** is a flowsheet for the two-stage rectification of air, wherein the condenser-reboiler is located within a double rectifying column between the medium-pressure and loW-pressure columns; and

FIG. **2** is a partial flowsheet similar to that of FIG. **1**, with a plate condenser-reboiler located outside the rectifying columns.

DESCRIPTION OF PREFERRED EMBODIMENTS:

FIG. **1** shows the known double column consisting of medium-pressure column **1**, low-pressure column **2** and condenser-reboiler **3** located between the two columns. The air to be separated enters the plant through line **4**, heats the sump liquid of medium-pressure column **1** by means of heating coil **5** and discharges into medium-pressure column **1** through line **6**. The resultant crude liquid oxygen enters low-pressure column **2** through line **7** and the liquid nitrogen through line **8**. From low-pressure column **2**, pure nitrogen is withdrawn through line **9**, while liquid oxygen enriched with krypton and xenon accumulates in the sump. This sump liquid is vaporized by gaseous nitrogen in medium-pressure column **1** which condenses in condenser-reboiler **3**.

Due to the high liquid-to-vapor ratio (1.30 to 1.45) in the lower portion of rectifying column **2**, the entire krypton and xenon content of the gaseous phase is washed down out of the rising gas. A part of this gas is withdrawn as product oxygen above condenser-reboiler **3** and conducted into separator **12** through line **11**. In separator **12**, it flows up through several rectifying trays **13** on which liquid oxygen is dumped from channel **10** in column **2** by pump **14** through line **15**. The liquid volume of this reflux is selected so that a liquid-to-vapor ratio between 0.05 and 0.2, preferably 0.1, is created. This reflux is capable of washing out the krypton and xenon present in the rising oxygen gas, whereas the methane also present in the oxygen gas partially remains in the gaseous phase due to the low liquid-to-vapor ratio.

The reflux ratio may be adjusted so that the amount of methane leaving the air separation plant with the gaseous product oxygen Is equal to the amount that enters the plant with the process feed air. In this way, a certain methane level will establish itself in the liquid oxygen.

If the methane level exceeds the given limit, the reflux ratio is reduced so that a lower level establishes itself in the liquid oxygen. A loss of rare gases will occur only if the reflux ratio is reduced to a value which is lower than that required for retaining the rare gases; i.e., the liquid-to-vapor minimum is equal to $K = y/k = 1/15 = 0.066$.

The gaseeus product oxygen, thus freed of krypton and xenon, then leaves separator **12** through line **17**.

Thus, it is possible to keep the krypton and xenon trapped in the liquid oxygen accumulating as a pool in separator **12** and passing thence through line **18** and valve **16** back into the sump of column **2**. As the plant continues operating, the amount of trapped krypton and xenon will increase. Through line **19**, a part of the crude concentrate is then withdrawn as a liquid for further processing.

FIG. 2 shows a variation of the invention wherein heating of the sump liquid of the low-pressure column takes place in an aluminum plate condenser-reboiler located outside both rectifying columns, as is often the case in modern air separation plants. Similar plant components are makred in FIG. 2 with the same reference numerals used in FIG. 1.

Low-pressure column 2 has lines 7 and 8 which, respectively, feed liquid crude oxygen and liquid nitrogen from the medium-pressure column which is not shown. Part of the liquid oxygen containing krypton and xenon, which accumulates in the bottom of column 2, is withdrawn by pump 20 and conducted into plate condenser-reboiler 22 through line 21. There, the liquid oxygen is vaporized by condensing gaseous nitrogen from the medium-pressure column which enters through line 23 and leaves as liquid through line 24 and then is dumped in part into the top of low-pressure column 2 through line 8; the remainder of the liquid nitrogen leaving through line 24 returns to the top of the medium-pressure column as reflux. The liquid oxygen is pumped through plate condenser-reboiler 12 in excess to prevent dry evaporation. Consequently, a liquid and vapor mixture enters separator 12 through line 25. The gas rises through rectifying trays 13 countercurrent to the wash liquid which pump 14 withdraws through line 15 from channel 10 located at the level of the lowest rectifying tray in the bottom section of rectifying column 2. Krypton and xenon are washed into the liquid accumulating in the bottom of separator 12 and are returned therewith to the sump of rectifying column 2 through line 18 and valve 16 which is used to control the liquid level. The greater part of the hydrocarbons, particularly the methane, is not washed out on the rectifying trays in separator 12 due to the selected low liquid-to-vapor ratio, and leaves separator 12 through line 17 together with the gaseous product oxygen. A partial stream of the gaseous phase separated in separator 12 is not conducted up through rectifying trays 13 but is withdrawn through line 26 and returned into the bottom of low-pressure column 2. This partial stream provides the necessary reboil vapor for low-pressure coumn 2. The krypton, xenon and hydrocarbons in this partial stream are washed out completely on the rectifying trays of low-pressure column 2 and end up in its sump. Again, as in the process of FIG. 1, a relatively high concentration of krypton and xenon in the liquid oxygen in the sump of low-pressure column 2 is obtained before the rising hydrocarbon content puts an end to any further concentration of krypton and xenon. The concentrate is withdrawn through line 19 and subjected to further concentration processes which are known and do not form a part of this invention.

The relatively high krypton and xenon concentration obtained in the first concentration by this invention reduces the cost of further concentration. Since a large percentage of the hydrocarbons leave the plant through line 17 together with the gaseous product oxygen, the known process for removing hydrocarbons from the krypton and xenon concentrate becomes simpler and cheaper as well.

What is claimed is:

1. In the process of separating oxygen and nitrogen in an air rectifying column, the improvement of recovering a concentrate of krypton and xenon which comprises discharging into the top of a krypton and xenon concentrating rectifying column liquid oxygen containing small quantities of krypton, xenon and hydrocarbons drawn from a level near the bottom tray of said air rectifying column before said liquid oxygen flows into the sump of said air rectifying column, passing a stream of oxygen containing increased quantities of krypton, xenon and hydrocarbons from below the bottom tray in said air rectifying column to below the bottom tray in said concentrating rectifying column, adjusting the discharge of said liquid oxygen into the top of said concentrating rectifying column to provide a liquid-to-vapor ratio at which krypton and xenon are substantially completely washed out of the vapor rising through said concentrating rectifying column, withdrawing gaseous oxygen containing some of said hydrocarbons but substantially free of krypton and xenon from the top of said concentrating rectifying column, returning liquid from the sump of said concentrating rectifying column to the sump of said air rectifying column, and recovering liquid from the sump of said air rectifying column as said concentrate of krypton and xenon.

2. The process of claim 1 wherein the stream of oxygen containing increased quantities of krypton, xenon and hdyrocarbons from below the bottom tray in the air rectifying column is liquid from the sump of said air rectifying column, said liquid is partially vaporized before being passed to below the bottom tray in the concentrating rectifying column, and part of the vapor of the partially vaporized liquid is passed from below the bottom tray in said concentrating rectifyIng column to below the bottom tray in said air rectifying column.

3. The process of claim 1 wherein the adjustment of the discharge of liquid oxygen into the top of the concentrating rectifying colomn provides a liquid-to-vapor ratio in the range of about 0.05 to 0.02.

4. The process of claim 1 wherein the air rectifying column is the low-pressure column of a double rectifying colomn, and vapor in the top of the medium-pressure column of said double rectifying column indirectly transfers heat to liquid in the sump of said low-pressure column.

5. The process of claim 4 wherein the adjustment of the discharge of liquid oxygen into the top of the concentrating rectifying column provides a liquid-to-vapor ratio in the range of about 0.05 to 0.2.

6. The process of claim 5 wherein the indirect transfer of heat from vapor to liquid is conducted outside the low-pressure and medium-pressure columns and effects partial vaporization of said liquid, the partially vaporized liquid is passed to below the bottom tray in the concentrating rectifying column as the stream of oxygen containing increased quantities of krypton, xenon and hydrocarbons, and part of the vapor of said partially vaporized liquid is passed from below the bottom tray in said concentrating rectifying column to below the bottom tray in said low-pressure column.

7. In an air rectifying plant wherein liquid oxygen collects in the sump of a rectifying column and is reboiled, the improvement of means for concentrating krypton and xenon in said liquid oxygen in said sump which comprises an auxiliary rectifying column, first means for drawing liquid from a level just below the bottom tray in said rectifying column and introducing said liquid on the top tray in said auxiliary rectifying column, second means for passing a stream drawn from a lower level below said bottom tray to below the bottom tray

in said auxiliary rectifying column, an outlet at the top of said auxiliary rectifying column for gaseous oxygen, and a valved pipe connecting the bottom of said auxiliary rectifying column to said sump.

8. The air rectifying plant of claim **7** wherein the first means for drawing liquid includes a pump with a variable pumping rate.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,751,934 Dated August 14, 1973

Inventor(s) Klaus Frischbier

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 45, correct "aobve" to -- above --.

Column 5, line 6, correct "makred" to -- marked --;
line 22, correct "12" to -- 22 --.

Column 6, line 36, correct "0.02" to -- 0.2 --.

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

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