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Schuftan

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[54] **AIR SEPARATION**

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[58] **Field of Search** 62/22, 23, 24, 26, 62/27, 28, 30, 18, 31, 12

[56] **References Cited**

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[57] **ABSTRACT**

Krypton and xenon are recovered from air by passing oxygen vapour into a rectification column to produce a krypton/xenon concentrate. The concentrate is kept substantially free from hydrocarbon impurities by withdrawing a small liquid oxygen fraction, containing most of the impurities, from the separation unit producing the oxygen. The rectification column has an upper section and a lower section, the ratio of the number of trays in the upper section to the number of trays in the lower section being in the range 6 to 12.

13 Claims, 2 Drawing Figures

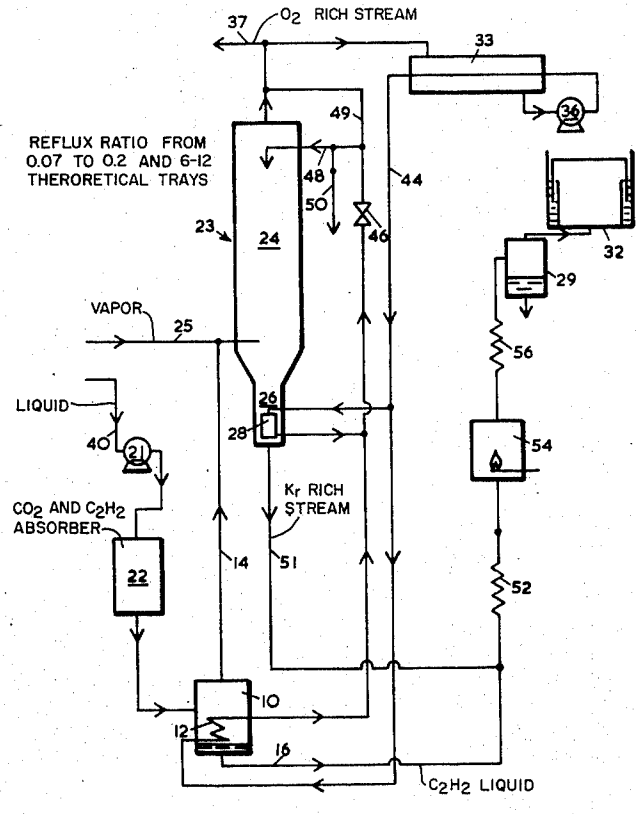
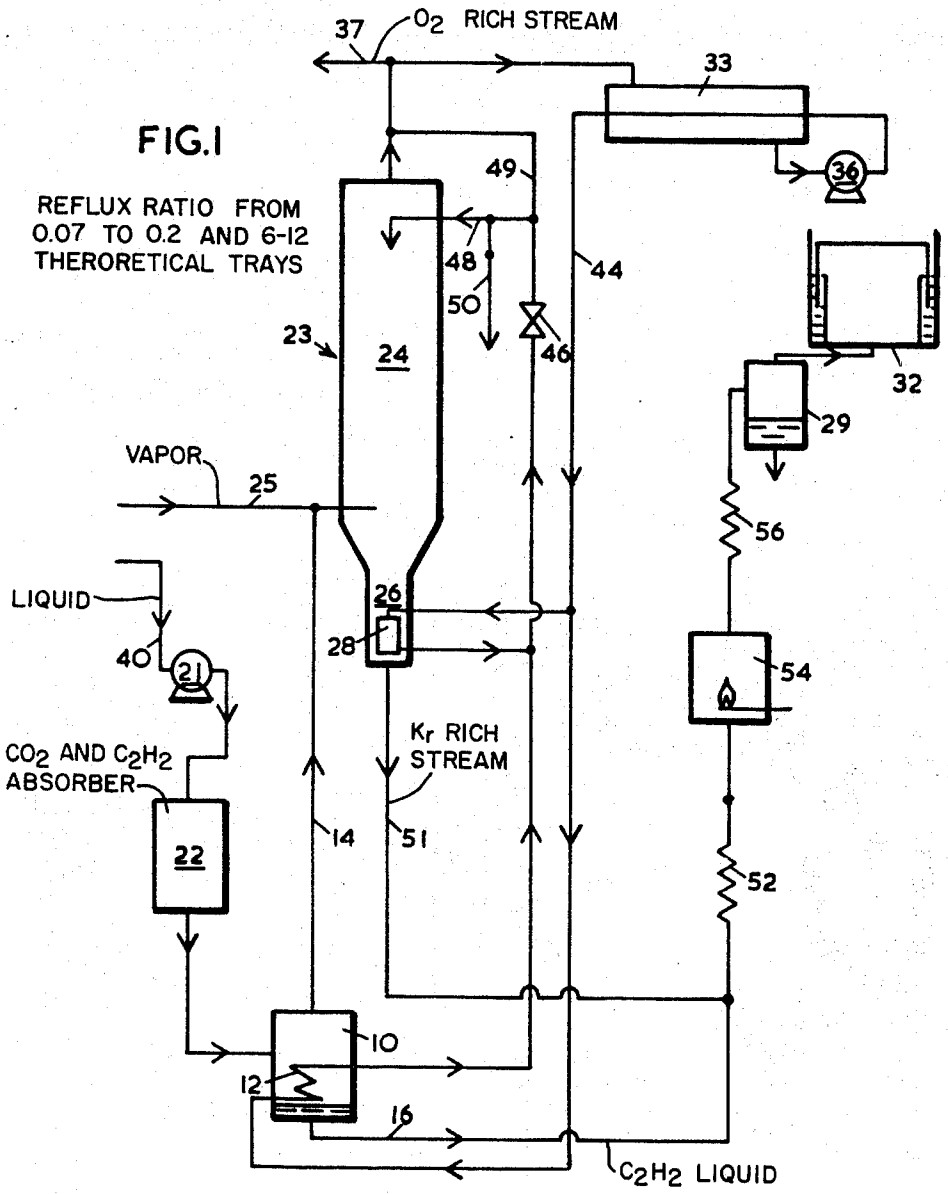
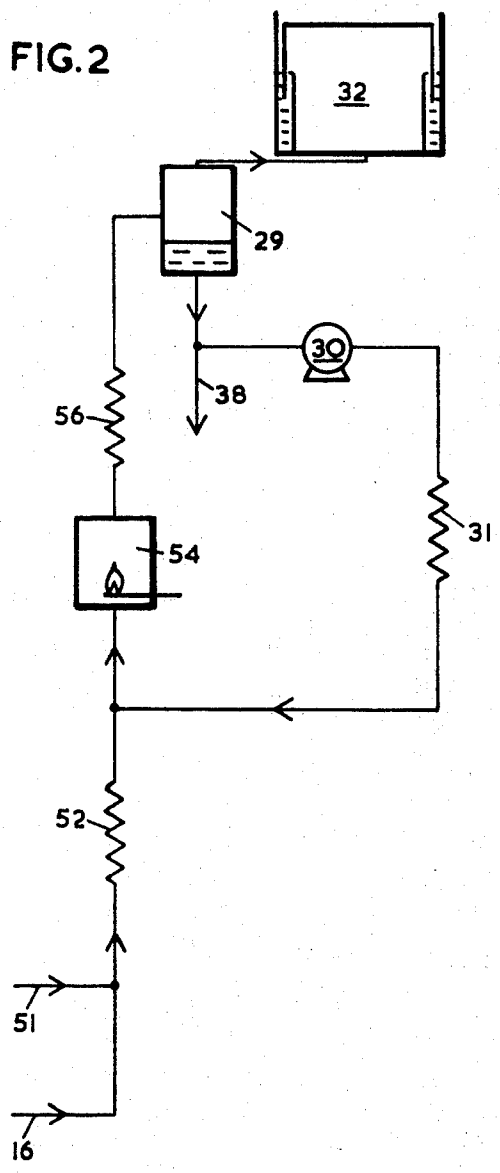


FIG.1



REFLUX RATIO FROM 0.07 TO 0.2 AND 6-12 THERORETICAL TRAYS

FIG. 2



AIR SEPARATION

FIELD OF INVENTION

This invention relates to air separation, in particular to the recovery of krypton and xenon from oxygen containing hydrocarbons obtained in the reboiler of an air separation plant.

DESCRIPTION OF THE PRIOR ART

In copending UK patent application 48 402/70 there is described a process for the recovery of krypton and xenon from the oxygen produced in an air separation plant, the oxygen being first freed from at least the bulk of acetylene and the other higher hydrocarbons, using a single rectification column with a reflux ratio sufficient to remove substantially all of the krypton and xenon from the ascending vapour but too low to remove all the methane from the ascending vapour. In the lower section of the rectification column a crude primary krypton/xenon concentrate is to be obtained containing at least 10 percent Kr having a methane content substantially below the explosion limit. A small fraction of the oxygen from the reboiler of the air separation plant is preferably added as liquid, after passing through an adsorber, to the reflux liquid leaving the upper section of the rectification column so as to balance the cold losses of the rectification column and to prevent accumulation of heavy hydrocarbons in the reboiler of the air separation plant.

With a methane content of the oxygen approximately equal to its krypton content, such a process gives a crude krypton/xenon concentrate having a methane content of about 1 percent and normally an acceptably small content of residual heavy hydrocarbons.

In certain locations, however, the methane content of the oxygen is considerably higher and there is also a risk that an excessive amount of residual heavy hydrocarbons, especially methane, may pass through the adsorber employed to remove the bulk of them from the liquid oxygen fraction, particularly during the changeover operation of this adsorber. In addition, traces of carbon dioxide may also pass through the adsorber and cause solid obstructions during concentration of the liquid in the lower section of the rectification column. The combined effect of the presence of residual heavy hydrocarbons and traces of carbon dioxide may cause enrichment of the heavy hydrocarbons in the reboiler of the rectification column beyond the permissible safety limit, and thus could render the process unsafe under such conditions.

SUMMARY OF THE INVENTION

The present invention relates to an improved method for the recovery of krypton and xenon which also permits dealing with oxygen containing a relatively high content of hydrocarbons again using such a single rectification column. It is based on the observation that the saturated oxygen leaving the reboiler of an air separation unit contains the bulk of the methane while the coexisting liquid contains the bulk of the heavy hydrocarbons and any carbon dioxide. As for several reasons a relatively small fraction of the oxygen to be processed has in any case to be withdrawn in the liquid state from the reboiler of the air separation unit, a solution of the hydrocarbon problem is achieved according to this invention in two distinct steps, i.e., dealing separately with the gaseous and liquid fractions and not jointly as in the preferred case of the co-pending application.

The liquid fraction is first passed through an adsorber which removes the acetylene and the bulk of the heavy hydrocarbons and of any carbon dioxide, and then through a vaporiser in which more than **90%** is vaporised, leaving a small amount of a weak liquid concentrate containing virtually the whole of any residual heavy hydrocarbons and carbon dioxide. The vapour so produced, which is practically free from these constituents, is admixed with the bulk of the oxygen that is withdrawn as saturated vapour from the reboiler and only this gaseous mixture is introduced at or near the base of the upper section of a rectification column. In this way it is possible to obtain at the base of the rectification column a strong primary concentrate which is also free from these constituents. The concentration factor of the krypton should be kept as high as possible in the upper section (where the reflux ratio is low) but as low as possible in the lower section (where there is practically total reflux). This can be achieved by proper matching of the reflux ratio and the ratio of the number of trays in the upper section to the number of trays in the lower section. The term "reflux ratio" as used herein is defined as the ratio of the liquid volume to the vapour volume in the rectification column both measured under standard conditions.

According to the present invention there is provided a process for the recovery of krypton and xenon from oxygen containing hydrocarbons obtained in the reboiler of an air separation column, wherein a major part of the oxygen to be processed is withdrawn from the reboiler as saturated vapour and a small fraction is withdrawn as liquid, the latter being passed through an adsorber to remove the acetylene and the bulk of the other heavy hydrocarbons and of any carbon dioxide and then vaporised to give a vapour fraction and a small volume of a weak concentrate containing substantially all of any residual heavy hydrocarbons and carbon dioxide, admixing the vapour fraction with the oxygen withdrawn as saturated vapour, passing the mixture into a rectification column having a reboiler at the base and an upper and lower section operating at the same pressure at a point at or near the base of the upper section and withdrawing from the base of the rectification column a strong concentrate containing at least 10 percent of krypton substantially free from heavy hydrocarbons and carbon dioxide, and from the top of the column gaseous oxygen substantially free from krypton, the methane content of the strong concentrate being kept at a minimum by using in the upper section a reflux ratio within the range 0.07 to 0.2 and a ratio of the number of theoretical trays of the upper section to the number in the lower section being within the range 6 to 12.

The invention also provides air separation apparatus comprising an air separation column with a reboiler, and adsorber to remove the acetylene and the bulk of the other heavy hydrocarbons and of carbon dioxide from a small liquid oxygen fraction withdrawn from the reboiler, a vaporiser to produce from the liquid leaving the adsorber a vapour fraction and a small volume of weak concentrate containing substantially all of any residual heavy hydrocarbons and carbon dioxide, a rectification column having a reboiler at the base and an upper and lower section operating at the same pressure and adapted to receive at a point near the base of the

upper section the said vapour fraction in admixture with saturated oxygen vapour withdrawn from the reboiler of the air separation column and to produce for withdrawal from the base a strong concentrate containing at least 10 percent of krypton substantially free from heavy hydrocarbons and for withdrawal from the top gaseous oxygen substantially free from krypton, the ratio of the number of trays in the upper section to the number in the lower section being within the range 6 to 12.

The reflux ratio in the upper section of the rectification column is preferably about 0.1 and the ratio of the number of theoretical trays is preferably about 9. Under these conditions the methane content of the crude concentrate can be kept below 0.3 percent even when the oxygen has a methane krypton ratio of 3. Practically all the methane is then contained in the gaseous oxygen leaving the top of the column with a krypton content of the order of only 0.5vpm.

The heat required for the reboiler of the rectification column and of the liquid oxygen vaporiser is in general, preferably supplied by condensing oxygen, at least a part of the liquid thus obtained being introduced into the upper section to act as reflux. The oxygen to be condensed is preferably a part of the gaseous oxygen withdrawn from the top of the rectification column and compressed to the pressure required for condensation.

Where, however, the compressor used for transmitting the gaseous oxygen product from the plant to the place of application has not the capacity for dealing with the additional amount of oxygen required for reboil and reflux in the rectification column a separate compressor would have to be provided. This would have to compress the requisite amount of oxygen from near atmospheric pressure to the pressure required at the reboiler. Such a compressor is relatively expensive as the compression of oxygen also requires special safety precautions.

In such cases, the use of air or nitrogen in the recycle system would normally be more economical, in spite of the fact that the rectification column would then require a condenser. The throughput of the recycle compressor would then be somewhat larger than when using oxygen but, in view of the different thermodynamic properties of air or nitrogen, both suction and delivery pressures would be higher thus reducing the size of the machine. This would then normally be of the reciprocating type. The power consumption would be virtually the same as for an oxygen recycle.

If at least one theoretical tray is provided in the vaporiser the weak concentrate will contain most of the xenon and can then, if desired, be treated separately for the recovery of the xenon.

Alternatively the strong concentrate and weak concentrate can be combined for further treatment. The volume of the combined concentrates is a very small proportion of the total oxygen being processed. For example, even when the strong concentrate obtained at the base of the column contains only 20 percent krypton, the volume of the combined concentrates amounts to only about 1/20,000 of the oxygen processed. The oxygen content of the crude product is therefore quite small and it has been found economical to remove at least the bulk of this residual oxygen by reaction with hydrogen. Such removal can for example be effected in a burner or over a catalyst. Any residual hydrocarbons will be converted into carbon dioxide at this deoxidation step.

Normally a burner would be water cooled and steam would preferably be admixed to the concentrate prior to introduction into the burner so as to reduce the oxygen concentration to the order of 15 to 20 percent. The water vapour formed by the reaction, together with the added steam, is condensed in a cooler downstream of the burner and, if desired, part of the water so obtained is then recycled, revaporised, slightly superheated and admixed to the concentrate. If catalytic deoxidation is employed steam is also preferably admixed to the concentrate prior to treatment, a greater volume of steam then being required in order to avoid an excessive temperature rise in the catalyst. Catalytic deoxidation can also be used in series with a burner in order to remove an unreacted hydrogen or oxygen leaving the burner.

The deoxidised product can contain over 80 percent krypton and xenon and can be stored in a gasholder from which it can be compressed intermittently into cylinders. It would usually be most convenient for a central station to carry out the final purification into saleable products. For final purification, after removal of the carbon dioxide and moisture, the gas is preferably liquefied and fractionally vaporised at 1 bar, the vapour formed being passed at about 120°K through an adsorbent, e.g., active charcoal, silica gel or a molecular sieve. Due to the combined separation effects of the fractional vaporisation and selective adsorption the gas leaving the adsorber first contains any residual constituents of low boiling point, such as nitrogen, argon and oxygen. This fraction is rejected until krypton appears at the outlet from the adsorber. A pur krypton fraction can then be collected, the xenon being retained on the adsorbent from which it can be obtained by a desorption step.

The accompanying figures illustrate the features of the invention for the case of oxygen recycle.

FIG. 1 is a simplified flow diagram of one form of apparatus suitable for carrying out the process of the invention,

FIG. 2 is a simplified flow diagram of a modified portion of the apparatus shown in FIG. 1.

In the apparatus shown in FIG. 1 gaseous oxygen from the reboiler of an air separation unit (not shown in the accompaning figures) passes through a conduit **25** into the upper section **24** of a rectification column **23**, which also has a lower section **26** and a reboiler **28**. The ratio of the number of theoretical trays in the upper section **24** to the number in the lower section **26** is 8.8.

Liquid oxygen from the reboiler of the air separation unit passes through a conduit **40** and a pump **21** into an adsorber **22** for removal of the acetylene and the bulk of the other higher hydrocarbons and of any carbon dioxide. The liquid oxygen leaving the adsorber **22** is passed to a vaporiser **10** fitted with a "reboiler" vaporising coil **12**. Gaseous oxygen formed in the vaporiser **10** is passed through a conduit **14** leading to the conduit **25** and mixes with gaseous oxygen therein to be introduced into the upper section **24**. The small amount of unvaporised liquid oxygen (the weak concentrate) from vaporiser **10** leaves through conduit **16** for further treatment.

Some of the gaseous oxygen leaving the top of the column **23** is withdrawn through a conduit **37**. The rest passes through an exchanger **33** and a blower **36** in

which it is compressed to the required condensation pressure. It is then returned through a conduit **44**, a major part being passed through the reboiler **28** and the remainder being passed through the reboiler **12**. Both parts, now liquid, are then recombined and expanded in a valve **46**. The expanded liquid obtained after flash evaporation is introduced through conduit **48** into the upper section **24** to provide reflux, the flash vapour being passed through a conduit **49** and combined with the gaseous oxygen leaving the top of the upper section **24**. If production of liquid oxygen is required this may be withdrawn through a conduit **50**.

Crude strong primary concentrate withdrawn from the base of the column **23** passes through a conduit **51** and is combined with the weak concentrate passing through the conduit **16**. The combined concentrates are then passed through a vaporiser **52**. Most of the oxygen and the hydrocarbons are removed by combustion with hydrogen in a water-cooled burner **54**. The product stream is then cooled in a cooler **56**, freed from water in a separator **29** and collected in a gasholder **32** to await final treatment.

In the modification shown in FIG. **2**, a pump **30** and heater **31** provide for recycle of water from the separator **29**. The heater **31** converts the water to steam and slightly superheats the steam which is then mixed with the concentrate leaving the vaporiser **52**. Any water not required for production of steam is withdrawn through a conduit **38**.

The operation of the apparatus described above will now be exemplified by reference to the processing of an oxygen stream containing methane and krypton in the ratio of **3:1**. Unless otherwise specified the proportions of methane, krypton, xenon and heavy hydrocarbons are expressed as volumes per million.

18,672 m^3 of gaseous oxygen containing 4.9 krypton 15.8 methane and 0.07 xenon were fed to the column **23** through conduit **25**, whilst 245 m^3 of liquid oxygen containing 56.1 krypton, 26,2 xenon, 53.0 methane and 2.1 heavy hydrocarbons were introduced through conduit **40** and, after passing through the adsorber **22** to remove the acetylene and the bulk of the other heavy hydrocarbons and of any carbon dioxide, were fed to the vaporiser **10** in which 244.6 m^3 were vaporised by oxygen condensing in the reboiler **12**. This vapour was almost free from heavy hydrocarbons and was admixed with the gaseous oxygen introduced through conduit **25** giving 18916.6 m^3 with 5.4 krypton, 0.28 xenon and 16.3 methane. 21,134 m^3 of gaseous oxygen containing 0.5 krypton and 16.3 methane left top of the column **23**. Of this 2,300 m^3 were warmed in the exchanger **33** and compressed in the blower **36** to 3.2 bars. After recooling in the exchanger **33**, the recycled oxygen passed through the conduit **44** to be condensed in the reboilers **12** and **28**. Of the liquid oxygen thus obtained 82 m^3 was withdrawn as product from conduit **50** while the remainder provided the reflux in the column **23**. 464 litres of a strong krypton/xenon concentrate in liquid oxygen, measured as gas under standard conditions, obtained at the base of column **23** contained 20 percent krypton, 1.15 percent xenon and 0.22 percent methane.

From the vaporiser **10** there are withdrawn 400 litres of liquid oxygen containing 0.06 percent krypton, 0.60 percent xenon, 0.13 percent heavy hydrocarbons and traces of residual carbon dioxide. The hydrocarbon contents of both concentrates were far below the explosion and solubility limits. These two concentrates when combined in advance of the vaporiser **52** formed 864 litres of liquid containing 10.8 percent krypton, 0.9 percent xenon, 0.12 percent methane and 0.06 percent heavy hydrocarbons. The vapour stream emerging from the vaporiser **52** was admixed with 3.2kg of slightly superheated steam and the bulk of the oxygen and the hydrocarbons were converted into water and carbon dioxide by reaction with 1.5 m^3 of hydrogen in the watercooled burner **54**.

After passing through the cooler **56** the condensed water was removed in the separator **29** and the product amounting to **111** litres contained 84 percent krypton, 7 percent xenon, 1.9 percent carbon dioxide and 7.1 percent oxygen. This was stored in a gasholder whence the gas was compressed into cylinders in advance of the final purification stage.

When providing one theoretical tray in vaporiser **10** about 80 percent of the xenon was recovered in the weak concentrate withdrawn therefrom and this could be processed separately for xenon production.

We claim:

1. A process for the recovery of krypton and xenon from oxygen containing hydrocarbons obtained in the reboiler of an air separation column, wherein a major part of the oxygen to be processed is withdrawn from the reboiler as saturated vapour and a small part is withdrawn as liquid, the liquid part is passed through an adsorber to remove the acetylene and the bulk of the other heavy hydrocarbons and of any carbon dioxide and then vaporised to give a vapour fraction and a small volume of weak liquid concentrate containing substantially all of any residual heavy hydrocarbons and carbon dioxide, admixing the vapour fraction with the oxygen withdrawn as saturated vapour, passing the mixture into a rectification column having a reboiler at the base and an upper and lower section operating at the same pressure at a point at or near the base of the upper section and withdrawing from the base of the rectification column a strong primary concentrate containing at least 10 percent Kr substantially free from heavy hydrocarbons and carbon dioxide, and from the top of the column gaseous oxygen substantially free from krypton, the methane content of the strong concentrate being kept at a minimum by using in the upper section a reflux ratio within the range 0.07 to 0.2 and a ratio of the number of theoretical trays of the upper section to the number in the lower section being within the range 6 to 12, and the said weak liquid concentrate is treated separately for the recovery of xenon.

2. A process as claimed in claim **1**, wherein the reflux ratio in the upper section of the rectification column is about 0.1.

3. A process as claimed in claim **1**, wherein the said ratio of the number of theoretical trays is about 9:1.

4. A process as claimed in claim **1**, wherein the heat required for the reboilers is supplied by condensing oxygen, at least a part of the liquid thus obtained being introduced into the top of the upoer section of the rectification column to act as reflux.

5. A process as claimed in claim **4**, wherein the oxygen to be condensed is a part of the gaseous oxygen withdrawn from the top of the rectification column and compressed to the pressure required for condensation.

6. A process as claimed in claim **1**, wherein the heat required for the reboilers is supplied by condensing air

or nitrogen and the rectification column is provided with a condenser.

7. A process as claimed in claim 1, wherein residual oxygen in one or both of the weak and strong concentrates is removed by reaction with hydrogen.

8. A process as claimed in claim 7, wherein residual oxygen is removed in a water cooled burner and steam is admixed to both the strong concentrate and weak concentrate prior to introduction into the burner so as to reduce the oxygen concentration to the order of 15 to 20 percent.

9. A process as claimed in claim 1 wherein residual oxygen in one or both of the weak and strong concentrates is removed over a catalyst.

10. A process as claimed in claim 1, wherein oxygen and residual hydrocarbons are removed from the primary concentrates to yield a secondary concentrate that is then condensed and fractionally vaporised at about 1 bar, the vapour formed being passed at about 120°K through an adsorbent.

11. Air separation apparatus comprising an air separation column with a reboiler, an adsorber to remove the acetylene and the bulk of the other heavy hydrocarbons and of any carbon dioxide from a small liquid oxygen fraction withdrawn from the reboiler, a vaporiser to produce from the liquid leaving the adsorber a vapour fraction and a small volume of weak concentrate containing substantially all of any residual heavy hydrocarbons and carbon dioxide, a rectification column having a reboiler at the base and an upper and lower section operating at the same pressure with means providing a reflux ratio within the range of 0.07 to 0.2 and adapted to receive at a point near the base of the upper section the said vapour fraction in admixture with saturated oxygen vapour withdrawn from the reboiler of the air separation column and to produce for withdrawal from the base a strong primary concentrate substantially free from heavy hydrocarbons and for withdrawal from the top gaseous oxygen substantially free from krypton, the ratio of the number of trays in the upper section to the number in the lower section being within the range 6 to 12.

12. Apparatus as claimed in claim 11, wherein the said ratio of the number of theoretical trays is about 9.

13. Apparatus as claimed in claim 11 wherein the vaporiser contains at least one theoretical tray.

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