

[54] **IMPROVED KRYPTON XENON RECOVERY METHOD**

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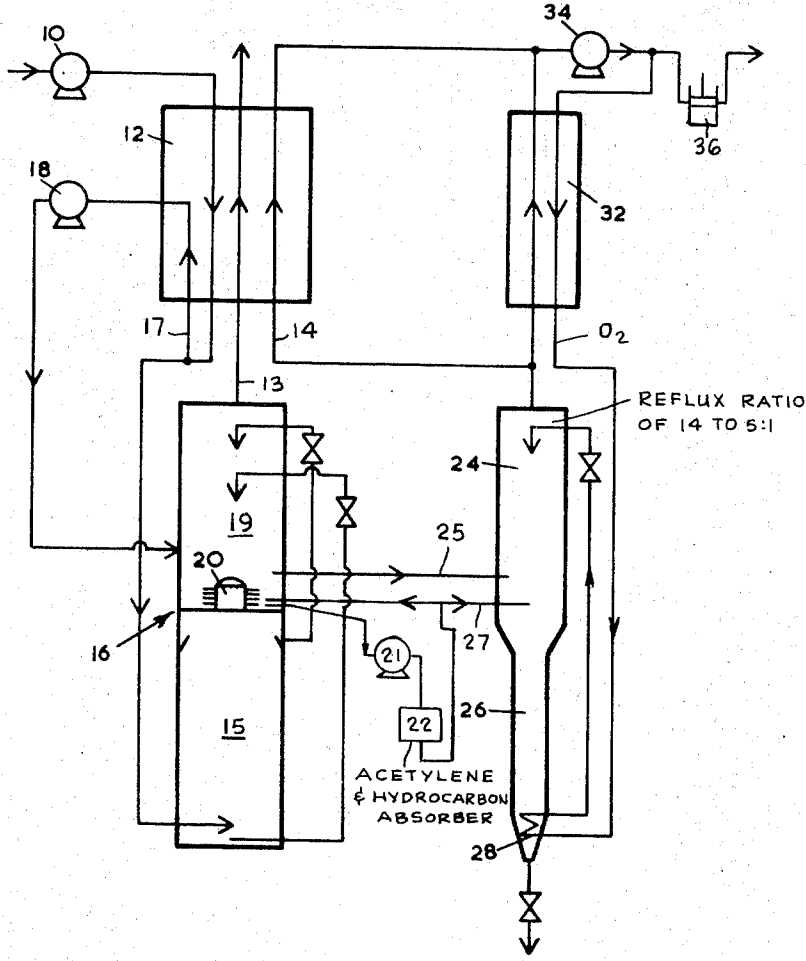
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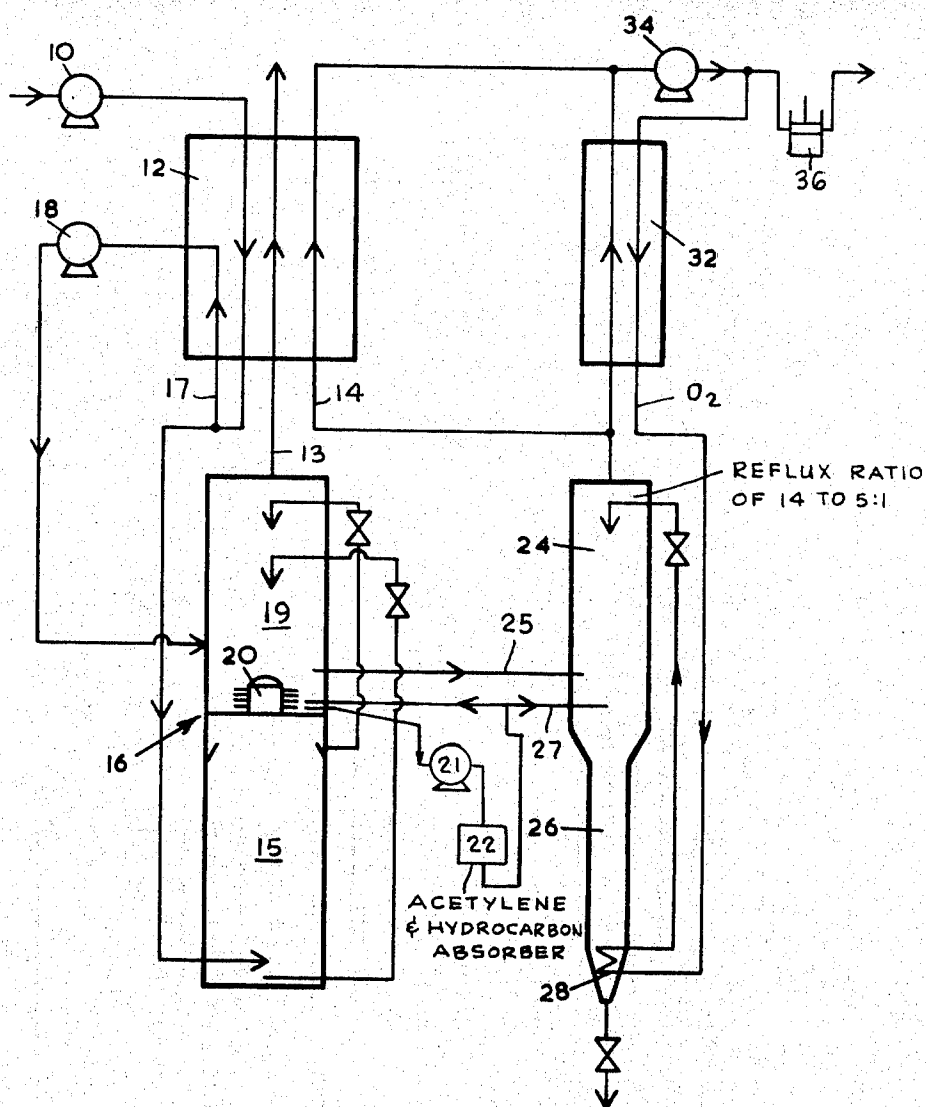
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[57] **ABSTRACT**

Krypton and xenon are recovered from the oxygen produced in the reboiler of an air separation unit by passing the oxygen into a two-section rectification column having at least one reboiler and in which the reflux ratio is selected to give a primary krypton/xenon concentrate of low methane content and containing at least 10 percent krypton.

14 Claims, 1 Drawing Figure





IMPROVED KRYPTON XENON RECOVERY METHOD

FIELD OF THE INVENTION

This invention relates to air separation. In particular it relates to the recovery of Krypton and Xenon from oxygen obtained in an air separation plant.

DESCRIPTION OF THE PRIOR ART

The oxygen product from an air separation plant usually contains about 5.5 vpm of krypton together with about the same amount of methane and smaller amounts of acetylene and other heavier hydrocarbons, and in addition about 0.42 vpm of xenon. The krypton and xenon are separated together, their production requiring a concentration factor of about 180,000. Although acetylene and the bulk of other higher hydrocarbons can normally be removed from the oxygen to a sufficient extent by adsorption, the presence of methane especially necessitated carrying out the concentration process in several steps in order to avoid concentrating the methane up to its explosion limit in oxygen.

In previous proposals a primary concentrate containing about 1 percent krypton is usually produced from which the methane has to be removed before further concentration steps are possible. This methane removal step is cumbersome and expensive as it involves heating the primary concentrate, passing it over a catalyst to bring about combustion of the methane, re-cooling and removing the carbon dioxide and water formed during combustion.

To avoid the combustion step it has been proposed to wash the gaseous oxygen with inert liquids, such as fluorocarbons or argon, but this requires several rectification columns and a sufficient replacement of the oxygen by the inert liquid is difficult to achieve.

It has also been suggested to produce a liquid primary krypton extract substantially free from methane in a first rectification column, passing this extract to the reboiler of the air separation unit to effect a gradual impoverishment in methane of the reboiler liquid and subsequently concentrating the reboiler liquid in two further rectification columns operating at different pressures. The suggestions that the methane content of the krypton extract from the first rectification column is substantially lower than that of the reboiler liquid and that its admixture with the reboiler liquid impoverishes it in methane are wrong. In fact more than about one third of the incoming methane would still be contained in the first column extract with about the same methane content as the reboiler liquid in such a procedure and this would have to be removed in the two subsequent columns.

SUMMARY OF THE INVENTION

The present invention allows almost complete elimination in a single rectification column of the methane input from a krypton concentrate, the column consisting of an upper and a lower section and provided with a reboiler at its base. Gaseous oxygen, freed from at least the bulk of acetylene and the other higher hydrocarbons, passes through the upper section of the column and leaves it with very little krypton and xenon but with almost all of the methane originally present. At the base of the column a crude primary krypton/xenon concentrate is obtained with a methane content well below the explosion limit. This crude primary concen-

trate can contain up to 60 percent or more of a krypton/xenon mixture, the remainder being oxygen and small amounts of methane and residual higher hydrocarbons.

According to the invention there is provided a process for recovery of krypton and xenon from the oxygen produced in an air separation column wherein

a. gaseous oxygen freed from at least the bulk of acetylene and the other higher hydrocarbons, is passed from the reboiler of the air separation column into a rectification column having an upper section and a lower section operating at the same pressure, the lower section having a reboiler at or near the base and the gaseous oxygen being introduced at or near the base of the upper section, yielding a crude primary krypton/xenon concentrate containing at least 10 percent of krypton

b. in the upper section there is employed a reflux ratio sufficient to remove substantially all of the krypton and xenon from the ascending vapours but too low to remove all of the methane from the ascending vapours,

c. the liquid obtained at the base of the upper section with at least the same krypton, xenon and methane contents as the liquid oxygen in the reboiler of the air separation column is concentrated in the lower section to give at the base of the lower section the crude primary krypton/xenon concentrate having a methane content substantially below the explosion limit and at the top of the lower section a vapour of relatively low krypton and xenon content which ascends into the upper section, and

d. the gaseous oxygen is withdrawn from the top of the upper section and the crude primary krypton/xenon concentrate is withdrawn from the base of the lower section. The gaseous oxygen can be freed from at least the bulk of acetylene and other hydrocarbons by circulating liquid from the reboiler of the air separation column through an external adsorber and then back to the column. An additional adsorber can be located at an appropriate position in the lower section of the rectification column if required to ensure that the acetylene concentration does not exceed the permissible limit. It may then be convenient to provide an additional reboiler at an intermediate point in the lower section of the rectification column.

The term "reflux ratio" as used therein refers to the ratio of the vapour volume to the liquid volume in the rectification column measured under standard conditions. It is preferably maintained within the range 14 to 5:1, most preferably at about 10:1.

A small portion of the liquid oxygen from the reboiler of the air separation plant is preferably added 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 the accumulation of heavy hydrocarbons in the reboiler of the air separation column.

The reboil in the rectification column is preferably provided by condensing gaseous oxygen, the liquid oxygen thus obtained being introduced into the upper part of the upper section of the rectification column to act as the reflux. The gaseous oxygen feeding to the rectification column reboiler is preferably a portion of the gaseous oxygen withdrawn from the top of the rectification column. Since the withdrawn oxygen is usually compressed in several stages to the required supply line

pressure, the portion returned to the reboiler can conveniently be removed at an intermediate pressure suitable for the reboil.

This procedure offers the advantage over providing reboil by condensation of air or nitrogen that by taking oxygen at elevated pressure from the oxygen supply compressor a higher reboil temperature and higher krypton concentration in the crude primary concentrate can be achieved. Moreover the use of liquid oxygen as reflux gives the advantages over air or nitrogen that a reflux condenser is not needed and that an increased oxygen yield is obtained from the air separation plant.

Where 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 recycle 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.

The reflux ratio can be conveniently adjusted by providing a valve in the line supplying the reflux liquid to the upper part of the section. The valve can be automatically controlled by a ratio controller between a flowmeter in the reflux supply line and a flowmeter in the gaseous oxygen withdrawal line. The reflux ratio also determines the requisite amount of reboil. During the concentration of the liquid obtained at the base of the lower section its boiling point, initially about 95K, increases. At a krypton content of 60 percent the boiling point is about 105K. If an oxygen recycle is used, the required condensation pressure for the oxygen in the reboiler rises correspondingly to a maximum of about 4.6 bars. The rate of reboil and the reflux oxygen can be kept constant by controlling the condensation pressure, for example by a flowmeter in the liquid reflux supply line controlling a valve in the line supplying gaseous oxygen to the reboiler. Alternatively the condensation pressure can be kept constant at its maximum value whilst the effective heat transfer area of the reboiler is adjusted by controlling, for example by means of a flowmeter in the liquid reflux supply line, the liquid level around the reboiler. The base of the lower section is preferably of small internal diameter and provided with a reboiler in the form of a block of the plate and fin type. In fact the volume provided for liquid surrounding the reboiler should be as small as possible, the crude primary krypton/xenon concentrate being a small volume relative to the volume of reflux liquid.

Removal of oxygen and the hydrocarbons from the crude primary krypton/xenon concentrate yields as a

secondary concentrate a mixture of pure krypton and xenon which can then be separated from each other.

For the removal of the oxygen and the residual hydrocarbons from the primary concentrate a hydrogen blowpipe is suitable. Alternatively, the hydrocarbons can be catalytically oxidised by copper oxide and the oxygen subsequently removed by reaction with manganoxy oxide. In either case, the resulting gas mixture has to be dried and freed from carbon dioxide.

The resulting secondary concentrate is a mixture of krypton and xenon that will normally not be sufficiently pure for sale. For final purification this secondary concentrate is preferably condensed and fractionally vapourised at 1 bar, the vapour formed being passed at about 120°K through an adsorbent, e.g. active charcoal, silica gel or molecular sieve. Due to the combined separation effects of the fractional vapourisation 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 pure krypton fraction can then be collected, the xenon being retained on the adsorbent from which it can be obtained by a desorption step.

The invention also provides apparatus for recovery in the manner specified above of krypton and xenon from the oxygen produced in an air separation plant.

The trays in at least the lower section of the rectification column are preferably of the bubble cap type. This is helpful in preventing accidental mixing of the liquid in the lower section trays with the liquid concentrating at the base of the section.

A preferred embodiment of this invention for the case of an oxygen recycle is described in the following example with reference to the attached simplified diagram. This refers to a double column air separation plant producing 610 tons/day of oxygen of 99.5 percent purity.

100,000 m³/h of air are compressed to 6.35 bars in a turbocompressor 10 and cooled to its dew point in a reversing exchanger 12 by nitrogen introduced through a conduit 13 and oxygen introduced through a conduit 14. The bulk of the air is passed into the lower column 15 of an air separation plant (indicated generally by the numeral 16) while a balancing stream 17 is partly warmed in the exchanger 12 and then work expanded in a turbine 18 to provide the cold requirements of the process. The upper column 19 has a reboiler 20 operating at 1.6 bars. For the removal of the bulk of the acetylene and the other higher hydrocarbons part of the liquid in the reboiler 20 is circulated by a pump 21 through an adsorber 22 provided in duplicate for alternate operation.

A rectification column, indicated generally by the numeral 23, consisting of an upper section 24 and a lower section 26 with a reboiler 28 is linked to the upper column 19 by a gas conduit 25 and a liquid conduit 27. Any residual acetylene can if desired be removed by an additional adsorber (not shown) in the lower section 26.

18672 m³/h of gaseous oxygen with 4.9 vpm of krypton and 5.2 vpm of methane are passed through the conduit 25 from the reboiler 20 into the section 24, and 245 m³/h of liquid oxygen with 56 vpm of krypton and 17.4 vpm of methane are withdrawn after the adsorber 22 from the liquid passing through it and introduced through the conduit 27 into the section 26.

21317 m³/h of gaseous oxygen containing 0.5 vpm of krypton and 5.4 vpm of methane leave the top of the section 24. The crude primary krypton/xenon mixture obtained (155 l/h measured as gas under standard conditions) at the base of section 26 contains 60 percent krypton, 4.5 percent xenon and 1 percent methane, the remainder being oxygen and small amounts of residual heavy hydrocarbons.

The gaseous oxygen leaving the top of section 24 is warmed to near ambient temperature, 18917 m³/h passing through the exchanger 12 and 2,400 m³/h through the exchanger 32. These two streams are then combined and compressed in a turbocompressor 34. 2400 m³/h are then withdrawn at an intermediate pressure of 4.6 bars and returned through the exchanger 32 into the reboiler 28 and then are expanded into the top of the section 24 to serve as reflux. The remaining 18917 m³/h are further compressed in the turbocompressor 34 followed by a piston compressor 36 to the required supply pressure of 30 to 40 bars.

When using as the reboiler a block of the plate and fin design in a tight circular enclosure the liquid surrounding the block enriches within about one week under the conditions of this example to a krypton content of 60 percent by volume.

The output of 155 litres/h of the crude primary krypton/xenon concentrate in the gaseous state corresponds to a liquid rate of about 0.24 litres/h. Such a small rate necessitates an intermittent withdrawal of the crude product from the sump of section 26 of the column 23. A weekly withdrawal yields about 40 litres of liquid, an amount which can be sent to a central station for further processing, for example with similar batches from other air separation units. Alternatively, the crude primary krypton/xenon concentrate can after compression be stored and transported in cylinders. In this case the liquid concentrate can either be compressed by a pump and then vaporised, or vaporised and then compressed at ambient temperature.

We claim:

1. A process for recovery of krypton and xenon from the oxygen produced in an air separation column wherein

- a. gaseous oxygen freed from at least the bulk of acetylene and the other higher hydrocarbons, is passed from the reboiler of the air separation column into a rectification column having an upper section and a lower section operating at the same pressure, the lower section having a reboiler at or near the base and the gaseous oxygen being introduced at or near the base of the upper section, yielding a crude primary krypton/xenon concentrate containing at least 10 percent of krypton,
- b. in the upper section there is employed a reflux ratio within the range of 14 to 5:1 sufficient to remove substantially all of the krypton and xenon from the ascending vapours but too low to remove all of the methane from the ascending vapours,
- c. the liquid obtained at the base of the upper section with at least same krypton, xenon and methane contents as the liquid oxygen in the reboiler of the air separation column is concentrated in the lower section to give at the base of the lower section the crude primary krypton/xenon concentrate having a

methane content substantially below the explosion limit and at the top of the lower section a vapour of relatively low krypton and xenon content which ascends into the upper section, and

- d. the gaseous oxygen is withdrawn from the top of the upper section and the crude primary krypton/xenon concentrate is withdrawn from the base of the lower section.

2. A process as claimed in claim 1, wherein any residual acetylene is removed by an adsorber located in the lower section of the rectification column.

3. A process as claimed in claim 2, wherein an additional reboiler is provided at an intermediate point in the lower section of the rectification column.

4. A process as claimed in claim 1, wherein the reflux ratio is maintained within the range of about 10:1.

5. A process as claimed in claim 1, wherein a small portion of the liquid oxygen from the reboiler of the air separation column is added 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 the accumulation of heavy hydrocarbons in the reboiler of the air separation column.

6. A process as claimed in claim 1, wherein the reboil in the rectification column is provided by condensing gaseous oxygen, the liquid oxygen thus obtained being introduced into the upper part of the upper section of the rectification column to act as the reflux.

7. A process as claimed in claim 6, wherein the gaseous oxygen feeding to the rectification column reboiler is a portion of the gaseous oxygen withdrawn from the top of the rectification column and after compression recycled into the reboiler.

8. A process as claimed in claim 1 wherein the reboil in the rectification column is provided by condensing air or nitrogen and providing a condenser in the rectification column.

9. A process as claimed in claim 6, wherein the reflux ratio is adjusted by providing a valve in the line supplying the reflux liquid to the upper part of the upper section.

10. A process as claimed in claim 9, wherein the valve is automatically controlled by a ratio controller between a flowmeter in the reflux supply line and a flowmeter in the gaseous oxygen withdrawal line.

11. A process as claimed in claim 1, wherein oxygen and residual hydrocarbons are removed from the crude concentrate by a hydrogen blowpipe.

12. A process as claimed in claim 1 wherein residual hydrocarbons contained in the crude primary concentrate are catalytically oxidised by copper oxide and oxygen is subsequently removed by reaction with manganese oxide, and the resulting gas mixture is dried and freed from carbon dioxide.

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

14. A process as claimed in claim 1, wherein the crude primary krypton/xenon concentrate contains about 60 percent krypton.

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