Review Article

Critical Methods of Purification for Cryogenic Applications

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Abstract

This article focuses mainly on the critical purification methods in especially oil and gas industries describing various phenomenon to be used based on the critical applications so that desired product is achieved with efficiency.

Keywords: Purification; CO_2; Circuit

Introduction

Purification is a process that separates unwanted particles from the desired product. The unwanted particles are of wide range that can be harmful environmentally and also effect the yield of the product for desirable purity. The same purifications are termed as adsorption, absorption in terms of distillation. Also condensation and solidification are considered to be the other process of purification.

Critical purifications methods

We have seen that cooling, air, down to its dew point (nearly -170°C under 6 bar) in exchangers is necessary before sending it in the distillation columns.

But then, if air is not purified, as temperature decreases, one can observe in exchangers (before air liquefaction starts):

- Vapour condensation (inevitably present in ambient air),
- Liquid water solidification (ice) at 0°C,
- Gaseous CO_2 condensation (appearance of carbonic snow): actually ambient air can content as much as 400 ppm of CO_2 ; and then under a 6 bar pressure, air CO_2 settles directly in solid from nearly -130°C.

Thus if no system of vapour and gaseous CO_2 elimination is planed, ice and carbonic snow will progressively plug up air passages in the exchanger.

Thus a purification system is required to maintain a continuous operation in a facility. Water and CO_2 will next be called impurities.
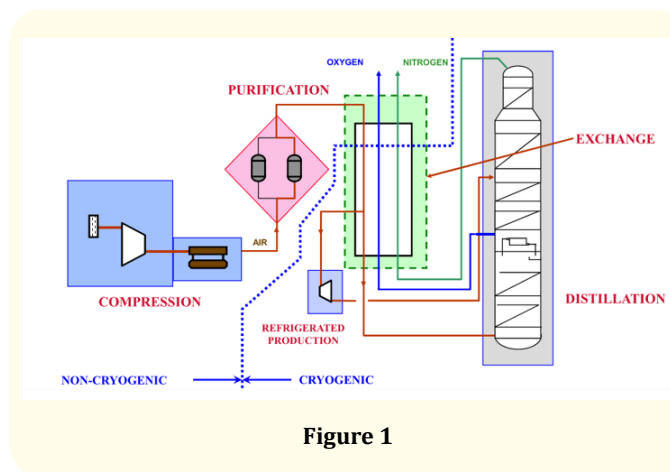

Figure 1

On the other hand, elimination as far as possible of hydrocarbons present in the air at concentrations of a few ppm (acetylene, methane, ethane, etc.) will still be necessary; they could concentrate in columns and, with oxygen, cause explosions.

Summarising panel of ambient air components and their respective proportions.

Figure 2

A part of purification can take place in the pre-cooling step (air/water tower).

Front end purification takes place in the adsorption technology.

This is a discontinuous process because of the "saturation" phenomenon of adsorbents.

Figure 3

Figure 4

The distillation process imposes us an air pressure called "average", about 6 abs. bar.

In order to reach this pressure, a compressor is used and liquid water is observed in draincocks placed at discharges of different device floors after coolers. Steam partially condenses during the compression, after cooling [3].

Let us consider liquid and vapour domains, corresponding to our devices working temperatures and pressures.

It is noticeable that to each temperature corresponds one saturated steam pressure, which is pressure at which steam start to condense.

This pressure can be related to maximal water quantity in liquid form that can be obtained at the considered temperature in a set volume.

When at this temperature, water quantity present in the air is higher than the content corresponding to saturated steam pressure, this water excess condenses. Of course, to maintain a constant temperature, for instance in a calorimeter, a cold source is needed (note: moisture content can not exceed 100%) [2].

Let us now consider an air volume at atmospheric pressure and at temperature T_1. It contains a certain quantity of water in vapour form corresponding to a partial pressure.

At this temperature T_1 corresponds a maximal water partial pressure, which is saturated vapour pressure of liquid water, or saturation pressure, under which air contains a maximal water quantity in vapour form. Every contained additional water quantity can only be in liquid form [1].

In this way, if this wet air quantity is condensed and cooled, water partial pressure reaches vapour pressure at saturation.

Water will condense once its partial pressure is equal to its saturated vapour pressure at temperature T_1.

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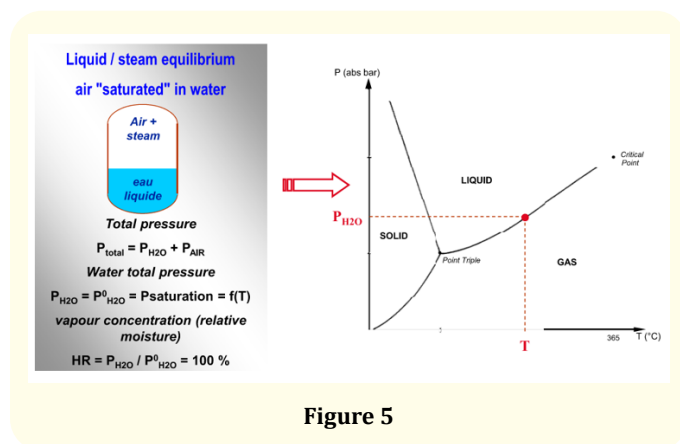
Figure 5

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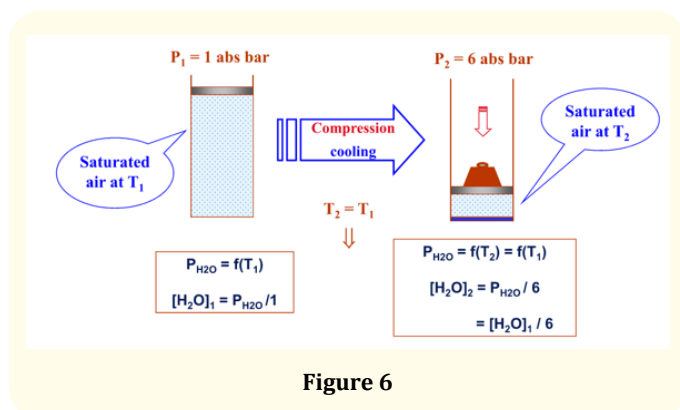Water will condense once its partial pressure is equal to its saturated vapour pressure at temperature T_1.

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Let us consider a two-stages compressor with intermediary cooler which compresses air from 1 to 5 abs. bar.

Generally, coolers are water exchangers, water itself is cooled by atmospheric air in an air/water tower.

By cooling from + 50°C to + 20°C (point 2 and 3 of the diagram), a part of water condenses. This water will be eliminated in the draincock. This is one of the interests of cooling down air after having compressed it to eliminate as much water as possible before the purification device.
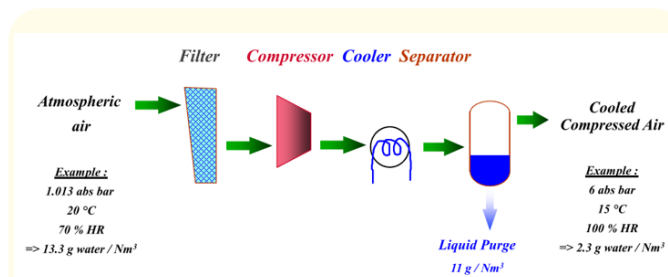

Figure 7

Note: fluid cooling after each compression floor is also necessary to avoid an excessive heating (which could for instance cause oil ignition, etc….) and it also allows to reduce energy consumption.

Reversible exchangers have a double role: cooling air to its dew point by exchange with gaseous products from columns (oxygen, nitrogen and impure nitrogen), and purify air from its water and CO_2.

Purification principle is refrigerated trapping.

During air cooling from ambient temperature to its dew point, water condenses in liquid state then solidifies, and CO_2 condenses in solid form. In the exchange line, at a temperature of nearly 0°C, water condenses and settles in liquid form, then in ice form at lower temperatures.

Actually, as air is at saturation at about 20°C in inlet, it contains a certain quantity of water (in gaseous state) which will decrease as temperature decreases.

Thus the difference between the quantity it contains at 20°C and the lower quantity it contains at a lower temperature ends up as deposit in exchanger (liquid or ice depending on the temperature) [5,6].

Concerning CO_2, we have seen that it condenses at about -130°C (for air under a 6 bar pressure).

Thus this condensation occurs at a temperature at which air does no more contain water: actually, there is hardly any water in vapour form in the air from -80°C upwards.

In practice, a reversible exchanger is divided into two exchangers (for technological reasons) separated by what is called the break.

Air temperature at the break is of about -80°C. It can be deduced that: water settles in the hot exchanger, and CO_2 deposits in the cold exchanger.

Thus in the outlet of the reversible exchanger, we have available air that can be called purified from its water and CO_2 (for instance, under 6 abs bar at -170°C, air contains only 0.2 ppm of CO_2).

The problem is that ice and carbonic snow progressively plug up passages in exchanger; in consequence they will have to be cleaned - it is said: regenerated -, thanks to impure nitrogen that will go upstream in passages containing deposits.

During this time, air will be sent to clean passages that impure nitrogen has just regenerated.

It is by this way noticeable that air and impure nitrogen passages are not fixed, and that they are inverted frequently enough (about every 15 minutes) to avoid air passages to be plugged up.

That is why we speak of reversible exchangers.

There are two very different types of passages in reversible exchangers:

- Fixed passages called like this because they are always passed through by the same gases. Pure products (oxygen and nitrogen) pass through these fixed passages.

- Reversible passages through which pass alternatively air under medium pressure and impure nitrogen under low pressure. Circuits inversion is made automatically by an inversion equipment.

Inversion is the automatic operation which consists in inverting air and impure nitrogen passages in reversible exchangers [7]. It is realised with shut-offs placed at the exchangers warm end, and with plugs placed at the exchangers cold end.

Shut-offs are automatic leak tight throttle valves. Four shut-offs are used for inverting circuits through which air comes in and impure nitrogen comes out. A fifth shut-off (E) is used for balancing circuits pressures before inversion.

Check-valves boxes: each cold exchanger is equipped with two pairs of plugs grouped together in a box at the cold end of the exchanger. Air and impure nitrogen are distributed between the pipes just because of their differences in pressure. Different operations are triggered 3 or 4 times an hour (at a normal rate) with a timer: KJV (timer control). Whole inversion operation lasts generally 5 to 10 seconds [8].

One of the important constraints is that air flow towards the cold box is totally null for about 7 seconds. In order to not disturb cold box working, two cold and hot exchangers groups are settled, and inversions of both batteries are brought forward of a half period. Total air flow is then distributed between both batteries. When one of them comes to inversion phase, air is directed towards a single battery (for about 7 seconds). Then the flow becomes of about 70% of its nominal value. At each inversion, air flow entering the M.P. column changes. This change can be prejudicial to both M.P. and B.P. columns stability (particularly in case of argon production).

Two-battery system allows, in case of problem on one of the exchangers batteries (for instance a de-icing), to still go on getting the facility work, even if the operation is disturbed: 70% of air flow at maximum and total cancellation of this air flow in each inversion for about 7 seconds. A vent valve is foreseen in order to flow out the compressor flow during the insulation needed to inversion.

Contrary to reversible exchangers, adsorption purification or front end purification has only a role of purification. Air cooling downstream will be assured by a classic exchanger (with set passages and no more reversible ones, what leads to a better sizing).

Conclusion

Its very important to choose the different types of critical purification methods for various applications for better productivity with atmost efficienciency in terms of operation and cost.

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