



CRYOGENIC CONDENSATION TECHNOLOGY

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INTRODUCTION

The cryogenic condensation technology developed by Polaris is a proven technique for the separation of volatile organic compounds from vent gases.

The principle of the technology is based on the decrease of vapour pressure at low temperature and consequent condensation of VOC's, by cooling the stream with liquid nitrogen or other cryogenic fluid. Due to the low operating temperature, some compounds can be separated in form of solid frost, depending on combination of melting point and vapor pressure equilibrium curves (vapor/liquid and vapor/solid equilibria). Polaris has developed a reliable design that allows a good separation of the condensed phases and a controlled fouling due to solid phase accumulation.

Each unit is specifically designed and customised for the required separation and VOC recovery, and the operating temperature is selected accordingly. The process and equipment configuration depends on several factors, considering the characteristics of the stream at the required operating temperature. The unit can include where necessary and/or convenient some pre-treatment steps, e.g. precooling, drying, washing, etc.

The units are fully automatic, thanks to a control system (PLC based) that monitors and adjusts the process parameters in order to get the required operating temperature and a stable and reliable working cycle. The operator interface is user friendly and includes useful features like automatic troubleshooting guide, records of events and process data, etc.

Due to the process principle, the technology is better applicable to process streams and to relatively VOC rich streams, for flowrates up to 5.000 Nm³/h, with no limits for inlet VOC concentration. The final concentration achievable for common VOC's are in the order of few ppm, and in compliance with the more strict requirements expressed by the European norms.

The cryogenic condensation process is apparently a "trivial" cooling application, but actually it involves some potential issues that have required some efforts to be overcome. In fact the standard approach for design of heat exchangers cannot be applied successfully. The maximum advantages have been got, from the great potential of cryogenic treatment, thanks to proprietary heat exchangers which are characterised by high fractionating capacity of vapours and gases.



PROCESS FEATURES

The effluent to be treated, containing volatile organic compounds at different concentration levels, is progressively cooled in counter-current in the vertical condensers below the dew point of the mixture. Therefore the pollutants are separated by simple condensation in a first phase, as far as physically possible. If the residual concentration of the pollutants in the effluent, at such condensation conditions, still results more than the allowed emission limits, the cooling is carried out at temperatures below their freezing point, in order to get a higher decrease of the pollutants residual vapour pressure, based on the sublimation equilibrium.

Due to the very low temperature of coolant, the skin temperature of the condenser is in any case lower than the melting point of the compounds to be separated, and consequently there is formation of solid onto the heat exchange surface. For this reason the condensers are designed and built with a special configuration that allows the formation of hard and soft solid deposits without any negative impact on the overall process performances.

In particular, when the effluent cooling temperature required by the process is below the freezing point, the surface is covered by solid aerosols in form of a very soft “snow” of organic or inorganic particles, which are intentionally kept inside the Polaris plant in order to avoid their release to atmosphere, that would nullify the achievement of the required purification level. After some time (6 to 12 hours usually) the heat-exchange rate progressively decreases and the pressure drop increases, and the condenser must be regenerated by heating, in order to defrost it. If the process is continuous, a second condenser must be used, kept in stand-by, ready for service.

The system performances during the operative cycle are ensured by controlling and monitoring the final effluent temperature in condensation/sublimation phase. The reliability of the process is ensured by the plant control system, that, thanks to special algorithms, constantly checks the correct process conditions, detects and solves any malfunction, and eventually promptly puts in service the stand-by condensation line.

In its typical applications, the cryogenic treatment is based on the use of liquid nitrogen, with which practically all pollution cases can be faced and solved, even the more complex ones, like the most noxious and volatile gases, for which the required process temperatures are as low as $-165\text{ }^{\circ}\text{C}$. The liquid nitrogen is evaporated inside the heat exchangers, in a circuit under pressure, and can be reused, because uncontaminated, by entering into the factory gas distribution network.

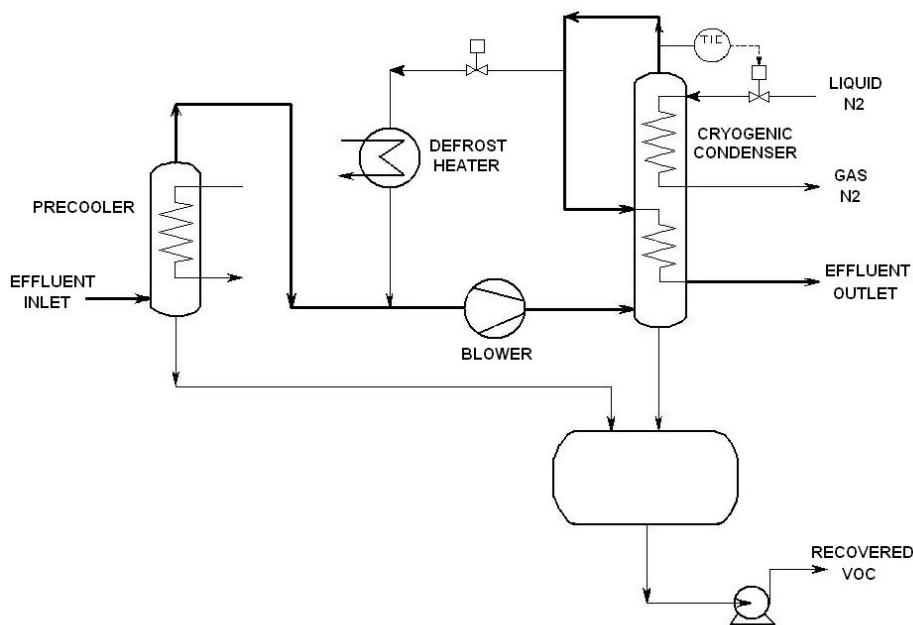
For easier separation cases, where the process temperature required for complying with the prescribed limits is higher, it can be sufficient the use of

other cooling fluids, like refrigerated solutions or refrigerated organic liquids, or directly expanded refrigerants.

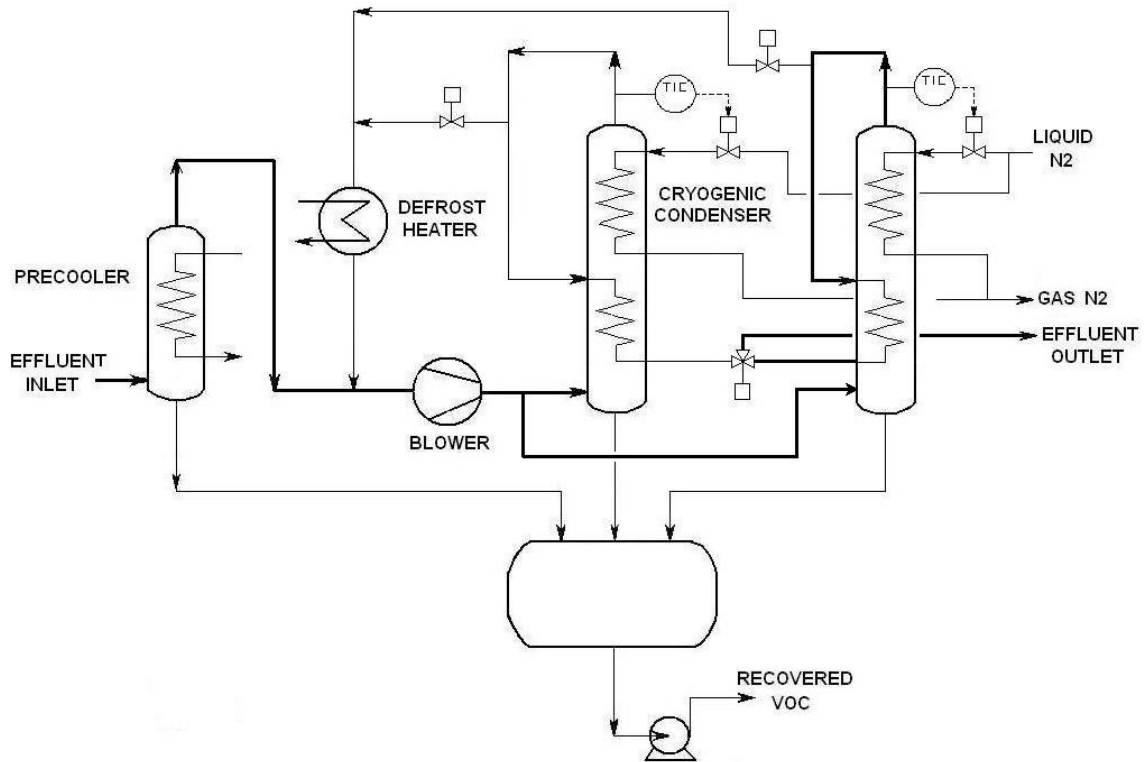
Polaris, in the course of years, has developed and optimised the cryogenic treatment of polluted emissions in all details, solving a wide number of technical, construction and control problems, by facing several cases with growing complexity, and making the technology effective and reliable, for fairly all types of pollutants, in particular for VOC.

Polaris has the experience of more than eighty units supplied, installed and running successfully in Europe and extra-Europe countries, in full respect of the more severe norms in force or in phase of approval, as well as of the more strict quality requirements imposed by customers for company ecological policy. Each system is supplied as a compact unit, skid mounted, complete and ready to run just after installation and external connections are completed and checked.

Picture 1: Typical scheme for a single condensation line unit



Picture 2: Typical scheme for a double condensation line unit





ENERGY CONSUMPTION

The cooling energy is the only significant consumption in the operation of the cryogenic treatment plant, with more relevant specific costs for lower condensation temperatures.

Besides a minor contribution due to insulation losses and to transitory start-up phases, the energy consumption is basically due to:

- a) cooling of the effluent, between inlet and outlet temperature in the unit (sensible heat to be removed)
- b) change of phase of the separated compounds (sensible and latent heat).

While it is practically impossible to save on the second energy consumption (excluding some processes where the pollutant is re-evaporated and separated in vapour phase), it is possible to carry out an efficient recovery on the first one's cryogenic energy, also in the order of 95 %, by cooling the inlet effluent with the same cold treated effluent, coming from the cryogenic condenser, in a pre-cooler, and by using for defrosting the energy of the incoming polluted effluents.

Also it is possible to use a cheaper cooling system for preliminary cooling steps, in particular for process with high moisture content, due to the significant latent heat for the water condensation.

The process is normally optimised and configured taking into account the net consumption of the system, considering for liquid nitrogen the quantity of gas recovered in the factory network for other uses.

In fact it is a common practice of most chemical industry, and in general where solvents or other VOC are used, to use nitrogen as inert gas for blanketing or purging in production and storage systems. Most frequently the production of the gaseous effluent is associated with a purge or with a product transfer, and consequently with a gas nitrogen consumption, so that the used nitrogen corresponds to the carrier gas of the effluent itself. For such cases the liquid nitrogen required for the cryogenic treatment of the effluent is fairly always less than the flow-rate of the effluent itself, and consequently less than the quantity of recoverable nitrogen. In these cases the operating cost of the cryogenic treatment is very close to zero.



COMPARISON WITH OTHER ABATEMENT TECHNOLOGIES

The cryogenic treatment of vent gases is a recuperative technique, that allows the re-use of the separated compounds, or other ways of use or disposal to recover part of their value.

Compared with other recuperative techniques, based on activated carbons or resins adsorption, or, sometimes, on absorption with liquids, the cryogenic treatment results economically convenient, for investment and operation costs, when the concentration of the pollutants exceeds values between 1.000 to 3.000 mg/m³, depending on the type of pollutant.

Anyway, by integrating the cryogenic treatment with adsorption, as per another patented Polaris technology, the combined method results optimal also for lower pollutant concentration, and particularly when the compounds to be separated are in form of gas.

If compared with common activated carbon adsorption systems with steam regeneration, with the cryogenic treatment the production is avoided of significant quantities of polluted water (that must be than purified internally or by third party), as well as any other negative phenomenon resulting, in phase of regeneration, in other recuperative systems.

If the separated pollutants cannot be recovered anyway, but they are to be transferred to third party for disposal, the cryogenic technique is anyway competitive as it reduces the quantity, and consequent costs, of wastes.

It must be underlined that the use of non-recuperative techniques for vent gas treatment, like catalytic or regenerative combustion, to solve the same environmental problem, involves locally the problem of significant environmental impact, associated with risk situations to be evaluated with attention.

The combustion originates large volumes of flue gases, even often increased by the preliminary dilution of the effluent for safety or functional reasons, that contain, even if within the law limits, the new products of combustion (carbon oxides, nitrogen oxides, organic compounds originated by uncompleted combustion of VOC, often even very toxic) and the residual quantities of the original VOC present in the effluent. In particular, as the cryogenic treatment does not require any dilution, the final concentration refers normally to lower flow-rate than for such systems, so that the mass flow-rate is also lower. Even not taking into account the operating costs for support fuel and for purification of flue gases where necessary, there is an intrinsic difficulty in ensuring in all moments a perfect performance of combustion. In some industrial contexts, in particular near civil installations or inside chemical poles where the environmental conditions are already jeopardised by diffused emissions, the impact of a combustion plant for vent gases can result non tolerable. It is then much more appropriate to separate the pollutants in liquid form and to transfer the same to an adequate disposal centre, or to burn the



wastes in a captive incinerator for liquids, as this kind of system does not present particular safety problems and produces much lower quantities of flue gases, for same quantity of VOC to be incinerated.

As far as safety aspects are concerned, the cryogenic treatment technique is incomparably safer than any other, and while frequent accidents occur related to incinerators and conventional activated carbon adsorption systems, it never occurred an accident related to cryogenic treatment systems. In particular, it is not required to make dilution of the effluent with excess air or inert gas to avoid explosion problems of the organic mixtures, or the overheating of the adsorption or the catalytic beds. In fact, during the cryogenic process pathway, the effluent only meets surfaces at temperatures much lower than ignition levels, and where it is not possible to generate an ignition source for friction or accumulate electrostatic charges.

For the above described reasons, the cryogenic treatment appears as the ideal solution from the point of view of ecology and safety. The best application field is for medium and high VOC concentrations, where the economical convenience is more evident, but it can also be economically suitable for lower concentrations, as combined method. To support the application of cryogenic treatment, it is recommendable that the collection of emissions from the various points (reactors, mixers, centrifuges, dryers, tanks, and all other process and accessory industrial equipment) are made at source, in order to avoid any unnecessary dilution with ambient air. In this way the size of the treatment unit is reduced and the efficiency is increased, and consequently the investment and operating costs are reduced.



BENEFITS OF CRYOGENIC CONDENSATION (SUMMARY)

- In most cases the VOC's separated by the effluent can be recovered for further use;
- It is a "static" equipment, no machinery/mechanical equipment more than the blower and valves – low maintenance cost – higher reliability of components;
- It is a safe process, no addition of air is required, no risk of flammability is introduced;
- It is a flexible process, suitable for practically all VOC's;
- The VOC's are separated without addition of other chemicals or dilution with water, and consequently the further processing of the recovered VOC's is easier, and in case the condensate cannot be recovered the disposal costs are reduced;
- No secondary pollutants are produced in the process;
- The unit is compact and requires a relatively small footprint, the prefabrication allows lower installation and commissioning costs;
- The operating cost is low thanks to the reuse of nitrogen used for cooling;
- The investment cost is relatively low for application to process vent streams.



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PICTURES

- size 400 Nm³/h
- pollutant: mixed solvents



- size 400 Nm³/h
- pollutant: freon R11



- size 250 Nm³/h
- pollutant: DCM