

## **CRYOGENIC SOLVENT ABATEMENT (VOC's )**



## **1. Introduction**

The technology for removing volatile organic compounds (V.O.C.s) from gas has been developed to meet the emission limits, decreased during the last twenty years, to control the pollution and to take care of health.

The process varies from simple once through wash operations to complex multiple-step recycle systems.

In many cases the process complexities are due to the reuse of the material employed to remove it.

The primary operation of gas purification is generally included in one of the following unit operations:

- absorption into a liquid;
- adsorption on a solid;
- low temperature condensation;
- chemical conversion to another compound;
- permeation through a membrane.

To put the requirements of V.O.C.s removal it is useful to compare the purity levels that are required, the flow rates, the utilities that are available, the V.O.C. chemical characteristics, the energy balance etc.

To give an idea of the process differences in succession there is a brief description of any unit operation that is in competition with low temperature condensation.

## 1.1 Absorption

The process consists in compound transfer from a gas phase to a liquid phase in which is soluble.

The absorbed compound can be stripped and recovered.

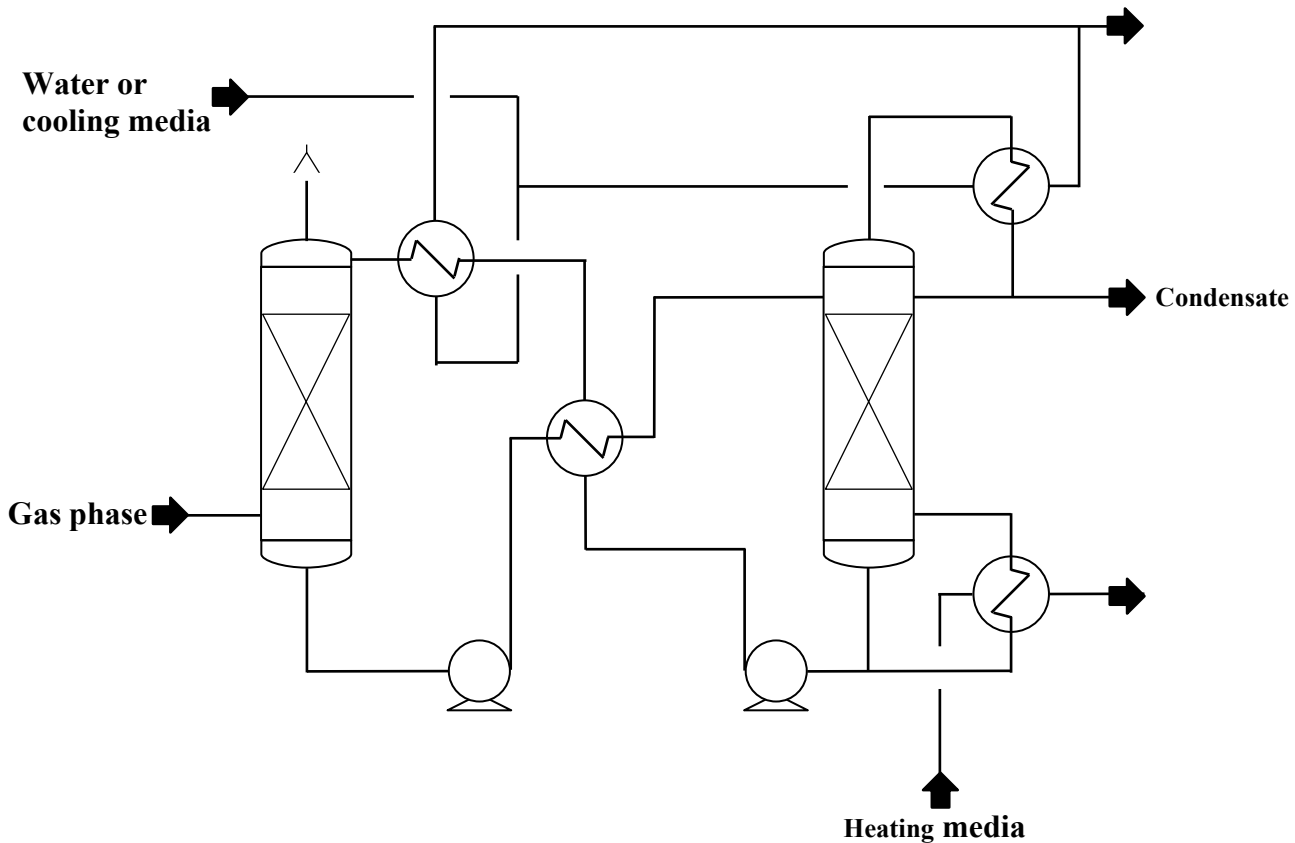


Figure 1.1 Typical absorber

The absorption depends on the solvent vapour pressure to be recovered over the absorbent liquor.

## 1.2 Adsorption

The process is based on the selective concentration of one or more compounds (adsorbates) of a gas mixture on a microporous solid surface (adsorbent) .

The attractive forces keeping the adsorbate on the adsorbent are weaker than those of a chemical bond.

The adsorbate can generally be desorbed by raising the temperature or reducing the partial pressure of the compound.

When an adsorbed compound reacts chemically with the adsorbent the operation is called chemisorption and the desorption is generally not possible.

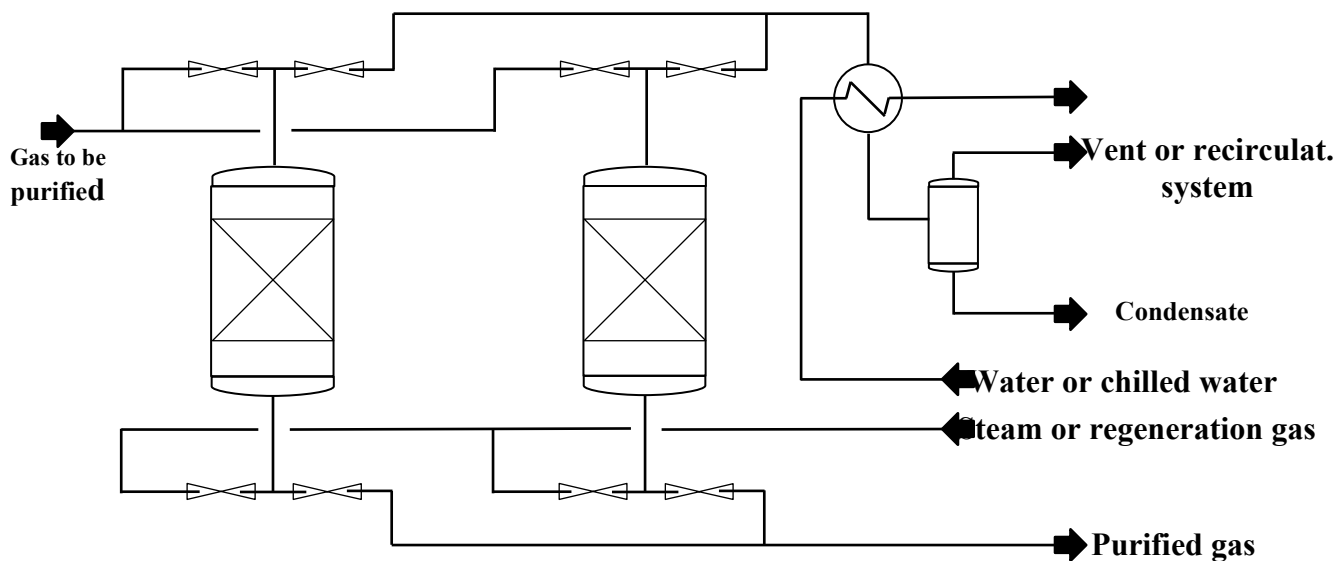


Figure 1.2 Typical Adsorber

### **1.3 Permeation through a membrane**

This technology is relatively new in the field of gas purification. The process forecasts a selective permeation of gaseous compounds through a polymeric membrane from one side of a membrane to the other side.

The mechanism of a solution diffusion involves the following steps:

- a) adsorption of the gas on the membrane surface;
- b) solution of the gas into the membrane;
- c) diffusion of the gas through the membrane;
- d) release of the gas at the opposite surface;
- e) desorption of the gas from the surface.

The term permeation is used to describe the overall transport of the gases through the membrane.

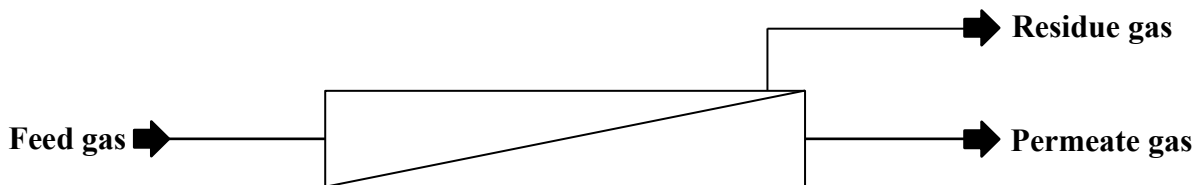


Figure 1.3 Typical Permeation

## **1.4 Chemical conversion to another compound**

This denomination includes a wide variety of processes, including catalytic and non catalytic gas phase reactions (thermal or regenerative) that are the main processes that are included in this category.

The processes involve the chemical reaction of one or more gas phase species, including the impurities to be removed, to form new species which remain in the gas.

In the catalytic processes the reaction rate is accelerated to a low or moderate temperature by the presence of an active catalyst.

In the thermal or regenerated processes the reaction to have an exceptionally high rate must operate with an elevated temperature.

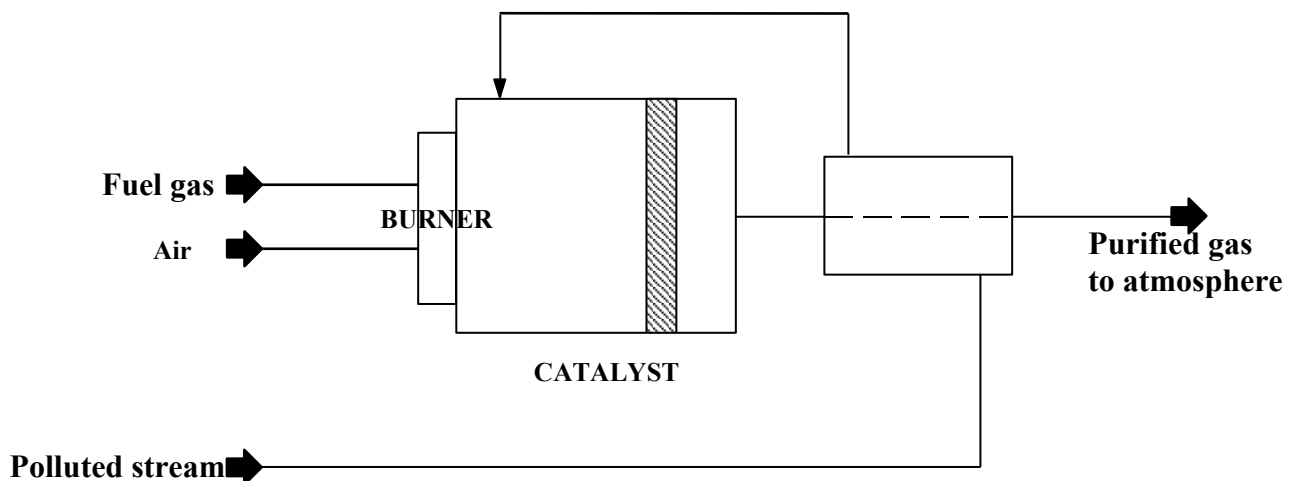


Figure 1.4a Typical catalytic oxidaton

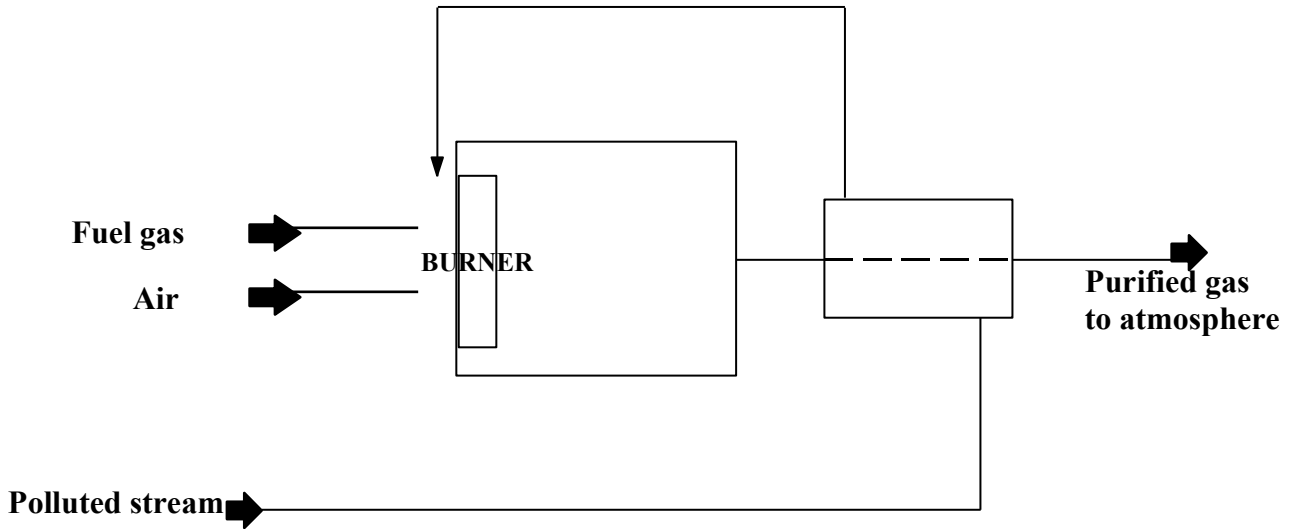


Figure 1.4b Typical thermal oxidation

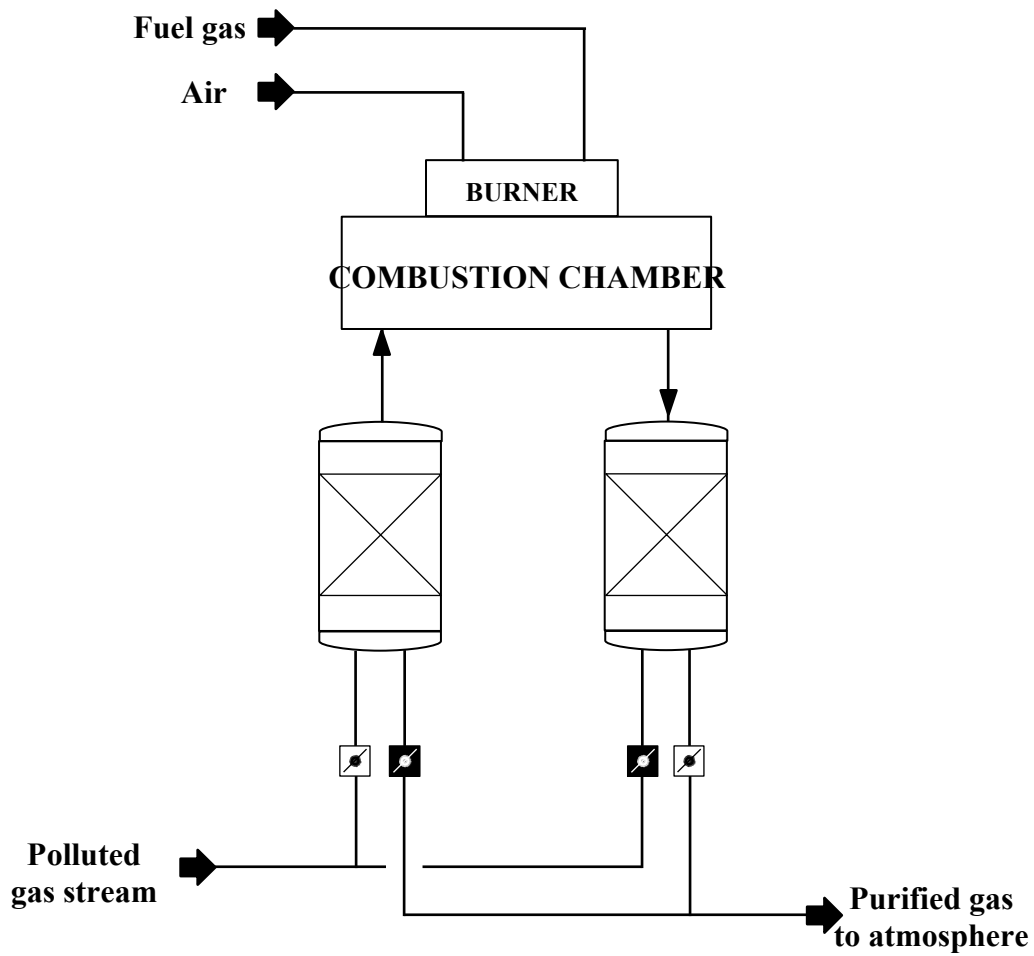


Figure 1.4c Typical regenerative oxidation

## **2. Low temperature V.O.C.s gas purification**

This operation of the mixture of V.O.C.s with condensation at low temperatures has been experimented extensively in the last years starting from industrial cryogenic process such as:

- 1) hydrogen purification for ammonia synthesis and other uses;
- 2) nitrogen removal from natural gas;
- 3) carbon dioxide and hydrogen sulphide removal from natural gas.

Normally the technology is called cryogenics when the operating temperature is below  $-75^{\circ}\text{C}$ . Table 2.1 shows the very low temperature that must be reached to condense solvents from a stream sufficiently well to make it fit to work in or, assuming TA luft or some similar regulations become the international standard, to discharge into the atmosphere.

In many cases the required low temperature is below a pure solvent's freezing point.

Figure 2.1 shows a 24h cryogenic plant using liquid nitrogen as bringing frigorities to the system. The plant has a pre-cooler in which the frigorities of the cooled gas and of gaseous in frozen are recovered, followed by a final condenser using liquid nitrogen to reach the final gas temperature.

The fan guarantees the gas removing (low pressure drop).

It is possible to insert a carbon activated guard, that can either be or not be regenerated to be sure of the plant limit observance.

Once every 8-12h, or as required, the procedure and final condenser should be defrosted using an electric resistance.

There are many different plant arrangements starting from only one condenser (8h working day) up to the diagram explained in Figure 2.1 depending on the different situations.

The plant safety is very high because the low temperature condensers are refrigerated flame arrestors of great depth. The vapour passes through 4-6m lined frost covered surface as cold as  $-181^{\circ}\text{C}$ .

The vapour passes through the explosive range at greatly reduced temperature.

The tubes are made in aluminium or stainless steel. In the case of acidity present especially given by hydrochloride acid it is necessary to insert a tower by using a basic solution to neutralise the gaseous stream to avoid the possibility of equipment corrosion. The refrigerant is non-flammable. The refrigeration as far as the system of recovery is safe.

### **3. Low temperature condensation advantages**

The condensation system has the following advantages :

a) Low Capital cost

Our unit in the range of 100-1000 Nmc/h has a very competitive investment with the absorption system that is the cheapest system.

b) Low power cost

The plant operates on demand only and the consumption of liquid nitrogen depends on the energy necessary to condense water and solvents that must be increased by 10-20% to compensate the frigorific dispersion plus frigorific expelled from the system (outlet temperature).

The energy consumption is equal to fan energy power plus energy used for the defrosting. Generally the demand of liquid nitrogen is less than the normal consumption of a chemical or pharmaceutical factory.

c) Low maintenance cost

The maintenance cost is very low and limited to fan, automatic valves and instrumentation.

It is also possible to hire the service including the supply of liquid nitrogen from a technical gas manufacturer.

d) Plant safety

The equipment considered in the reasons explained in point 2, have a very low possibility of a fire or explosion.

e) High flow rate variation

The plant can support a wide variation of flow rate without any problem. In general we suggest to regulate the insertion in the abatement plant of the vacuum pumps that in general rapport the very high amount of solvents.

f) Ease of performance monitoring

The outlet temperature is read and is correlated with a vapour pressure chart as accepted by EPA 40 CFR parts 9 and 63 dated 14/12/94.

g) Low pressure drop

The plant has a maximum pressure drop of 300mm of water.

h) Solvent recovered in a liquid state

The solvent recovered can be easily measured and re-employed if the humidity can be acceptable.

i) No significant additional pollution problem created

The processing of nitrogen or air at room temperature adds, by means of atmospheric pressure, only 15-20 grams/Nmc of water.

**4.Process selection**

For the V.O.C.s removal it is necessary to consider the following parameters :

- a) limits to be respected and toxicology;
- b) flow-rate
- c) flow-rate variation
- d) stream pressure
- e) physical, chemical and biological properties of the compounds to be removed

The processes in competition have the following limits:

	Observation Limit	Flow-rate Limit	Flow-rate variation	Compound Influence Property	Capital Cost
Incineration	++++	++++	++++	+	+
Absorption	++	++++	+++	++++	+
Cryogenic condensation	++++	+++	++++	+	++
Membrane	+	++	+	+++	++++
Adsorption	+++	++++	+++	+++	++++

+ low    +++++ high

The cryogenic condensation flow rates up to 1000 Nmc/h is the best choice.



### 5. Form

Composition:	min.	max.	%vol %weight
Flow-rate	min. max. norm.		Nmc/h Nmc/h Nmc/h
Acidity			
Pressure			
Limits to be guaranteed			
Solvent recovered can be reused	YES		NO
Water humidity to be respected in case of solvent reuse			



**CRIO&ENG** S.R.L.