CONTROL OF CARBON MONOXIDE AND VOLATILE ORGANIC COMPOUNDS, INCLUDING CONDENSATION

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Summary

This chapter treats three different subjects that have little in common:

- Condensation is a major thermal unit operation in heat transfer technology that can be used to recover solvents and other condensable vapors from off-gas streams. Volatile solvents require very low operating temperatures in order to attain typical emission threshold values, so that cryogenic condensation becomes mandatory, with its concomitant technical and operating problems. The process is only economically feasible for rather concentrated off-gas streams. Dilute streams are first concentrated by adsorption.

- Carbon monoxide, CO is an important industrial gas, with lethally incapacitating properties. It is a component of numerous industrial gases, such as generator gas, synthesis gas, coking furnace gas, wood gas and also an intermediate in numerous chemical processes, such as the Fischer-Tropsch synthesis, the synthesis of oxo-alcohols and aldehydes, the production of phosgene, etc. From industrial gases it is removed by:

    - Scrubbing by a highly corrosive copper chloride solution. The industrial application of this method has long been discontinued.
    - Catalytically converting CO into CO_2, according to the water gas shift reaction.
    - Catalytic methanation of CO with hydrogen to methane, forming a synthetic natural gas.
    - Scrubbing with liquid nitrogen, which dissolves almost all gas impurities.

- Carbon monoxide is also a major product of incomplete combustion. It can be decreased by clean combustion techniques or by thermal or catalytic post-combustion (see *Pollution Control through Efficient Combustion Technology*).
- Volatile Organic Compounds may be controlled by a variety of means:

    - Prevention;
    - Condensation;
    - Adsorption (see *Adsorption of Gaseous Pollutants* and *Adsorbents and Adsorption Processes for Pollution Control*);
    - Thermal or catalytic post-combustion (see *Pollution Control through Efficient Combustion Technology*)
    - Membrane processes; these are at an R&D-stage and discussed at the end of this article.

1. Condensation

3.7 Technical Importance of Condensation

Condensation is a purely physical transformation, referring to the change of phase from vapor to liquid and accompanied by both the liberation of latent heat of condensation and significant reduction in volume. Because of the large heat effect and the use of heat exchangers condensation is often treated in manuals on Heat Transfer. Important applications are the condensation of steam in the thermodynamic cycle of a power plant (see *Pollution Control through Efficient Combustion Technology*), production of potable water using multiple effect and multi-flash seawater desalination units, and in crystallization processes - concentration and super saturation of the solutions of sugar, salts, etc.

Compound	Formula	Enthalpy of Vaporization, $\Delta_{vap}H$ (25° C) kJ mol^{-1}
Water	H_2O	43.99
Methanol	CH_4O	37.43
Acetone	C_3H_6O	30.99
Ethanol	C_2H_6O	42.32
n-hexane	C_6H_{14}	31.56
Chloroform (trichloromethane)	$CHCl_3$	31.28
Methylene chloride (dichloromethane)	CH_2Cl_2	28.82
Perchlorethylene (tetrachloroethylene)	C_2Cl_4	39.68
Methylethylketon (2-butanone)	C_4H_8O	34.79
Diethyl ether	$C_4H_{10}O$	27.10

[Source: Lide David R., “CRC Handbook of Chemistry and Physics”, 74th Edition 1993-1994, CRC Press]

Table 1: Selected values for the latent heat of condensation

In solving pollution problems the major application of condensation is in separating solvents from a concentrated off-gas stream. However, this is normally not the case in applications such as that of drying printing inks, paints and varnishes, glues, the application of coatings on paper or plastics, etc. After their application in this wide variety of industrial operations, the solvents can conveniently be recovered and often also reused. Reusing the solvent is not so straightforward, since an enterprise using inks, glues, or coatings is not the same as the enterprise manufacturing such commodities. Moreover, the solvent may be a complex mixture, very much diluted and possibly polluted with dust and water vapor.

Condensation is not only a Method of Gas Treatment but also a potentially Clean Technology, involving Resource Recovery, since the solvent - in principle - can be recovered for further use, rather than to be thermally or catalytically destroyed, oxidized, adsorbed, absorbed, or worse - vented to the atmosphere.

There is an important thermodynamic aspect in such processes, since heat of evaporation is required when drying the solvent and liberated during condensation. The latent heat is normally transferred to cooling water and hence lost in the process.

3.7.1 Film Condensation and Dropwise Condensation

Film condensation takes place when a vapor is in contact with a surface at a temperature well below its saturation temperature. The vapor then typically condenses to a continuous, liquid film that covers the cooling surface and runs off from it. Such a film constitutes a sizeable supplemental resistance to conductive heat transfer, markedly reducing the rate of heat transfer, and calling for much larger and hence more expensive heat exchangers.

In *dropwise condensation* the condensate appears in many small and discrete droplets formed at various points of the cold surface, which is no longer uniformly wetted. The absence of a continuous liquid film considerably reduces resistance to heat transfer at the cold wall. The individual droplets grow, coalesce with adjacent droplets to form rows of rivulets flowing down the surface, which on their way collect droplets and leave a dry surface in their wake. Dropwise condensation is promoted by impurities in the vapor stream. The presence of air in the condensing vapor must be avoided at all cost, since such air dilutes the condensing vapors and adversely affects the quality of heat transfer. Hence, both the rate and extent of condensation are reduced. Air must always be purged carefully out of all heat exchangers.

3.7.2 Solvent Recovery

Solvent recovery is applicable mainly when the solvent concentration is quite high, its vapor pressure and volatility limited, and the gas flow relatively small (below 1000 $m^3 h^{-1}$). It is important to collect such effluents as concentrated as possible, i.e. at the source and diluted with only a minimum of air. This can best be realized in a completely closed plant, in which the solvent is used in a cyclic mode, such as the one in Figure 1, showing a typical tunnel dryer, as used in printing, coating and other operations involving a solvent as a carrier. An inert gas enters the dryer at the end, gradually becomes charged with solvent vapors, and is withdrawn at the entrance of the tunnel.

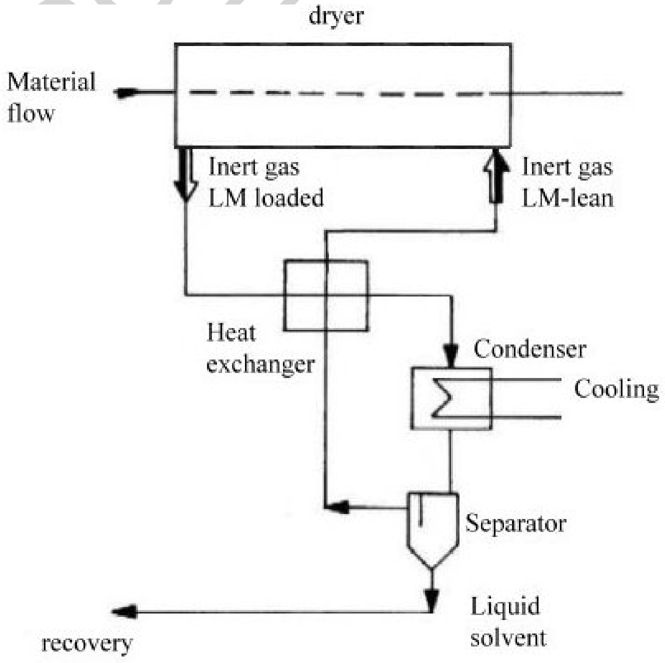

Figure 1: Solvent recovery from a dryer using an inert gas cycle

The solvent laden gas first is cooled in a heat exchanger (while heating the circulating drying gas) and finally further and deeply cooled in a separate and dedicated condenser, so that the solvent vapors are largely condensed and recovered. In favorable cases the solvent can be reused directly, in others it requires preliminary drying and cleaning:

Some interesting design and operating aspects are:

- Such operations usually perform best, when operating in countercurrent, i.e. when the material flow in the dryer and the cycle gas move in opposite directions.
- The solvent is condensed to the liquid phase. However, the cycle gas still contains solvent vapor, ideally (i.e. in the thermodynamic equilibrium state) that concentration corresponding with the solvent vapor pressure at the operating temperature in the condenser. The lower this temperature, the deeper the condensation, but the higher the operating cost.
- Sometimes, the vapor converts into a vapor mist that is not separated by the condenser. In that case it is essential to provide a suitable demister (see *Wet Scrubbers*).
- In principle, the recycle gas can be completely freed from vapors, by leading the recycle stream through a fixed bed adsorber. This simple addition improves the efficiency, but increases the investment and operating costs.

In most cases, it is impractical to enclose a drying line completely. Indeed, most drying tunnels need to provide free access to the stream being dried, e.g. films or other coated or printed materials. The same holds for other solvent-based operations, such as degreasing parts before they are being painted or coated.

[Source: Bank M. (2000) “Basiswissen Umwelttechnik : Wasser, Luft, Abfall, Lärm und Umweltrecht” – 4., komplett neue, bearbeitete Auflage, Wurzburg: Vogel, ISBN 3-8023-1797-1]

Off-Gas												
		Concentrate					Thermal Conversion					
Methods		Condensation	Activated Carbon				Catalytic Combustion		Thermal Combustion		Thermal Oxidation	
		Cryogenic	Wheel type	Annular	Fixed Bed		Regenox	Catox	Thermal air Cleaning	Combustor	Thermo Reactor	Combu Changer
Characteristics	Pollutant Concentration (g per Nm³)	10 - 1000 (3000)	0.1 - 15	0.1 to 15	0.1 to 15	Pollutant Concentration (g per Nm³)	< 5	< 10	< 20	No Limit	< 10	< 5
	Concentration Factor	Solvent	1/20	1/20	1/15	Autothermal Operation Limit (g per Nm³)	0.8	3.5	-	-	1.7	0.8
	Flow Rate (kNm³ per h)	< 1.2	< 30	< 80	< 450	Flow Rate (kNm³ per h)	< 0.3	< 0.3	0.5 - 80	No Limit	5 to 250	Low
	Inlet Temperature ° C	< 30	< 30	< 30	< 30	Inlet Temperature ° C	190 - 450	200 - 380	780	800 - 1000	800 - 1000	1000
Final Result		Solvent Recovery					Thermal destruction with regenerative or conventional heat exchange					

Table 2: Areas of application of solvent recovery and thermal destruction.

3.8 Safety Aspects

Drying with air generates a safety hazard when the solvent is flammable.

Safety requires avoiding the occurrence of flammable solvent/air mixtures, as well as that of ignition sources. Static electricity may be especially problematic, e.g. when processing plastics or other materials that are poor electric conductors. Indeed, once dried many substances see their electric resistance enhanced, so that electrical charging becomes problematic and even hazardous.

Vapors only condense after becoming supersaturated, i.e. when their concentration exceeds the vapor pressure at the given temperature. For safety reasons this concentration must not exceed at most 50 % and preferably 25 % of the Lower Explosion Limit (L.E.L.) of a flammable vapor. The relation between the actual concentration and the L.E.L.-value can be verified using a pellistor (see *Effluent Gas Monitoring*).

As a safe but expensive alternative, an inert carrier gas (e.g. nitrogen, carbon dioxide or oxygen lean combustion gases) sometimes replaces air.

3.9 Cryo-condensation

Solvent recovery from a gas stream is practically feasible with concentration levels of > 25 g m^{-3} for indirect or of > 50 g m^{-3} for direct condensation. Usual solvents, depending on their volatility, range from circa 10 (low volatility) to circa 1000 g m^{-3} (highly volatile, e.g. dichloromethane) when saturated in air or gas at ambient temperature. The residual concentration can be further decreased using *cryo-condensation*.

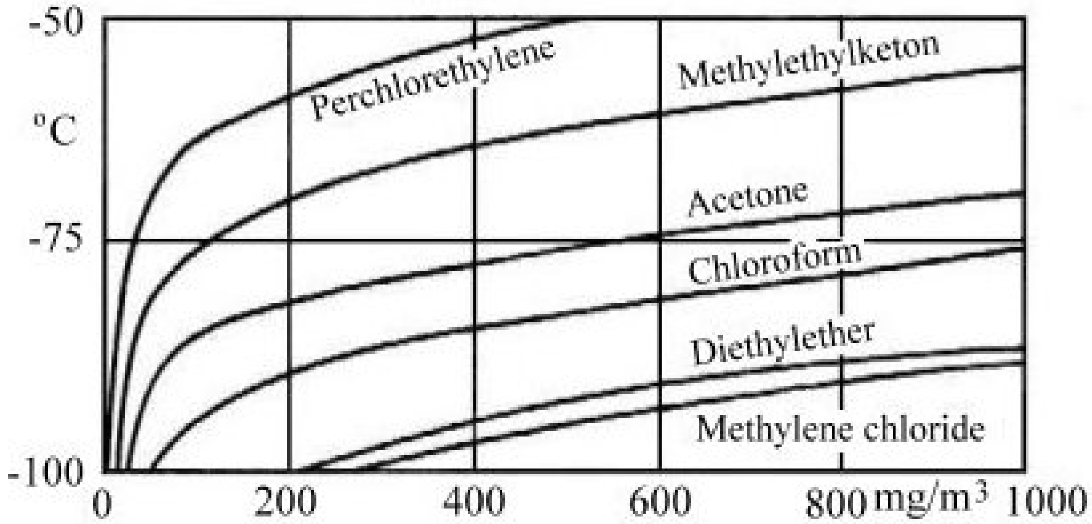

Figure 2: Operating Temperature vs. Concentration for low to highly volatile solvents

Figure 2 shows examples of saturation curves at cryogenic conditions for a number of widely used solvents.

Condensation may be combined with another operation, e.g.:

- Condensation, with *subsequent adsorption* of the residual vapors on activated carbon, molecular sieves, or other adsorbents, to eliminate the residual content to the very low limit emission values required. Condensation separates the bulk of the stream before adsorption, thus safeguarding expensive adsorption capacity. Conversely, adsorption allows attaining very low limit values that would require excessively deep cryogenic cooling temperatures. Periodically, during regeneration the adsorbent yields a concentrated flow of solvent that, after cooling, can be treated by (cryo-) condensation, as in the second possible combination.

- Solvents from air or gases are subjected to a preliminary *pre-concentration*, using activated carbon adsorption. The regeneration of the carbon, e.g. with steam, generates a concentrated stream of solvent, that is recovered by condensation. Such systems should always consider carefully the nature and amount of impurities entering into the system and eventually requiring their elimination as a bleed stream. In drying applications, for example, it must be verified whether the inks, adhesives or coatings will liberate pure solvent, or solvent loaded with impurities, thermal decomposition products, moisture, etc. Regenerating the adsorbent with steam is the preferred operating method with water insoluble solvents, such as toluene or chlorinated solvents. Nevertheless, the steam condensate contains traces of solvents, the solvent traces of water. Treating wastewaters and drying solvents add considerably to both complexity and investment and operating costs.

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Biographical Sketch

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).