LIQUID AIR

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Table of Contents

Amendments to Doc 197/21

Section	Change
4.2	Prevention of accumulation of contaminants

Note Technical changes from the previous edition are underlined

1 Introduction

Starting from the 1990s a number of applications for the use of liquid air, particularly within the food industry, were identified and as such there was an increase in its production and use.

In recent years liquid air has been proposed as an “energy vector”, in both the electricity grid and in transport.

Liquid air can also be used as raw material to fill compressed air gas cylinders, for industrial and breathable applications.

Liquid air has properties that differ from those of other cryogenic liquids, such as liquid oxygen or liquid nitrogen, and which can give rise to specific safety hazards.

The European Industrial Gases Association (EIGA) has therefore recognised the need for a publication addressing safety in production, storage, distribution and use of liquid air.

2 Scope and purpose

2.1 Scope

This publication applies to the production, permanent storage and transportation of liquid air.

General guidelines for the application of liquid air are also covered, but it is not the intention of this publication to review specific applications.

Breathing applications may require additional safeguards or be covered by additional legislation.

2.2 Purpose

This document is intended to provide guidance to EIGA members and their customers for the safe production, storage, transportation and use of liquid air.

It is intended to explain the specific nature of this two-component product and the need for expert involvement in all aspects of production and use of liquid air.

3 Terminology and definitions

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May and need not

Indicates that the procedure is optional.

3.1.4 Will

Used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Definitions

3.2.1 Liquid air

Air in a cryogenic liquid state, having a typical composition of 21% (by volume) oxygen, with the balance essentially nitrogen.

3.2.2 Tank

Thermally insulated tank that can be filled with a cryogenic liquid for storage purposes.

3.3 Tanker

Vehicle used for the transport of cryogenic liquid in an insulated vessel.

4 General

4.1 Physical properties of liquid air

The properties of liquid air vary slightly depending on the exact percentages of the components.

The table below gives the properties for a typical mixture.

Properties of mixture of 20% Oxygen, 80% Nitrogen, mixture by volume	
Boiling point (bubble point) at 1.013 bar absolute	78.7 K
Vapour Density at 0°C	1.29 kg/m^3
Molecular weight	28.81

Table 1: Properties of Liquid Air

4.2 Precautions

Because liquid nitrogen has a lower boiling point than liquid oxygen, if liquid air is stored in a closed vessel (tank or tanker) with a headspace containing gas above the liquid, the gas phase will have a higher concentration of nitrogen and the liquid phase will have a higher concentration of oxygen. When a release of gas occurs the oxygen content of the liquid phase will increase.

In a similar way, the concentration of contaminants such as hydrocarbons, carbon dioxide and nitrous oxide can increase in the liquid phase when the liquid is vaporized since the gas leaving the system does not contain the contaminants. Precautions should be taken to prevent accumulation of these contaminants to unacceptable levels. One common way to avoid high levels of enrichment is to ensure a withdrawal of some of the liquid air from time to time. This purge provides a way for the contaminants to leave the system.

It is because of these specific properties that liquid air shall be handled with care at any point where it is or may be liquid, since oxygen enrichment of the liquid and oxygen deficiency of the vaporised gas, can occur.

Precautions shall also be taken against the hazards associated with the low temperatures of cryogenic liquids. These precautions are detailed in documents such as:

Doc 44 - *Hazards of Oxygen Deficient Atmospheres* [1] [1]

Doc 224 - *Static Vacuum Insulated Cryogenic Vessels Operation and Inspection* [2]

Doc 33 - *Cleaning of Equipment for Oxygen Service*. [3]

Doc 04 - *Fire Hazards of Oxygen and Oxygen Enriched Atmospheres*. [4]

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[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section

Doc 13 - *Oxygen Pipeline and Piping Systems*. [5]

Local legislation and gas company standards shall be complied with.

4.3 Training and protection of personnel

All personnel involved in the production, handling and use of liquid air, including customer staff, delivery drivers, production, quality control and maintenance personnel shall receive a specific training.

The training shall cover the properties of the product and the dangers of venting or release of gas, as well as the risks, common to all cryogenic liquids, associated with low temperatures.

4.4 Analysis of liquid air

The analysis of liquid air is more complex than the analysis of pure cryogenic liquids, since it is possible that the composition of the mixture changes during sampling and analysis.

Samples shall be taken from the liquid phase and care shall be taken to ensure that a representative sample is taken.

The liquid sample shall be completely evaporated before it reaches the analyser, because, should the liquid evaporate partially at the sampling point, the analysis will be incorrect or analysers shall be located as close as possible to the sample point, in order to prevent flash separation of the two primary components.

A continuous flow shall be taken through the analyser, and a steady reading obtained, since intermittent sampling is likely to give incorrect readings. Liquid sampling systems which allow venting as the sample is collected will not give a correct analysis for liquid air.

The accuracy of the analysis system shall be in coherence with the target specification and tolerances.

Analysers shall be calibrated and operated under approved procedures by qualified personnel. Records of the analysis should be approved and retained.

There is a significant difference between the oxygen percentages measured by volume and those measured by mass. For example:

	Oxygen	Nitrogen
Percentage by volume	20 %	80 %
Percentage by mass	22.2 %	77.8 %

Table 2: Content by volume and mass

5 Production of liquid air

There are two common methods of production of liquid air:

- by mixing of liquid oxygen and liquid nitrogen;
- by liquefaction of atmospheric air. In this case it will contain nitrogen, oxygen, a small amount of argon and traces of other gases.

5.1 General

All equipment in the production process that may come in contact with liquid air shall be oxygen compatible and cleaned accordantly. See EIGA Doc 33. [3]

5.2 Liquid air production by mixing

There are different methods of batch and continuous mixing, in tanks or in tankers. Examples of these methods are shown in the diagram in Appendix A.

Mixing processes are often based on the weight of the two components, but it is possible to mix on a volume basis as well.

Continuous mixing, where the final composition is controlled by adjusting the flow rates of the two components, is possible, but requires accurate on-line analysis to ensure that the final composition can be guaranteed.

5.2.1 Prevention of back feed contamination

When mixing liquid oxygen and liquid nitrogen to form liquid air there is a risk that the storage tanks for the oxygen and nitrogen can become contaminated by back flow, therefore it is recommended that the mixing is via intermediate storage and not directly from the main storage tanks.

5.2.2 Control of mixing

The amounts of liquid oxygen and nitrogen required to make liquid air with a particular oxygen content can be calculated from the properties of the two liquids.

If venting occurs during mixing, allowance shall be made for the fact that the gas boiling off will not be at the same concentration as the remaining liquid.

The following parameters have to be considered during mixing:

5.2.2.1 Temperature

The liquid oxygen and liquid nitrogen will be at different temperatures before they are mixed.

Mixing should start with nitrogen (lower boiling point) to prevent flash evaporation. During mixing, boiling off of nitrogen rich gas is to be expected.

5.2.2.2 Equilibrium pressure

The equilibrium pressure of the liquid is directly related to the temperature of the mixture. Any heat addition during the production process will increase the pressure or, if venting of gas occurs, will increase the oxygen content of the remaining liquid.

For example, when liquid air is transferred from a storage tank to a tanker, and the tanker vent is open during filling, the oxygen percentage (by volume) in the liquid in the tanker will be greater than that in the tank.

5.2.2.3 Relative densities of oxygen and nitrogen

It is easier to correct non-conforming product by adding oxygen to liquid which is low in oxygen than by adding nitrogen to liquid which is high in oxygen, since the oxygen is denser than the mixture and will tend to fall and mix better than nitrogen, which is less dense.

5.2.3 Sizing of relief devices

All vents and safety devices shall be sized for the maximum possible flow rate of boil off gas.

5.2.4 Analysis

A final quality analysis of the oxygen content of the liquid shall be carried out before the liquid is transferred to the tanker or the storage tank, or supplied to the application.

Before taking the analysis, the analysis line should be thoroughly purged.

A second analysis is recommended, because the mixture can take some time (depending on the equipment used) to reach equilibrium. A second analysis will show whether the final equilibrium concentration has been reached. The second analysis will also assist in validating the analytical process. (See 4.4)

If liquid air is used as raw material for compressed air cylinders filling, it should be analysed before starting to fill the packages. Final cylinders should be also analysed after filling, using statistical quality control techniques, accordingly to the specific risks and the intended cylinders application.

5.2.5 Out of specification product

Out of specification product may be corrected by adding oxygen or nitrogen (see 5.2.2). After the correction the same analysis procedure shall be followed as after mixing a fresh batch.

5.2.6 Batch mixing in a tanker

In case the batch mixing of liquid oxygen and liquid nitrogen is done directly in a tanker, additional precautions shall be taken.

The trailer shall be pre-cooled using liquid air or nitrogen. Pure nitrogen is colder and of lower density than liquid air at the same pressure, and does not change in composition, while liquid air used for cooling is likely to change in composition.

Most tankers are low pressure vessels (below 4 bar) so it is probable that there will be some boiling off of gas during mixing. The vent and relief valve sizing should be checked to ensure they are sufficient for the maximum gas flow.

The final liquid composition after mixing shall be analysed since this can change owing to the boiling off of nitrogen rich gas.

A minimum journey time may be required to ensure homogenous mixing of the liquid in the tanker.

6 Transport of liquid air

This section lists the factors which shall be considered in the safe transport and delivery of liquid air in tankers.

6.1 General

When transported by road liquid air shall be clearly identified. The UN number for the product is 1003. The tanker shall carry a yellow oxidiser label (ADR 5.1) and a green non flammable non toxic gas label (ADR 2.2). [6]

Tankers for liquid air service shall be oxygen compatible and carry all necessary type approvals.

6.2 Operational controls

6.2.1 Analysis

The tanker shall be analysed before the liquid is transferred in the customer’s tank or used in the application, to confirm that it is within the required oxygen concentration range and an appropriate certificate shall be issued. If liquid air has been produced by mixing in the tanker, it is recommended that a minimum journey time is set to ensure complete mixing in the tanker.

6.2.2 Pressure relief

Venting through the tanker pressure relief devices can produce an oxygen enrichment of the liquid in the tanker, because operation of safety relief valves leads to venting of nitrogen rich gas. If venting occurs after the tanker has been analysed, the liquid shall be re-analysed before it can be used in an application.

In order to reduce the likelihood of enrichment because of venting, a time limit (typically 24 hours) may be set between the filling of the tanker and the delivery and, if the liquid is not delivered within this time, it shall be re-analysed.

6.2.3 Couplings

A dedicated coupling unique to liquid air should be used whenever possible for tanker filling and delivery hoses. The EIGA DN60 coupling, Code No 5, is assigned to the product [7]. There is currently no DN40 coupling assigned to the product.

For regular deliveries to customer tanks, unique couplings should be used. If the liquid air supply is on a ‘one-off’ basis and the application is under gas company control, adapters may be used. This practice is potentially hazardous and should be evaluated and controlled.

6.2.4 Delivery

It is recommended that the pressure in the receiving vessel be controlled by using top filling through the gas connection as required, to re-condense nitrogen rich gas in the headspace.

Delivery to more than one customer from a single tanker load is not recommended, because the liquid remaining in the tanker after the first delivery could be high in oxygen, because of preferential boil off of nitrogen into the gas space, or may require intermediate analysis.

7 Storage of liquid air

This section covers the storage of liquid air in tanks, both at customer and gas company premises.

7.1 Hazards and risks

The hazard is that the oxygen concentration of the liquid stored in the tank moves outside the range which is considered acceptable for the application and for the personnel.

Low oxygen concentration could potentially lead to asphyxiation of personnel in the area where the liquid is used.

High oxygen concentration increases the risk of combustion in the tank, pipe work or application equipment.

Possible causes of oxygen level outside acceptable range include:

- Filling of liquid outside specification into the tank.
- Venting of vapour from the gas space in the tank leading to enrichment in oxygen of the remaining liquid.
- Stratification in the tank, in which layers of liquid with different compositions are formed over time. It may be possible, for particular combinations of filling and operation, that stable layers at different compositions are formed in the tank. However this situation is not likely to occur because as the top layer in the tank becomes enriched in oxygen, it will be denser than the lower layer and so it will move down and mix, giving a homogenous liquid composition.
- If the liquid in the tank drops to a low level, evaporation caused by heat exchange with ambient will lead to oxygen enrichment of the liquid. This is more likely to occur when the low liquid level is accompanied by a low liquid usage.

Tank geometry will have an effect on oxygen enrichment.

When small amounts of liquid are used to cool down a tank, the liquid will be enriched in oxygen. It is recommended to dispose of the residual liquid and then fill with fresh liquid air into the cold, empty tank.

7.2 Design considerations

7.2.1 General

The same materials and standards of cleanliness and construction for oxygen tanks shall be used.

Connections to obtain a liquid sample for analysis shall be included.

A coupling unique to liquid air should be used and product identification notices shall be clearly displayed on the tank.

7.2.2 Minimising changes in composition

Storage tanks should be designed to minimise changes in composition. Points which should be considered during design include:

- Methods to eliminate the possibility of withdrawal of gas by the customer. This may include locking of valves or removal of hand wheels.

- Methods to minimise gas venting during normal operation.

- Activation of pressure relief devices should be monitored in order to detect gas venting and take the necessary actions.

Remote pressure and level indication can assist in monitoring these parameters.

- Setting a minimum level below which the liquid cannot be withdrawn. This minimum level can be calculated theoretically by performing ‘worst case’ calculations on the enrichment of the liquid if the pressure in the tank rises to the pressure protection set point. Tank geometry will influence this calculation.

- A mechanical method (for example, a control valve that trips shut) to stop liquid supply to the process when low level or off specification liquid is present in the tank (e.g. triggered by tank low level or by continuous analysis in application line after vaporisation, etc.).

- Risk assessment of the design shall include the assessment of the probability and consequence of leaks.

7.3 Operational controls

Procedures should ensure that gas venting is minimised during liquid transfer into the storage tank.

Vessel maintenance procedures shall include checks for leaks.

The length of time for which the liquid air can be stored before the pressure relief devices operate depends on the heat in leak into the storage tank.

For tanks in which liquid air is stored for some time, for example at production sites or at a customer site where the usage is low or intermittent, oxygen enrichment will occur in the liquid phase.

Procedures shall be in place for action to be taken, should the oxygen level move outside the acceptable range.

The procedure for commissioning the tank shall take into account the possibility of enrichment when liquid is filled into a warm tank.

Operational procedures should take into account the risk of change in composition due to the activation of pressure relief devices.

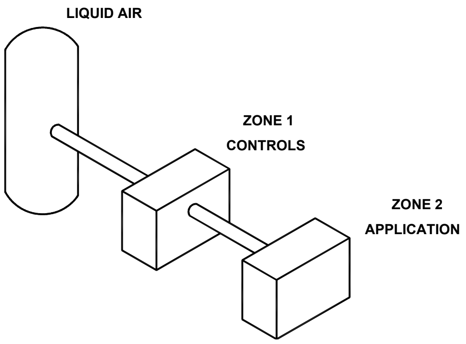
Non-conforming product procedures shall be in place, to cover identification and safe disposal of liquid outside specification.

The procedure for decommissioning the installation shall take into account the possibility that residual product composition may be very high in oxygen or nitrogen.

8 Applications

This section covers the use of liquid air for refrigeration and other applications.

The applications system, which includes all pipework and equipment downstream of the storage tank or tanker used to supply the liquid, can be divided into two zones, for each of which different design considerations apply - see diagram below.



8.1 General considerations

All potential uses of liquid air, including compressed air cylinders filling and its intended application shall be considered and a detailed risk assessment of any new applications equipment shall be carried out, to ensure that it is safe for the intended purpose and cannot be misused.

The risk assessment shall also take into account the process and any hazards specific to the actual location of the equipment.

Once liquid air is fully vaporised, it can be treated as atmospheric air.

8.2 Hazards and risks

The main hazards for liquid air applications are:

- Oxygen enrichment leading to increased risk of combustion, both in equipment and at point of use.
- Oxygen deficiency which could lead to asphyxiation in an area in which people are present.
- Extremely cold temperatures: unevaporated liquid or very cold gas can cause cold burns.
- The composition of liquid air in the tank can change due to boil off of nitrogen resulting in oxygen enrichment in the liquid phase and deficiency in the gas phase. Therefore when filling cylinders from the liquid phase there is the hazard potential that the down-stream equipment is not compatible with the oxygen enriched product; or the cylinders may be filled with oxygen enriched product.

Additionally, when liquid air is injected into a room, as the air in the room is cooled, moisture in the atmosphere will condense, leading to fogging and poor visibility.

8.3 Application Zone 1

Zone 1 consists of pipeline, valves and control equipment between the storage tank and the point of use of liquid air.

8.3.1 General

All pipelines, components, insulating materials, equipments and fittings shall be oxygen compatible.

Maintenance activities shall be carried out to the same standard as for oxygen supply lines. Phase separators shall not be used on liquid air pipelines.

8.3.2 Potential for venting

The design should minimise potential for venting.

Where (thermal) relief valves are installed, the risk assessment shall consider the amount of oxygen enrichment that may occur if they operate and whether this is acceptable. For example, a small volume of oxygen enriched liquid air mixing with a large volume of air (e.g. a cold store) is unlikely to present a hazard.

Pressure relief vents shall be run to atmosphere at a safe location free from combustion or asphyxiation risk.

8.3.3 Other factors to be considered in design

Control valves and nozzles shall be sized for all envisaged flow conditions. The liquid velocity should be safe for oxygen (see EIGA Doc 13 [5]).

Particular consideration should be given to any aspects of the design which could lead to change in composition of the liquid. For example, intermittent flow to the application, branching pipework at different levels or long sections which could contain a boiling column of liquid, all have the potential for gas to boil off in one part of the system.

8.4 Application Zone 2

Zone 2 is the point of use of the liquid air. For example liquid air may be injected through nozzles into a large room or a small cabinet. Liquid baths shall not be used because they allow liquid to partially vaporise.

8.4.1 General

Besides the general hazards (see 8.2), the risk assessment for Zone 2 shall consider the potential for liquid to be present. Where such potential is identified, any risk associated with oxygen rich liquid coming into contact with non oxygen-compatible materials shall be analysed.

Factors such as the amount of liquid and the material with which it could come into contact will determine the hazard associated with the proposed design.

For example, cold grinding, where liquid could come into contact with small particles of flammable material, is not an acceptable application for liquid air.

In Appendix B guidelines are given for the calculation of theoretical evaporation distances for droplets. This information will assist in the risk assessment for applications involving nozzles.

When liquid air is injected through nozzles, the possibility of the nozzles becoming partially blocked or shrouded with ice should be considered. This can lead to liquid dripping from the nozzles.

8.4.2 Operational controls

The risk assessment shall consider what control mechanisms are required for the application.

Controls and precautions which may be appropriate include:

- Use of fans to ensure complete mixing. Interlocks should be considered to stop the flow of liquid air if the fans are not operating correctly.
- Detection of incomplete vaporisation by a temperature probe on a surface, for example the floor of a cabinet. If this temperature drops below the operating temperature, suggesting liquid could be present; the liquid air supply should be stopped.
- A means to stop the supply of liquid air in case of an emergency.
- Atmospheric monitoring in the area in which the liquid air is used, which is set to alarm and/or shut-off the air delivery when the oxygen concentration moves outside acceptable limits.
- Continuous product analysis to trigger an alarm and/or shut-off the air delivery when the oxygen concentration moves outside acceptable limits.
- Signs placed in the application area warning of hazards and forbidding smoking and naked flames.

9 References

[1] EIGA Doc 44 - *Hazards of oxygen deficient atmospheres*, www.eiga.eu.

[2] EIGA Doc 224 - *Static vacuum insulated cryogenic vessels operation and inspection*, www.eiga.eu.

[3] EIGA Doc 33 – *Cleaning of Equipment for Oxygen Service*, www.eiga.eu.

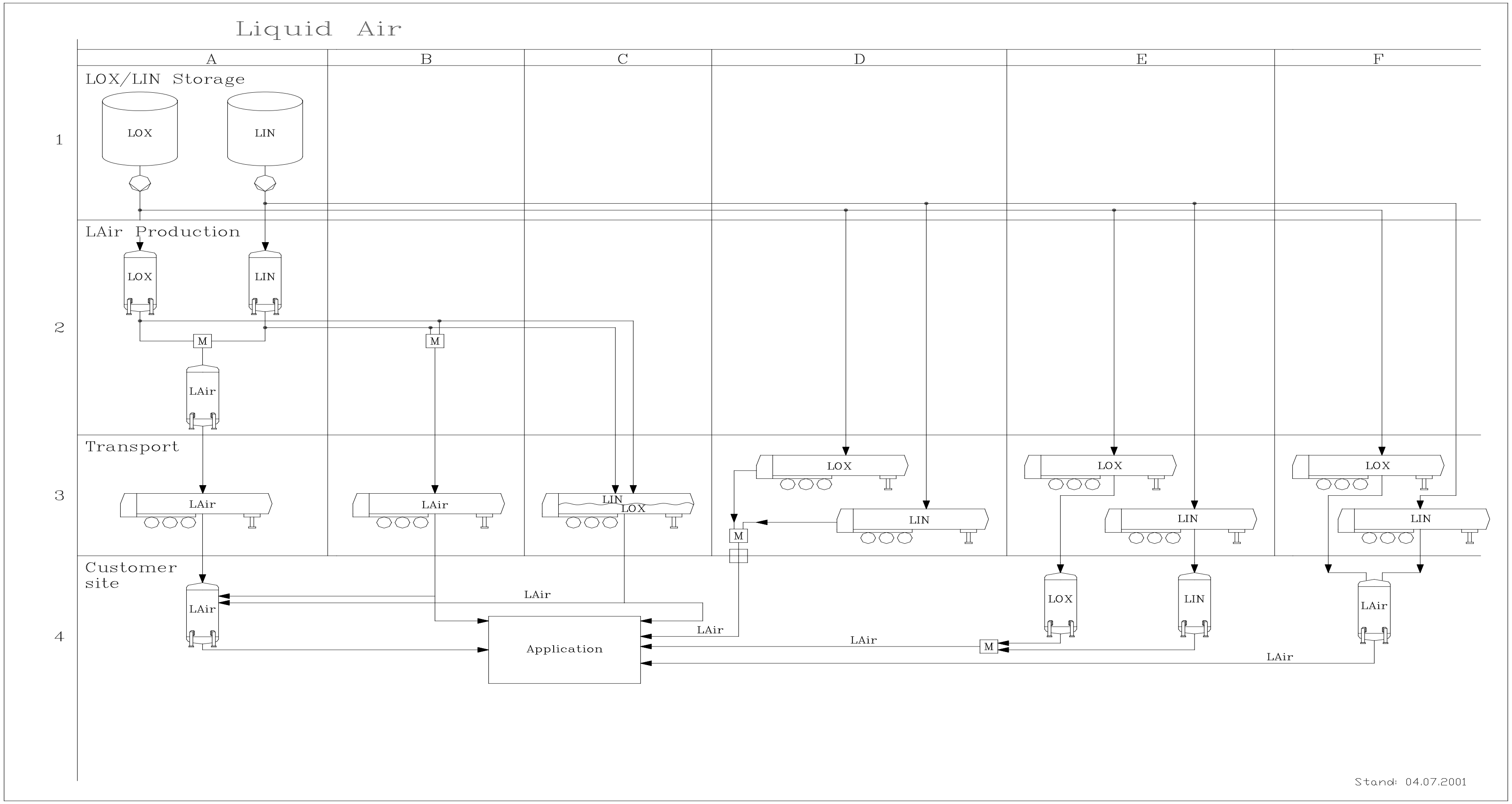
[4] EIGA Doc 04 – *Fire Hazards of Oxygen and Oxygen Enriched Atmospheres*, www.eiga.eu.

[5] EIGA Doc 13 – *Oxygen Pipeline and Piping Systems*, www.eiga.eu.

[6] *The European Agreement concerning the international carriage of dangerous goods by road (ADR)*

[7] EIGA Doc 909, *EIGA Cryogenic Gases Couplings for Tanker Filling*, www.eiga.eu.

Appendix A - Production Methods for liquid air



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Appendix B - Droplet Evaporation Calculations

The charts below show the results of calculations for evaporation time for droplets generated by a nozzle. The results are valid for a pressure drop across the nozzle of up to 3 bar. To find the distance to evaporate the speed of the droplet shall be estimated, and multiplied by the time to give the distance. The curve for the correct ambient air temperature should be selected.

Chart 1 can be used when the flow coefficient (CV) of the nozzle is known.

Chart 2 can be used if the initial size of the droplet is known or can be estimated.

Chart 1 Liquid Air Droplet Evaporation Time Plotted Against Nozzle Flow Coefficient, for Different Ambient Temperatures

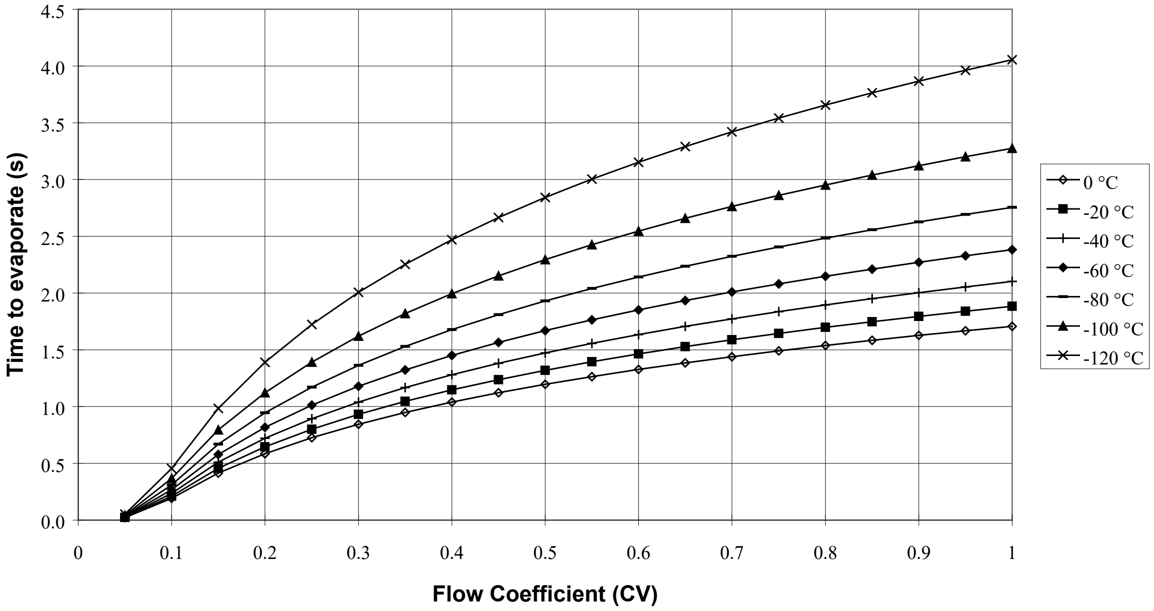

Chart 2 Liquid Air Droplet Evaporation Time Plotted Agianst Droplet Diameter, for Different Ambient Temperatures