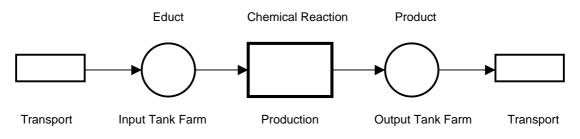
# Application Note

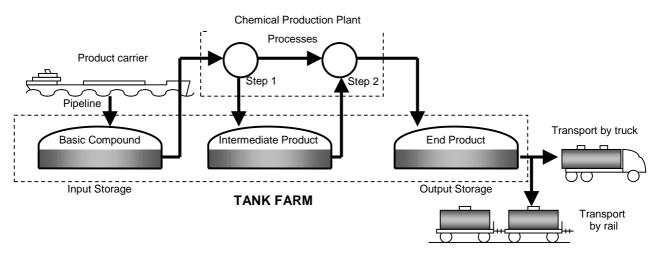
# **Tank Farms and Liquefied Gases**

# **Introduction**

We can consider a chemical plant very simply as a facility needing great amounts of basic compounds (reactants or educts) which are converted to the required products also in a great amount.



Input and output of a chemical plant is realized by a more or less continuous mass flow from the input storage to the output storage. In case of gases or liquids the storage area is a tank farm. To increase the mass of gases these are either compressed or even liquefied.



Essentially there are **three different types** of storage tanks: Pressure Tanks, Cryogenic Tanks, and Atmospheric Tanks.

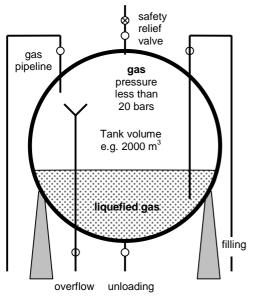
#### **Pressure Tanks**

These are mostly horizontal or vertical cylindric tanks but also spherical tanks. Spherical tanks are optimal concerning the surface/volume-ratio and ensure homogenous tension load. Because of this the wall thickness can be half of the cylindrical tanks only. However, the disadvantage is that because or their height they cannot easily be installed underground. Big spherical tanks are used for pressures up to 25 bars (vapour pressure of the liquefied gas) where a lot of gases can be kept in the liquefied





state. As liquefied gases need a very much lower volume than the gas itself there is a great mass of gas being stored, e.g. 1 m<sup>3</sup> of gaseous butane at 20 °C weighs 2.5 kg, 1 m<sup>3</sup> of liquefied butane weighs 580 kg, so the same volume contains the 230-fold mass in the liquefied state!



Spherical tank for liquefied gas storage

Typical gases stored in pressure tanks are ammonia, amines such as methyl amine, dimethyl amine, ethyl amine, and trimethyl amine,

 $C_3/C_4$ -hydrocarbons such as propane, cyclopropane, propylene, butanes, butylenes, and butadiene, mixtures of propane and butanes called LPG (liquid petrol gas), ethyl chloride, ethylene oxide, chlorine, dimethyl ether, methyl chloride, phosgene, sulfur dioxide, nitrogen dioxide, and vinyl chloride.

Pressure tanks are equipped with a fill level indicator with alarm facilities and sensors to measure the interior temperature continuously to switch on a cooling sprinklersystem in case of temperature alarm.

Safety relief valves control the internal pressure, the gas is relased into atmosphere or into a flare-system to be burnt. Both these processes mean costly loss of product, the first one leading to potentially explosive of toxic atmospheres additionally - gas detection is needed.

Tank filling is made by two connecting tubes, one for the

gas, one for the liquid. The gas is sucked out from the storage tank and by means of a compressor it is pressed into the truck's tank. The resulting pressure forces the liquefied gas into the storage tank.

then. This is a more or less dangerous process, especially when making the necessary tube connections. Gas leaks can occur and gas detection is recommended.

In Germany there is even a regulation that LPG tanks containing more than 30 tonnes (more than 50 m<sup>3</sup>) LPG must be equipped with a gas detection system.

The most famous gases kept in a pressure tank are ammonia, chlorine and LPG.

Vapour pressure of some liquefied gases at 20 °C:

Ammonia	8.6 bar
i-Butane	3.1 bar
n-Butane	2.1 bar
n-Butylene	2.6 bar
cis-2-Butylene	1.8 bar
trans-2-Butylene	2.0 bar
Chlorine	6.9 bar

Cyclopropane	6.2 bar
Dimethyl amine	1.9 bar
Dimethyl ether	5.0 bar
Ethyl amine	1.2 bar
Ethyl chloride	1.3 bar
Ethylene oxide	1.4 bar
Methyl amine	3.0 bar

Liquefied gas is

compressed into

the storage tank

Methyl chloride	5.0 bar
Nitrogen dioxide	0.96 bar
Phosgene	1.6 bar
Propane	8.3 bar
Propylene	10.3 bar
Sulfur dioxide	3.3 bar
Trimethyl amine	1.9 bar

Filling a pressurized

tank with liquefied gas

from a truck tank

Compressor to press

gas into the truck's tank





#### **Cryogenic Tanks**

If liquefied gases have a vapour pressure of more than 25 bar, greater containments would involve an increased dangerous risk. In this case there is another way of obtaining liquefied gases: Cryogenic. When cooling down a gas below its boiling point it will liquefy.

Ammonia	- 33.4 °C	Cyclopropane	- 32.8 °C	Methyl chloride	- 23.8 °C
i-Butane	- 11.7 °C	Dimethyl amine	+ 7.4 °C	Nitrogen dioxide	+ 21.1 °C
n-Butane	- 0.5 °C	Dimethyl ether	- 24.8 °C	Phosgene	+ 7.6 °C
n-Butylene	- 6.3 °C	Ethyl amine	+ 16.6 °C	Propane	- 42.0 °C
cis-2-Butylene	+ 3.7 °C	Ethyl chloride	+ 12.3 °C	Propylene	- 47.7 °C
trans-2-Butylene	+ 0.9 °C	Ethylene oxide	+ 10.5 °C	Sulfur dioxide	- 10.0 °C
Chlorine	- 34.1 °C	Methyl amine	- 6.3 °C	Trimethyl amine	+ 2.9 °C

Boiling point of some liquefied gases at atmospheric pressure:

Cryogenic tanks need a complex cooling system and so cryogenic storage is more expensive than the pressurized storage, but it is safer because liquefication is gained at atmospheric pressure.

Also combinations of pressurized and cryogenic technique is common, e.g. liquefied carbon dioxide is stored at - 30 °C and a pressure of 15 bar. LNG carriers (LNG = liquefied natural gas) use cryogenic tanks containing liquefied methane at approx. - 161 °C. In most cases it would not be economic to ship natural gas in its compressed gaseous state if not by pipelines. LNG tankfarms often are in direct connection or vicinity to harbour terminals.

Also Gasoline stations have cryogenic LNG-tanks. It is important to know that gas detection is necessary in this application because leaks of LNG cannot be smelled. The reason is that odorants normally used cannot be added to liquefied methane.

Low temperature cryogenic tanks are effectively insulated and a big part of their volume is insulation only. These tanks contain liquefied gases such as argon ("LAr", - 186 °C), ethane (- 88 °C), ethylene (- 104 °C), helium (- 268 °C), methane (-161 °C), oxygen ("LOx", - 183 °C), and nitrogen ("LN2", - 196 °C) at temperatures near their boiling point and atmospheric pressure.

Besides oxygen and nitrogen ethylene is one of the world-wide mostly used products, so tank farms frequently are ethylene tank farms.

#### **Atmospheric Tanks**

Atmospheric tanks are used for substances which under normal conditions are liquid, in other words, which are stored at temperatures lower than their boiling point. Typical atmospheric tanks are used for flammable liquids (e.g. methanol, toluene, xylene), and hydrocarbon mixtures (e.g. gasolines, kerosine) produced in the refineries.

Atmospheric tanks commonly have wallthicknesses layed out for filling pressures from 100 mbar below up to 100 mbar above atmospheric pressure only. Loading and unloading of tanks with a fix roof would jowever cause higher pressure differences and this is the reason why there are relief valves with breathing openings to the outer atmosphere. If not inertized, the interior of tanks containing flammable liquids is zone 0. Atmospheric breathing is done by flame arrestors to avoid flash-back into the tank. Mostly vapours are fed via flame arrestors to a flare system, sometimes they are recondensed.

E.g. for an acrylo nitrile (ACN) tank of 3700 m<sup>3</sup> there is a loss by breathing of some tonnes ACN per year (!) if not recondensed.

As the vapour pressure of liquids is lower than atmospheric pressure mostly there is an inerting blanket of nitrogen (or other intering gases) added so that there is always a small over-pressure against atmosphere and air access into the tank is avoided. Sometimes also tanks with floating roofs swimming directly on the liquid surface are used.





## Market Segments and Development

Market segment is commonly chemical industry and petrochemcial industry.

In chemical tank farms billion of tonnes per year of liquids and liquefied gases are stored in bulk wordwide. Solely the worldwide production capacity of ethylene, the most important highly reactive basic compound, was 107 million tonnes per year (tpy) in 2002. Ethylene and propylene are mainly used for the plastics industry. Liquefied ammonia used for chemical industry processes and production of fertilizers is produced by 165 million tpy, and LNG, shipped and stored (gaseous natural gas not considered) about 100 million tpy.

#### Estimation:

If only 80 percent of liquefied ammonia is intermediately stored in bulk per year, and one tank is assumed to have a capacity of 2000 m<sup>3</sup> (diameter of 16 meters w/o insulation if spherical) and 1 ton ammonia equals to 1.6 m<sup>3</sup> we can estimate to have at least 100000 ammonia tanks worldwide.

### **Description of the Challenge**

Is it necessary to say that bulk storage of toxic and/or flammable substances, liquified and/or pressurized is dangerous? In many cases gas detection is a must. National laws and regulations require high safety standards when the amount of dangerous goods exceeds a given limit.

The NFPA regulation reads: Continuously monitored low-temperature sensors or flammable gas detection systems shall sound an alarm at the plant site and at a constantly attended location if the plant site is not attended continuously. Flammable gas detection systems shall activate an audible and visual alarm at not more than 25 percent of the lower flammable limit of the gas or vapor being monitored.

NFPA 59A (1996), Standard for the Production, Storage, and Handling of Liquefied Natural Gas (LNG), Chapter 9-4.2

There are two targets for gas detection. One is explosion protection, the other is early leak detection.

*Explosion protection* means being alarmed at concentrations of about 20 to 40 % LEL to promptly activate countermeasures at site (informing operators, technicians and fire brigade) and/or switching countermeasures (closing solenoid valves, activating cooling showers, water sprayers). Also loading and unloading might be accomplished by heavy leaks when connecting the appropriate pipes.

*Early leak detection* is preferably practised by detecting low concentrations (e.g. 10 % LEL). Although there are temperature and pressure gauge sensors small leaks (hairline cracks) cannot be detected. However in longterm consideration these leaks mean costly loss of mass and may tend to become a great leak with hazardous consequences. In a tank farm there must be a safety distance between the tanks so that in case of a fire the probability of affecting the other tanks is minimized.

Some applications even strip out the cooling water to monitor for dissolved flammable e.g. ethylene.

# Solution from Dräger

For an individual application you can find the proper gas detector in the gas list. Electrochemical sensors commonly are sensitive enough to detect a gas leak (e.g. ammonia, amines, sulfur dioxide, chlorine). For flammable gases and vapours the alarm trehsold should not be lower than 10 ... 20 % LEL if having a measuring range of 100% LEL. Otherwise environmental effects may cause false alarms.

As tank farms are out-door applications where always some natural ventilation exists and dilutes the gas concentrations, in many cases IR Ex with its lower measuring ranges is suitable. Also the 10% LEL sensor is a very good choice for ethylene and propylene tank farms.

Position the sensors in the vicinity and below a potential leak (filling nozzles, flanges, bellows, compressor connections). In some cases even continuous gas sampling from the interior of the insulation coat is practised.

Fence monitoring to avoid gas leaks to drift into unsafe areas can also be done by open path gas detection. For several hydrocarbons the Polytron Pulsar is very suitable.





### <u>USP's</u>

Polytron IR Ex:

For a lot of gases measuring ranges of 0...20 of even 0...10% LEL are possible. Constant sensitivity over time, no poisoning, theoretical unlimited lifetime, low cost of ownership, no consumables, 1 calibration per year, windspeed not a problem, fast response, 100% failsafe.

Polytron SE Ex and Polytron SE Ex LC (10% LEL): Reasonable sensitivity for ethylene and propylene, low price, also detects hydrogen leaks.

Prepared by: Dr. Wolfgang Jessel



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