

❁ Chemical Process Safety

Reference:

D.A. Crowl and J.F. Louvar, *Chemical Process Safety. Fundamentals with Applications*, Englewood Cliffs: Prentice Hall, 1990.

❖ Basic Concepts

Chemical plants contain a large number of potential hazards. Chemical hazards include fire, explosions and spills. There are also mechanical hazards that arise from things as simple as tripping, falling or moving equipment. Below are brief explanations of some common terms.

- **Hazard:** things that have the potential of producing injury or an accident.
- **Risk:** the probability of having a hazard that results in an accident.
- **Safety or loss prevention:** the prevention of accidents. Programs for identification and assessment of hazards; control and elimination of the hazards before an accident occurs; limitation of the loss when an incident occurs.

- **Ingredients of a safety program:**

- Safety knowledge
- Safety experience
- Technical competence
- Safety management support
- Commitment

- **Acceptable risk**

Risk cannot be eliminated. Everything, be it driving a car or running a chemical plant, has a certain risk associated with it. At some point in a design, someone will have to decide if the risks are acceptable.

- **Public perceptions**

The general public has great difficulty agreeing to the involuntary nature of acceptable risk. A manufacturer assumes that the risks are satisfactory to the people living near the plant, but frequently the civilians are not aware what the risks are.

- **Engineering ethics**

Most engineers are hired by companies who earn profits for their shareholders. While as an employee, an engineer must provide a service to the company by maintaining and improving the profits, the engineer also has the responsibility for minimizing losses and to provide a safe and secure environment for fellow workers, family and the community.

❖ Nature of accidents in chemical plants

Chemical plant accidents follow typical patterns. As shown in Tables 1 and 2, major accidents involve explosions, fires and dispersion of toxic chemical release. Among explosions, a large fraction of them are vapor cloud explosions (VCE) which are the most dangerous and destructive. Vapor cloud explosions are difficult to characterize, but they generally involve the sudden release and subsequent dispersion and ignition of a large quantity of flammable vapor, say, when a vessel or pipe containing a superheated and pressurized liquid ruptures.

Table 1. Types of loss for large chemical accidents

Type	Percentage
Vapor cloud explosion	42%
Fires	35%
Explosion, others	22%
Wind	1%

Table 2. Three types of chemical plant accidents

Type	Probability of occurrence	Potential for fatalities	Potential for economic loss
Fire	High	Low	Intermediate
Explosion	High	Intermediate	High
Toxic Release	Low	High	Low

Economic loss is also high for accidents involving explosions. Fires are less destructive. Toxic release (fugitive emission) typically results in little damage to capital equipment, but personnel injuries, legal compensation, and cleanup liabilities can be significant.

Many of the accidents are caused by mechanical failure and operational error. Mechanical failure frequently is a result of improper maintenance. Human errors contribute to both mechanical failure and operational errors. Among equipment types, piping systems and storage tanks are involved in a significant number of accidents. (See attached figures.)

A few examples (many more in Chapter 13 of Crowl and Louvar).

- Chemical reactivity
 - ◊ A pesticides manufacturing plant in Bhopal, India, 1984. A storage tank containing the intermediate methyl isocyanate (MIC) was contaminated with water. (MIC reacts exothermically with water.) A chemical reaction heated the MIC to a temperature past its boiling point. The vapors traveled past a non-functioning scrubber and flare system. An estimated 25-tons of toxic MIC vapor was released. No plant equipment was damaged, but the MIC vapor killed over 2,000 civilians and injured at least 20,000 more. Problem: large inventory of reactive intermediate; equipment failure; lack of emergency response procedure.
 - ◊ A reactor experienced a violent reaction resulting in the tank being driven through the floor, out the wall and through the roof of an adjoining building. The reactor was designed to contain sulfuric acid and nitrobenzene sulfonic acid which was known to decompose at 200 °C. Steam had leaked into the heating jacket and brought the temperature to 150 °C. Subsequent tests showed that decomposition occurs above 145 °C. Problem: lack of precise reaction decomposition data.
- Static electricity
 - ◊ A slurry containing a solvent mixture of methylcyclohexane and toluene was being fed into a basket centrifuge. When a foreman lifted the lid to take a look, a flame was released and the mixture exploded. The centrifuge was lined. Problem: accident investigation indicated that a flammable atmosphere was developed due to an air leak. The lined centrifuge was the source of ignition due to static accumulation and discharge.
- System designs
 - ◊ A process storage tank containing 6,500 gallons of ethylene oxide was accidentally contaminated with ammonia. The tank ruptured and dispersed ethylene oxide into the air. A vapor cloud was formed and immediately exploded with a force equivalent to 18 tons of TNT. Problem: lack of design protection to prevent the back-up ammonia into the storage tank.
 - ◊ Vibration from a bad pump caused a pump seal to fail in a cumene section of a phenol acetone unit. The released flammable liquids and vapors ignited and an explosion ruptured other process pipes adding fuel to the original fire. Damage to the plant exceeded \$23 million. Problem: lack of inspection and maintenance program. Potential design improvements include vibration detectors, gas analyzers, block valves and deluge systems.

❖ Fires and Explosions

Fire is the rapid exothermic oxidation of an ignited fuel. The major distinction between fires and explosions is the rate of energy release. The fuel can be in solid, liquid or vapor form. Combustion always occurs in the vapor phase; liquids are vaporized and solids are decomposed into vapor prior to combustion. Burning occurs when **fuel**, **oxidizer** and an **ignition source** are all present at necessary levels. Examples of each category:

- *Fuels*

Gases	acetylene, propane, carbon monoxide, hydrogen
Liquids	gasoline, acetone, ether, pentane
Solids	plastics, wood dust, fibers, metal particles
- *Oxidizers*

Gases	oxygen (air), fluorine, chlorine
Liquids	hydrogen peroxide, nitric acid, perchloric acid
Solids	metal peroxides, ammonium nitrite
- *Ignition sources*

Sparks, flames, static electricity, heat

Some other definitions:

- **Flash point (FP)** of liquids

The flash point of a liquid is the lowest temperature at which it gives off enough vapor to form an ignitable mixture with air. The combustion is rarely sustained because rarely enough vapor is produced. The *fire point* is a higher temperature at which the fire will continue to burn once ignited.

The flash point is used to determine the fire and explosion hazards of liquids. Flash points for pure components are determined experimentally and tabulated in handbooks. The flash point of a multicomponent mixture is calculated from the vapor pressure of the flammable component(s) in the liquid mixture.

- **Lower and upper flammability limits (LFL and UFL)** for vapors

Vapor mixtures only burn within a certain range of compositions. When the composition of the fuel is less than the lower flammable limit (*LFL*), the mixture is too lean for combustion. The mixture also will not burn when the mixture is too rich, with the composition above the upper flammable limit (*UFL*). A mixture is only flammable within the *LFL* and *UFL* which are measured using pure component experiments. The terms lower and upper explosive limits (*LEL* and *UEL*) are sometimes used in place of *LFL* and *UFL*. Common units are mole (or volume) percent fuel in air [moles fuel/(moles fuel + moles air)].

For multicomponents, the limits are calculated using the equations first proposed by Le Chatelier in 1891:

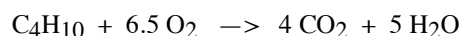
$$LFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{LFL_i}} \quad \text{and} \quad UFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{UFL_i}}$$

where the unit of the composition y_i is in volume percent, same as *LFL*.

- **Minimum oxygen concentration (MOC)**

The *LFL* is based on fuel concentration, but oxygen is also a key ingredient for combustion in air. There is a minimum oxygen concentration required to propagate a flame. Thus we can prevent combustion of a fuel by adding inert gases like nitrogen and carbon dioxide to reduce the oxygen concentration. This is the basis of the common practice called **inerting**.

Example: estimate the *MOC* for butane. The stoichiometry for the reaction is



Using *LFL* for butane from handbooks, 1.6 volume%, and stoichiometry,

$$MOC = 1.6 \left[\frac{\text{mole butane}}{\text{mole butane} + \text{mole air}} \right] \frac{6.5}{1} \frac{[\text{mole oxygen}]}{[\text{mole butane}]}$$

from which *MOC* for butane is 10.4 volume% oxygen. That is, we can prevent butane from burning by adding inerts to reduce the oxygen concentration below 10.4%, roughly half the amount in air.

- **Adiabatic compression**

The temperature of a gas increases under adiabatic compression. Accidents can be caused by flammable vapors being sucked into the intake of air compressors; subsequent compression may result in **autoignition**. For an ideal gas, the adiabatic temperature rise can be calculated easily:

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

where $\gamma = C_p/C_v$.

- **Boiling liquid expanding vapor explosions (BLEVE, pronounced ble'-vee)**

Boiling liquid expanding vapor explosions occur when a tank containing a liquid held above its atmospheric pressure boiling point ruptures, resulting in the explosive vaporization of a large fraction of the tank contents. If the materials are flammable, a vapor cloud explosion (VCE) may occur. If the materials are toxic, a large area will be contaminated. Often, BLEVE is caused by fire.

☞ Safety control techniques

Accidents in general involve a three-step sequence: initiation, propagation of events and termination. Safety engineering involves eliminating the initiating step and terminating the propagation steps. Some of the procedures are suggested in Table 3. The general idea is to work on all three steps to insure that accidents, even if initiated, do not propagate and will terminate quickly.

◆ Engineering tools for analysis

- Hazard and operability study (**HAZOP** study). A systematic technique to identify plant or equipment hazards and operability problems.
- **Fault-tree** analysis. Primarily a means of analyzing hazardous events after they have been identified by other techniques such as HAZOP. The use of a logic fault tree diagram provides a graphical representation between certain possible events and an undesired consequence and helps to estimate the likelihood of an accident. The analysis also helps to investigate the impact of alternative preventive measures.
- Hydrodynamic models to design for example two-phase flow through a vessel relief valve.
- Dispersion models to calculate the spread of a toxic substance after release through the plant or the neighborhood.

Table 3. Strategies to defeat the accident

<u>Step</u>	<u>Desired Effect</u>	<u>Design & Operating Procedures</u>
Initiation	Diminish	inerting (dilution, vacuum purging, pressure purging) grounding (eliminate or control static electricity) guardrails and guards good maintenance human factors design process design (ventilation, relief systems, substitution with less hazardous chemicals or technologies) awareness of dangerous properties of chemicals
Propagation	Diminish	emergency material transfer reduce inventories of flammables explosion proof electrical explosion proof equipment and instruments equipment spacing and layout nonflammable construction materials check and emergency shut-off valves
Termination	Increase	firefighting equipment and procedures relief systems sprinkler systems check and emergency shut-off valves

Safety Design, a few more words from Crowl & Louvar, and Kletz

Philosophy:

Instead of adding on equipment to control hazards in the later stages of design or even construction, make an effort to choose a basic design early in the project that is inherently safe. Such an effort could lower cost and save energy. The final cost may be lower because with reduced hazard, there is also less demand for protective equipment, alarms and control systems, emergency valves, and fire protection.

Objective:

- Minimize human errors.
- Design a fault-tolerant plant that can tolerate minor errors or deviations from specifications.
- Minimize impact and extent of equipment failure.

Inherently safer design features (additional comments):

1. Substitution

- Choose alternative reaction paths that use less hazardous chemical reactants or generate less hazardous intermediates.

Example 1. The Bhopal incident could be avoided if an alternative synthesis path is used.

Example 2. Toxic gases such as phosphine, diborane and silane used in the manufacture of microelectronic devices can be replaced by less hazardous liquids such as trimethyl phosphite, trimethyl borate and tetraethylorthosilicate. Phosphorous oxychloride can replace phosgene. According to J.C. Schumacher, these replacements have technical as well as safety advantages.

- If for some reasons we cannot use water or oil to replace flammable ethers or hydrocarbons (ethylene, propylene, etc.) as heat transfer media or refrigerants, try liquefied carbon dioxide or nitrogen. (There is a trade off between safety and cost.)

2. Attenuation — use chemicals under conditions that make them less hazardous

- Example. Store liquefied chlorine and ammonia as refrigerated liquid at atmospheric pressure as opposed to under pressure at room temperature.
- Common applications in storage and transportation: dissolve the hazardous compound in a safe solvent or put the hazardous material in form of a safer chemical. Acetylene as a solution in acetone; hydrogen as ammonia, chlorine (for swimming pools) as calcium or sodium hypochlorite, and light hydrocarbons being refrigerated and liquefied.
- A new catalyst (or new technology) that requires lower operating pressure or temperature can be used.
- Use vacuum (or reduce pressure) to lower the boiling point.
- Choose a reaction temperature that may reduce the chance for reactor runaway.

3. Isolation (containment) — prevent domino effects

- Make use of emergency isolation valves.
- 15 m wide corridors between units and sections.
- Blow-out walls.
- Handle flammable materials out-doors or in open construction—facilitates dispersion. (See also **ventilation**.).
- Consider leakage rate in the design (function of gas/liquid, pressure and temperature, etc.).
- In batch processing, use different vessel for different reactions.
- Effective fire fighting systems.
- Place control room away from operations.
- Removes sources of ignition.
- Spillage due to overfilling and relief valve should be discharged to a scrubbing, flare or collection system.

- Common (!) accident: corrosive liquid stored in plastic or plastic coated tanks and heated by electrical immersion heaters. If liquid level drops and expose heater, tank wall can catch fire. If unstable chemicals have to be kept hot, the heating medium should be incapable of overheating them. Limit the level of energy available—use hot water, steam or other low-energy heater.

4. **Intensification** (Note: this term can take on a different meaning under other circumstances.)

If there is less hazardous material to be dealt with, we can reduce the capital investment in vessels, pipes, structures, and so on. Hence, intensification in many circumstances provides good cost savings, more than just a safer plant.

"What you don't have can't leak," Trevor Kletz, author of *Plant Design for Safety*

- Reduce inventory of hazardous materials (both raw and intermediates).
- Where appropriate, consider the sizes of a smaller CSTR versus a large batch reactor and a tube reactor versus a CSTR. Warning: a compromise of a large reactor operating at low T&P versus a small reactor at high T&P might combine the worst of both ends.
- Improve mixing in the reactor (which includes the reactor vessel design itself). Reduce localized heating.
- Consider vapor phase versus liquid phase reactions (trade off is less mass when there is a leakage versus higher operating temperatures).
- Rework routing in the plant layout to reduce the need to move hazardous materials around.
- Put hazardous materials on the tube-side of shell-and-tube exchangers.
- Alternative technologies. For example, membrane separation. The more compact plate heat exchangers.

5. **Simplification**

- In a good number of cases, complex equipment is added on for control when design procedures fails to identify hazards or problems until it is too late. Then changes lead to more unexpected changes. The key is that safety concerns must be considered at the conceptual design stage.
- A simpler design could reduce human errors during operation.
- We want flexibility, but we have to draw a line somewhere. Asking for too much flexibility invariably increases the complexity of the design.

6. **Other miscellaneous pointers to eliminate hazards**

- Make incorrect assembly impossible. Example: compressor with different inlet and outlet connections.
- Vapor space in drains can be explosive. Use fully flooded (surcharged) drains.
- Sampling is hazardous.
- Maintenance is hazardous.
- **Tolerance** (to poor procedures or errors). Choose gasket that leaks (if there is a leakage) slower. Spiral-wound gaskets are better than fiber gaskets. Expansion loops are more tolerant of poor installation than bellows. Fixed pipe are better than hoses. Welded joints are better than quick-release coupling.
- **Make status clear.** On both the main control console and the equipment. Common mistake: wrong installation directions of check-valve, gate valve, and venturi-mixing.
- Ease of **control**. Where possible, we should use physical principles. Example: instead of using flow ratio controllers, let one fluid through an orifice and such in the other through a side arm.
- Smart controllers. With built-in expert systems or fuzzy logic.

Some questions to ask during the *conceptual* design stage

Many of these questions are related to substitution and attenuation.

- Is the product hazardous? Are there safer products which have comparable cost and effectiveness?
- Are the raw materials, intermediates, solvents, catalysts and so on hazardous? Alternatives?

- What side reactions are liable to occur? Will the intermediates or by-products hazardous?
- Can poor mixing cause undesired reactions or local overheating? Undesirable results?
- Problem with impurities?
- Plant site location considerations?
- Once we have settled on the chemical reaction pathway, we should make a list of all the materials. Identify:
 - flashing flammable liquid (flammable liquid under pressure above their normal boiling pt.)
 - flashing toxic liquids
 - flammable or toxic liquids below their normal boiling points
 - refrigerated flammable or toxic liquids
 - flammable or toxic gases
 - unstable materials
 - explosive dusts

Questions to ask during the *flowsheet* design stage

Many of these questions are related to intensification and simplification.

Questions to ask during the *detailed* design stage

Many of these questions are related to attenuation, isolation and plant layout, equipment selection, tolerance and control.