SKF4163: Safety in Process Plant Design

Major Hazards:
Fires, Explosions, Toxic Release

Mohammad Fadil Abdul Wahab

Chemicals' Hazards

- Flammable substances
  - Fire

- Explosive substances
  - Explosion

- Toxic materials
  - Toxic Release
  - Exposure to toxic substance

The 3 Most Common Chemical Plant Major Accidents

Fire, Explosion and Toxic Release

To prevent these accidents, engineers need to familiar with:

(1) Fire, explosion and toxicity properties of materials
(2) Nature of fire, explosion and toxic release process
(3) Procedures to reduce fire, explosion and toxic release hazards

Note: most common sources of fire and explosion are organics solvents

Toxic Release

- ❑ Toxic chemicals can cause harm by inhalation, skin absorption, injection and ingestion.

- ❑ Short term and also long term effect, identification, evaluation and control of toxicants are covered in chapters on Toxicity and Industrial Hygiene.

Seveso, Italy, 10/7/1976.

Release of material containing dioxin to atmosphere.

Incident after a series of not following specified procedure.

About 2 kg of dioxin was discharge through relief valve to atmosphere.
Heavy rain washed toxic chemical and then absorbed into soil.

600 people evacuated, 2000 given blood test and many people suffered from skin disease

Manfredonia, Italy, 26/9/1976.

Aerosol mixture containing 10 tons of potassium arsenite (K_3AsO_3) and Arsenious acid (H_3AsO_3) escaped from NH_3 cooling column.

Explosion resulted in 60 tons of water, 10 tons of arsenic trioxide and 18 tons of potassium oxide released into atmosphere.

Contaminated 15 km^2 of cultivated land from 2 km^2 area around the plant with arsenic.
Fishing prohibited and 30 people contaminated.
Area declared safe in Jan 1977.

Bhopal, India, 3/12/1984.

Runaway reaction caused release of methyl isocynate and possibly hydrogen cyanide.

2500 fatalities and 200,000 injuries.

Identified causes :

Inadequate design pipe work,

inadequate procedures,

inadequate emergency plan,

inadequate job supervision,

inadequate maintenance of protective equipment,

inadequate management capabilities,

and possibly sabotage.

Fire and Explosion

Fires

- Is a chemical reaction in which a substance combines with oxidant and releases energy.

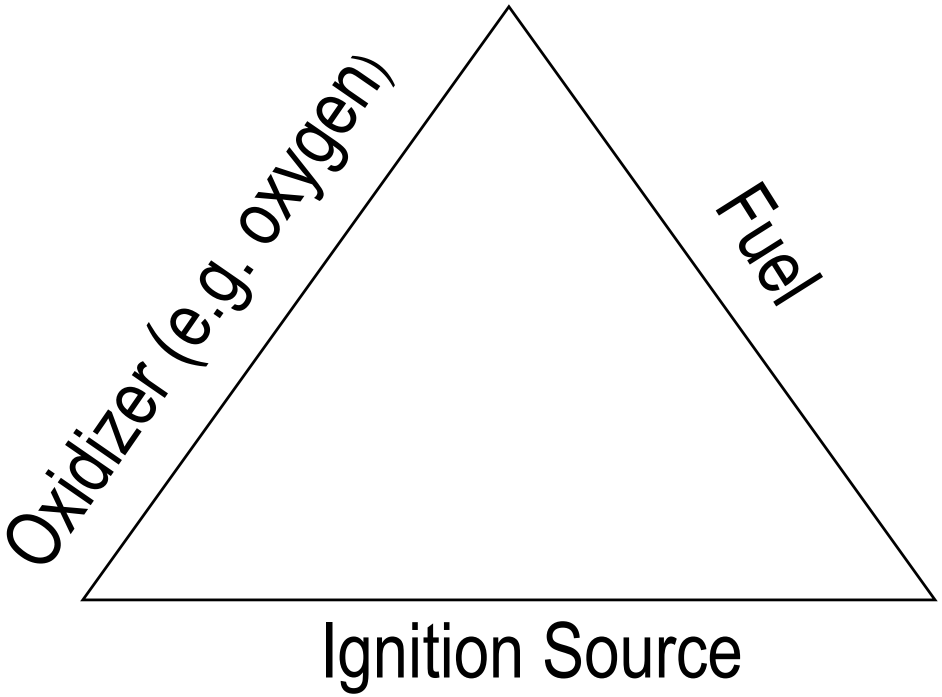
- The release of energy is slower than an explosion

- Fires could also results from explosion and vice versa.

Fire Triangle

3 elements for combustion to take place…

1) Fuel 2) Oxidizer 3) Ignition source



Fuels

- ✓ Liquids - gasoline, acetone, ether, pentane;
- ✓ Solids - plastics, wood dusts, fibers, metal particles, flour;
- ✓ Gases – methane, acetylene, propane, carbon monoxide, Hydrogen

- Note:

  Vapor and liquid fuels are easier to ignites than solid fuels (except dust)

Oxidizers

✓ Gases – oxygen (O_2), nitrous oxide (N_2O)

✓ Liquids - hydrogen peroxide (H_2O_2), nitric acid (HNO_3)

✓ Solids - ammonium nitrate (NH_4NO_3), metal peroxides

Oxidizers

- An oxidizing agent (also called an oxidizer or oxidant) is referred to as a chemical compound that readily transfers oxygen atoms

Note: The strict dangerous goods definition of an **oxidizing agent are substances that, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.**

Ignition Sources

- Sparks, flames, static electricity, heat (Hot surfaces).
- Various ignition sources as summarized in Table 6-5
- Impossible to identify and eliminate all sources.
- Identification and elimination should be a continuous activity.
- Particular attention to the ignition sources with greatest probability of occurrences.

Pool Fire

- ✓ Flammable liquid spills onto the ground and forms a pool.
- ✓ The liquid evaporates to atmosphere and soon form flammable mixture with air.
- ✓ Upon ignition, a fire will burn over the pool.
- ✓ The heat vaporizes more liquid and air is drawn in round to the side to support combustion.
- ✓ Danger to people is by direct thermal radiation and burn.

Flash Fire

- ✓ If spilled material relatively volatile (e.g. propane, butane, LPG) it would still form a pool but evaporation would be much more rapid.
- ✓ If ignition did not take place immediately to form pool fire, the vapor cloud would form, drifted away by wind, to form cloud within flammable range.
- ✓ If found source of ignition, flash fire will occur. People at risk from thermal radiation effects.
- ✓ Usually unexpected event and short duration

Torch/Jet Fire

- ✓ High pressure release of gas from a vessel or pipeline ignites almost immediately.

- ✓ This give rises to a giant burner of flame length tens of meters.

- ✓ Danger from thermal radiation and also impingement on adjacent pressurized vessel, such as LPG vessel, heating the content followed by pressure build up causing ‘boiling-liquid expanding-vapor explosion’ (BLEVE).

Explosive Chemical

- Gun powder
  - A mixture of sulfur, charcoal, and potassium nitrate - with the sulfur and charcoal acting as fuels, while the potassium nitrate works as an oxidizer
- Trinitrotoluene or TNT ($C_6H_2(NO_2)_3CH_3$),
- Nitroglycerine ($C_3H_5(ONO_2)_3$)
- C-4 or Cyclotrimethylene-trinitramine ($C_3H_6N_6O_6$),

TNT equivalency

- Is a simple method for equating a known energy of combustible fuel to an equivalent mass of TNT, see pg 270.
- Energy explosion of TNT is 1120 cal/g or 4686 kJ/kg

Method for Controlling Fires/Explosions

1. Elimination or reduction of ignition sources
   - In the past, this used to be the sole method of controlling
2. Preventing formation of flammable mixtures
   - Nowadays,
     - continuing elimination of ignition sources
     - and preventing formation of flammable mixtures.

Minimum Ignition Energy (MIE)

- The minimum energy required to ignite/initiate combustion
- All flammable materials (including dust) have MIEs.
- Depend on composition or concentration, pressure and temperature
- MIE decreases with increasing P
- MIE increases with increase N_2 concentration
- Many HC's have MIE about 0.25 mJ, see Table 6-4.
- Spark plug has a discharge energy of 25 mJ

Auto Ignition Temperature (AIT)

- Also known as Spontaneous Ignition Temperature.
- AIT is a fixed temperature above which a flammable mixture is capable of extracting enough energy from environment to self-ignite
- e.g. for CH_4 => 632°C Petrol => 246°C
- AIT is a function of ,
  - concentration of vapor, vapor volume, system pressure, flow condition, and presence of catalytic material
  - So need to exercise caution when using AIT data.
- See Appendix B for AIT values.
- So, a hot surface could be a source of ignition

Flash Point (FP)

- the lowest temperature at which the liquid gives enough vapor to form an ignitable mixture with air.
- e.g. for CH_4 => -222.5°C Petrol => -43°C

  Kerosene => 38 to 72°C
- determined using the open cup (Fig 6.3) or a closed-cup apparatus.
- the temperature at which the momentary flashing flame occur.
- But vapor might not be produced at a rate to sustain the fire.
- A higher temperature called ***fire point*** is required to produce continuous flame.
- See Appendix B for FP values.

- FP can be estimated using correlation by Satyanarayana and Rao,

$$T_f = a + \frac{b(c/T_b)^2 e^{-c/T_b}}{(1-e^{-c/T_b})^2} \qquad \text{unit in K}$$

- a,b,c are constants, see Table 6-1
- T_b is boiling point temperature in K
- For multicomponent flammable mixture, the FP should be determined experimentally

Fire Point

- The lowest temperature at which the vapor above liquid will continue to burn once ignited, fire point is higher than FP.

Flammability Limits (LFL and UFL)

- Vapor-air mixture will only ignite and burn over a specified range of compositions.
- Mixture will not burn if composition lower than **lower flammability limit** (LFL) : i.e. mixture is too lean for combustion
- Will not burn if composition higher than the **upper flammability limit** (UFL) : i.e. mixture is too rich for combustion
- LFL < **Composition of Flammable Mixture** < UFL

- Common unit used : volume percent of fuel in a fuel and air mixture.
- e.g. for CH_4 => LFL 5.3% UFL15.0%
  C_3H_8 => LFL 2.2% UFL 9.5%
- LFL and UFL are easily determined experimentally.
- Experimental determination is always recommended
- LFL and UFL for various HC are provided in Appendix B
- The range of flammability limits in pure O_2 are wider as shown in Table 6-3

Flammability Limits for Mixtures

- For mixture, they could be estimated by Le Chatelier eqn:

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

- y_i is mole fraction of component i
- n is the number of combustible species
- LFL and UFL are in % volume basis
- Note: For ideal gas mixtures, mole fraction equal volume fraction

Effect of T on Flammability limits

- Flammability range increases with temperature
- Estimated by

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_C}(T - 25)$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_C}(T - 25)$$

- T in ^oC
- ΔH_c is net heat of combustion (*kcal/mole*)

Effect of P on Flammability limits

- P has little effect on LFL
- However, the UFL increases significantly as P is increased

$$UFL_P = UFL - 20.6(\log P + 1)$$

- P is absolute pressure in megapascals
- UFL is the upper flammability limit at at 1 atm

Limiting O_2 Concentration (LOC)

- Also known as minimum O_2 concentration (MOC)
- O_2 is a key component in air for combustion
- There is minimum O_2 concentration required to propagate flame
- Below the LOC, the reaction cannot generate enough energy for the self-propagation of the flame
- Reducing O_2 concentration to below LOC to prevent fire and explosion is the basis of inerting.

- See Table 6.2 for LOC for a number of gases for N_2 and CO_2 as inert gases
- The unit are percentage moles of O_2 in total moles
- The LOC is from experiment but could be estimated using combustion stoichiometry and the LFL.
- Typical LOC is about 10%

$$LOC \approx \left(\frac{\text{Moles } \mathrm{O}_2}{\text{Moles Fuel}}\right)\left(\frac{\text{Moles Fuel}}{\text{Moles Fuel \& Moles Air}}\right)$$

$$LOC \approx \left(\frac{\text{Moles } \mathrm{O}_2}{\text{Moles Fuel}}\right) LFL$$

Stoichiometric Equation

$$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O$$

$$where, \quad z = \left(\frac{\text{Moles O}_2}{\text{Mole Fuel}}\right) = m + \frac{x}{4} - \frac{y}{2}$$

$so,$

$$LOC \approx z(LFL)$$

Example, for Butane (C_4H_{10})

z = 4+(10/4)-(0/2) = 6.5, LFL = 1.9% LOC ≈ 6.5x1.9 =12.35

Inerting

- Reducing O_2 concentration to prevent fire and explosion is the basis of inerting.
- N_2 and CO_2 are common inert gases.
- Water vapor could also be used but not really recommended as any condition that condense water vapor will move the O_2 concentration back above LOC.
- Usually the oxygen concentration is maintained at 4% lower than the LOC.
- Normally an O_2 analyzer (sensor) is connected to an inert gas control valve to maintain the O_2 concentration at a safe level.
- **Although usually non-toxic, inert gases can displace oxygen creating an asphyxiating atmosphere.**
- Details are in Chapter 7 (not covered in this class)

Example: Inerting a fuel tank

- An **inerting system** increases the safety of a fuel tank (e.g. aircraft fuel tanks), other sealed or closed-in tank that contains highly flammable material.

- An inert fuel tank is non-combustible.

- a fuel tank can be made inert by
  - (1) reducing the oxygen content of the ullage (space above the fuel that contains air and fuel vapors) below the LOC, or
  - (2) by reducing the air-fuel ratio of the ullage below the minimum threshold (Lower Flammability Limit) required for combustion, or
  - (3) increasing the fuel air ratio above the maximum threshold (Upper Flammability Limit) that can support combustion.

- fuel tanks are rendered inert by adulterating the ullage with an inert gas such as nitrogen, nitrogen enriched air, steam or carbon dioxide.

- Without sufficient oxygen in the tank, the fuel vapors in the ullage cannot ignite, and an explosion does not occur.

Flammability Diagram

- Concentration of fuel, oxygen and inert are plotted in volume or mole% on a triangle diagram
- Point A lies outside flammability zone, so this composition is not flammable
- The air line represents all possible combination of fuel plus air
- The stoichiometric line represents all stoichiometric combination of fuel plus oxygen.
  - For methane, $CH_4 + 2O_2 \rightarrow CO_2 + H_2O$

    this line intersect the oxygen axis (0% N_2) at

    $(2/(1+2))x100 = 66.7$

- Note the flammability limits for pure O_2 are wider (LFL 5.1%, UFL 61%)
- LOC line is at 12% oxygen
- Any gas mixture containing oxygen lower than LOC is definitely not flammable
- The size and shape of flammability zone as well as flammability limits and LOC depend on
  - Fuel type
  - Temperature
  - Pressure
  - Inert species

- Details on how to develop flammability diagrams are discussed in the textbook
- Example of inerting and purging with N_2 is discussed on page 302.

Explosion (chemical)

- Rapid chemical reaction leading to rapid release of energy (microsecond) and sudden expansion of gases resulting in rapidly moving pressure and shock wave to cause damage in its path.

- Energy dissipated through the formation of pressure wave, projectiles, thermal radiation and acoustic (sound) energy.

- Explosion can results from fires and vice versa.

- Note:

  Mechanical explosion is, on the other hand, due to sudden rupture of a pressurized vessel, calculation on mechanical energy explosion is on pg 276

Confined Explosion

- Occur in a confined space such as vessel and building
- Most common type of explosion
- Mostly due to vapor (e.g solvent vapor) or dust
- Results in injury to inhabitants and cause extensive damage to structure.

- Example:

  Abbeystead disaster - Build up of methane gas (from earth) within tunnels in a water pumping station ignited and several of visitors died as a result.

Unconfined Explosion

- Occur in the open
- Such as from flammable gas spilled
- Rarer than confined explosion due to dilution to below LFL by wind dispersion
- But the explosion could be destructive due to large quantity of gas and large areas involved

Vapor Cloud Explosion

- Occur due to
  - Sudden release of large quantity of flammable liquid and vapor from
    - Liquefied gases, volatile superheated liquid, compressed gases
  - Difficult to control once released
  - Dispersion of the vapor throughout the plant site while mixing with surrounding air
  - The flammable mixture find an unexpected ignition source
  - Increase frequency in recent time due to large inventory of flammable materials
  - For example, the Flixborough accident where the vapor cloud is cyclohexane

- Prevention
  - Keep low inventory of flammable material
  - Inherent safety design
  - Install detector that could detect low concentration
  - Install automatic block valve to shut system down while spill is at the incipient stage
- E.g. 6-9 shows equivalent amount of TNT for VCE of methane, the overpressure and damage on common structures

Example :

- Flixborough, UK, 1/6/74. Plant producing caprolactam for nylon manufacture and part of the process involved reaction of cyclohexane with air. Massive failure of a temporary bypass pipeline cause 40 -50 ton of liquid cyclohexane to escape and formed a large vapor cloud. Subsequent explosion cause damage up to 3 miles away. 28 killed, 36 injured on site, 53 off-site.

BLEVE

- Boiling-Liquid Expanding-Vapor Explosion
- Rupture of a vessel at high pressure containing hot liquid at a temperature above its *atmospheric pressure boiling point* (i.e. *NBP*)
- Then explosive vaporization of the vessel content.
- If the liquid is combustible, the vapor cloud explosion might result if found an ignition source.
- Usually occurs when external fire heats the content of a tank of volatile material.
  - The vapor pressure of liquid increases (hence the boiling temperature also increases)
  - As temperature increases, the structural integrity of vessel is weaken.
  - The vaporising liquid will ignite/explode as the tank ruptures

Examples:

a) Feyzin, France, 4/1/66. A leak on propane storage sphere ignited and caused fire which burned fiercely around the vessel and led to BLEVE. 18 death, 81 injuries.

b) Mexico City, Mexico, 19/11/84. A series of LPG explosions at LPG gas distribution plant resulted in 542 killed and over 7000 injured. LPG was stored in 6 spheres and 48 cylindrical bullets holding 4 million gallons of LPG.

Deflagration (low explosive)

- Explosion with resulting shock wave moving at speed less than speed of sound.

- Speed of sound is 344 m/s at 20°C for ideal gases.

Detonation (high explosive)

- Explosion with resulting shock wave moving at speed greater than speed of sound.

- You will see a glass window broken **before** you hear the explosion

Blast wave

- Explosion results in reaction front moving outward preceded by a shock wave or pressure wave.
- The impact of shock wave cause overpressure on objects on its path.
- E.g. 6-8 shows the estimation of overpressure at a distance from explosion.
- Blast wave is a combination of abrupt pressure wave (shock wave) that followed by strong wind
- Blast wave causes most of the damage such as from projectiles

Dust Explosion

- Explosion results from the rapid combustion of fines solid particles.
- Many solid materials (including metals such as iron and aluminum) become flammable when reduce to fine powder, e.g. coal, flour, wood dust, resin dust.
- Minimum explosive dust concentration, particle size and minimum ignition energy for various dusts are given in Table 6-8.
- Example: Series of explosions in silos at New Orleans in 1977. Forty five silos containing corn, wheat and soy beans involved… 35 to 50 people killed.

Videos

1. Propane released during transfer process leading to confined explosion inside a convenient store
2. BLEVE of a petrol tanker in Korea
3. Use of BLEVE to test the Castor® nuclear waste container in Germany
4. Confined space explosion during a welding process

Reference

- Crowl, Daniels A. and Louvar, Joseph F., Chemical Process Safety: Fundamentals with Applications, Prentice Hall, 1990, New Jersey, USA.