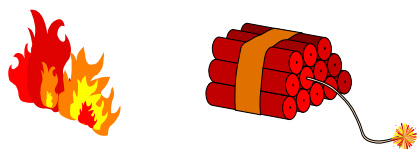


Chemical Process Safety

Chapter 6: Fires & Explosions



Case History

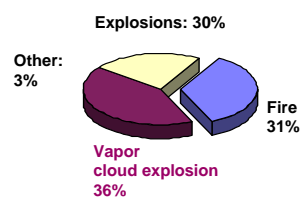


Case History



Accident Statistics

Evaluation of the largest chemical plant accidents:



Most of the large accidents are due to fires and explosions.

Introduction

FIRE rapid exothermic, oxidation, with flame
EXPLOSION higher energy release rate (mixture) pressure or shock wave

} may trigger each other

EFFECTS injuries / casualties
 property losses
 process interruption

} Thermal radiation,
 asphyxiation, toxic products,
 blast, fragments

REQUIRED KNOWLEDGE FOR PREVENTION

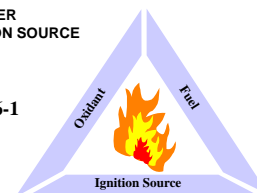
material properties
 nature of fire and explosion process
 procedures to reduce hazards (Ch. 7)

Fire Triangle

FIRE TRIANGLE

FUEL
 OXIDIZER
 IGNITION SOURCE

Figure 6-1



Oxidant may not be oxygen, i.e. chlorine.

Fire Triangle

FUELS	Gases	Acetylene, Propane, CO, H ₂
	Liquids *	Gasoline, Organic Solvents
	Solids *	Plastics, Wood Dust, Fibers, Metal Particles

OXIDIZERS	Gases:	O ₂ , F ₂ , Cl ₂
	Liquids: <td>H₂O₂, HNO₃, HClO</td>	H ₂ O ₂ , HNO ₃ , HClO
	Solids: <td>Peroxides, NH₄, NO₂</td>	Peroxides, NH ₄ , NO ₂

IGNITION SOURCE	Sparks, Flames, Static Electricity, Heat
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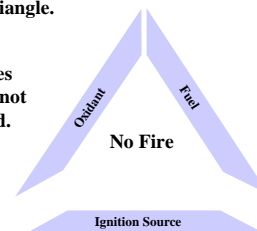
* Liquids are volatilized and solids decomposed prior to their combustion in the vapor phase

Sufficient quantity / energy required.

Application of the Fire Triangle

Fires and explosions can be prevented by removing any single leg from the fire triangle.

Problem: Ignition sources are so plentiful that it is not a reliable control method.



Robust Control: Prevent existence of flammable mixtures.

Combustion Behavior – Most Hydrocarbons



Smoke and fire are very visible!

Combustion Behavior – Carbon Disulfide



No smoke and fire, but heat release rate just as high.

Combustion Behavior – Methane



Methane burns mostly within vessel, flame shoots out of vessel.

Combustion Behavior – Dusts



Much of the dust burns outside of the chamber.

Definitions - 1

LFL: Lower Flammability Limit

Below LFL, mixture will not burn, it is too lean.

UFL: Upper Flammability Limit

Above UFL, mixture will not burn, it is too rich.

Defined only for gas mixtures in air.

Both UFL and LFL defined as volume % fuel in air.

Definitions - 2

Flash Point: Temperature above which a liquid produces enough vapor to form an ignitable mixture with air.

Defined only for liquids at atm. Pressure.

Auto-Ignition Temperature (AIT): Temperature above which adequate energy is available in the environment to provide an ignition source.

Definitions - 3

Limiting Oxygen Concentration (LOC): Oxygen concentration below which combustion is not possible, with any fuel mixture.

Expressed as volume % oxygen.

Also called: Minimum Oxygen Concentration (MOC)

Max. Safe Oxygen Conc. (MSOC)

Others

Typical Values - 1

	LFL	UFL	
Methane:	5.3%	15%	
Propane:	2.2%	9.5%	See Appendix B
Butane:	1.9%	8.5%	
Hydrogen:	4.0%	75%	

	Flash Point Temp. (deg C)
Methanol:	12.2
Benzene:	-11.1
Gasoline:	-43

Typical Values - 2

	AIT (deg. C)	
Methane:	632	Great variability in reported AIT values! Use lowest value.
Methanol:	574	
Toluene:	810	

	LOC (Vol. % Oxygen)	
Methane:	12%	Table 6-2
Ethane:	11%	
Hydrogen:	5%	

Flammability Relationships

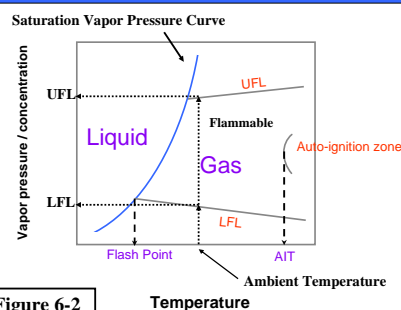


Figure 6-2

Minimum Ignition Energies

What: Energy required to ignite a flammable mixture.

Typical Values: (wide variation expected)

Vapors: 0.25 mJ

Dusts: about 10 mJ

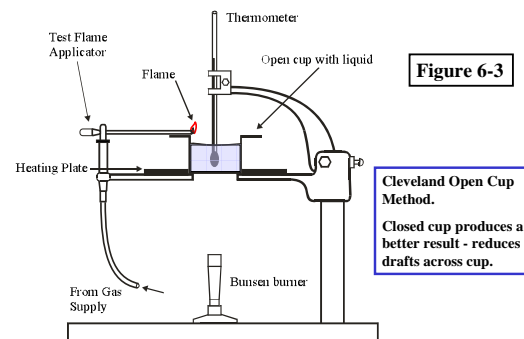
Dependent on test device --> not a reliable design parameter.

Static spark that you can feel: about 20 mJ



Table 6-4

Experimental Determination - Flashpoint



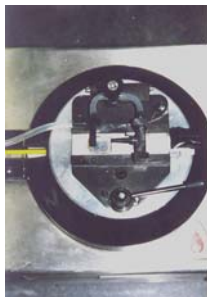
Experimental Determination - Flashpoint



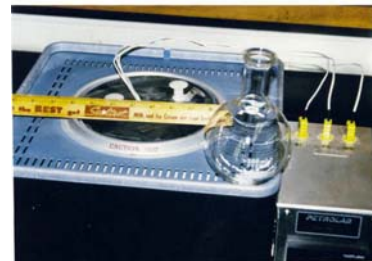
Setaflash Flashpoint Device



Setaflash Flashpoint Device - Close-up



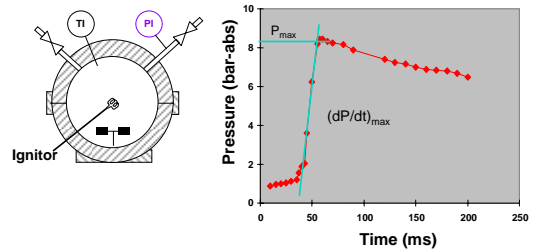
Auto-Ignition Temperature (AIT) Device



Auto-Ignition Temperature (AIT) Device



Experimental Determination: P versus t



Final experimental result: P_{\max} $(dP/dt)_{\max}$

Experimental Apparatus

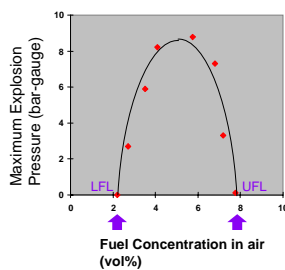


Experimental Apparatus



Experimental Determination - LFL, UFL

Run experiment at different fuel compositions with air:



Need a criteria to define limit - use 1 psia pressure increase. Other criteria are used - with different results!

See Figure 6-5

Flammability limits are an empirical artifact of experiment!

Flammability Limit Behavior -1

As temperature increases:

UFL increases, LFL decreases

--> Flammability range increases

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_c} (T - 25) = LFL_{25} - \frac{100C_p}{\Delta H_c} (T - 25)$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_c} (T - 25) \quad \text{Equations 6-4, 6-5}$$

$T : ^\circ C$

ΔH_c : kcal/mole, heat of combustion

Approx. for many hydrocarbons

Flammability Limit Behavior -2

As pressure increases:

UFL increases

LFL mostly unaffected

$$UFL_p = UFL + 20.6 * (\log P + 1)$$

P is pressure in mega-Pascals, absolute

No theoretical basis for this yet!

Pressure and temperature effects on flammability limits is poorly understood – estimation methods are poor.

Flammability Limits of Mixtures

Le Chatelier Rule (1891)

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

y_i on a combustible basis only

Assumptions: 1) Product heat capacities constant

2) No. of moles of gas constant

3) Combustion kinetics of pure species unchanged

4) Adiabatic temperature rise the same for all species

Details provided in *Process Safety Progress*, Summer 2000.

Flammability Limits - Le Chatelier

LeChatelier's rule shows that the LFL can be approximated by:

$$\left(\frac{LFL}{100} \right) \cong \frac{C_p \Delta T^*}{(-\Delta h_c)}$$

Where C_p is the product heat capacity, ΔT^* is the adiabatic temperature rise, and Δh_c is the heat of combustion.

1200 K is frequently used as the adiabatic temperature rise at the flammability limit.

A similar expressions is written for the UFL.

Adiabatic Temperature Rise:

$$\Delta T = \frac{n_{Fuel} (-\Delta h_{Comb})}{n_{Prods} C_p^{Prods}} \cong \frac{n_{Fuel} (-\Delta h_{Comb})}{n_{Total} C_p} \cong \frac{y_{Fuel} (-\Delta h_{Comb})}{C_p}$$

$$y_{Fuel} = \frac{C_p \Delta T^*}{(-\Delta h_{Comb})} = \left(\frac{LFL}{100} \right)$$

1200 K is frequently used as the adiabatic temperature rise at the flammability limit.

A similar expression is written for the UFL.

Flammability Limits of Mixtures

$$\left(\frac{LFL}{100} \right) \cong \frac{C_p \Delta T^*}{(-\Delta h_c)}$$

From this equation, a plot of the flammability limit vs. $1/(\text{Heat of Combustion})$ should yield a straight line if Le Chatelier's rule is valid.

If this is done, one finds that:

Le Chatelier's rule works better at the lower flammability limit than the upper flammability limit.

Assumptions are more valid at LFL.

Lower Flammability Limit and Heat of Combustion

