Flammable gas and vapour explosion hazards: Significance of flammability characteristics

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Introduction

Many products made in industry today require the use of flammable chemicals (gases and liquids) and flammable chemical mixtures during the manufacturing and processing stages. These flammable chemicals can pose a serious fire and explosion hazard during handling, processing, and storage. If containment is lost through a leak or a rupture, the gases or liquid vapours can readily mix with the surrounding air to form explosible mixtures. Since many gases and most vapours are heavier than air, they can travel across the floor or concentrate in low areas if there is minimal or no air movement or they can be lofted to higher levels by air currents. If the gas or vapour mixtures are in the flammable range, only a small amount of spark energy (typically less than 1.0 millijoule) is required to ignite the explosible mixture.

> **"The important difference between a fire and an explosion is the rate at which energy is released"**

The risk of a fire and explosion at a facility that handles flammable chemicals can be minimised if the site staff has knowledge of the following concepts:

- Requirements for a fire and explosion
- Flammability properties of the chemicals
- Effect of process conditions on the flammability properties of chemicals
- Explosion prevention and protection measures

Requirements for a Fire and Explosion

The necessary elements required for a fire include (a) fuel, (b) an oxidant, and (c) an ignition source. When all the three elements are simultaneously present in one location, then a risk of fire exists (see Figure 1). For propagating combustion (fire or flash fire) to occur, the fuel must be within the flammable range, the oxidant concentration must be capable of supporting combustion, and the ignition source must have sufficient energy. Two additional elements are required to create an explosion hazard (see Figure 2); they include (d) containment, and (e) mixing

The important difference between a fire and an explosion is the rate at which energy is released. In a fire, the rate at which energy is released is relatively low and the energy release may occur over a period of seconds

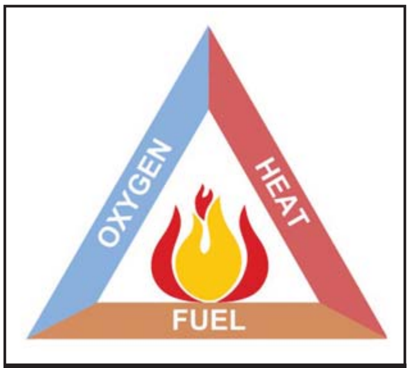

Figure 1: Fire Triangle

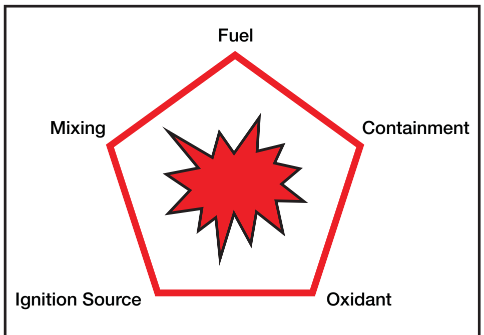

Figure 2: Explosion Pentagon

to hours. In an explosion, the energy is released in a very short time period, usually milliseconds or microseconds, and the rate at which the energy is released is very high. As the pressure increases in an explosion – as a result of confinement – the rate of the combustion reaction rapidly accelerates, but in a fire or flash-fire the pressure remains relatively constant.

Flammability Properties of the Chemicals – liquids, vapours, and gases

Flammable liquids, vapours, and gases can be characterised by the values of several combustibility properties. Knowledge of these properties is required to assess the risk of a fire or explosion at a facility and to determine the safety measures that would be needed to mitigate or control the hazards of a process.

Several test methods exist to determine the fire and explosion (flammability) properties of chemicals and chemical mixtures. The flammability properties needed to address the risk of a fire or explosion will depend on the nature of the chemical or chemical mixture, the type of process equipment, and the processing conditions and these factors may determine the selection of the appropriate test methods. The safety-critical flammability properties, the purposes of the flammability tests, and the standard test methods used to determine these properties are provided in the Table 1, below.

Effect of Process Conditions on the Flammability Properties of Chemicals

Process operating conditions such as (a) temperature, (b) pressure, (c) oxidant concentration, (d) equipment shape and size, (e) material of construction, and (f) turbulence/mixing – all affect the flammability properties of chemicals (liquids, vapours and gases).

Published data on the flammability properties of liquids, vapours, and gases can be found in safety data sheets (SDSs) and in other publications, such as NFPA 325. Most of these data are for common chemicals, and they usually have been determined in air at ambient conditions of room temperature and atmospheric pressure. Very limited data are available or exist at different process conditions. Many methods are available to estimate the flammability properties of chemicals – including estimation at elevated temperatures and pressures. However, these methods should be used only for initial estimations and should not be relied-upon for engineering safety design. Moreover, the estimation methods that are available usually cannot take into account the combined effects of process conditions. Hence, safety-critical data should be developed by conducting experiment(s) at – or as close as possible to – the actual process conditions.

Examples:

- **The flash point (FP) temperature of a liquid is lower at reduced pressure (vacuum)**
  Flash fires were noted in a process that used a pan filter containing a combustible liquid with a Flash Point

Table-1: Flammability Properties, Uses, and Test Methods

Flamm. Property [(1)]	Description and Use	Test Method(s) [(2)]
FP and/or LTL	FP is the lowest temperature at which sufficient vapors are present above a chemical (liquid) surface to form an ignitable mixture with air. LTL is the FP of a chemical determined under equilibrium conditions. The FP/LTL is a characteristic of a liquid fuel and may be used to specify storage, operation and material-handling procedures for liquids. They are also useful in specifying the packing requirements for shipping purposes.	ASTM D93 ASTM D56 ASTM D3828 ASTM E1232 EN 11 EN 57
LFL and UFL	LFL is the minimum concentration of a fuel vapor in an oxidant below which flame propagation will not occur. UFL is the maximum concentration of a fuel vapor in an oxidant above which flame propagation will not occur. LFL and UFL are used to specify storage, operation and material-handling procedures for flammable liquids and gases. LFL is particularly useful in specifying ventilation requirements for operations handling flammable gases and vapors.	ASTM E681 ASTM E918 EN 1839
AIT	AIT is the lowest temperature at which a material will spontaneously ignite in the absence of an ignition source, such as spark or flame. AIT is useful in specifying storage, operation and material-handling procedures. It is particularly useful if a material is handled in a process at an elevated temperature, as in drying.	ASTM E659 ASTM D2155 EN 14522
Flamm Property	**Description and Use**	**Test Method(s)**
LOC	LOC is the minimum concentration of an oxidant in a fuel-oxidant mixture, below which combustion will not occur. LOC data are used in explosion prevention or to reduce the severity of a combustion incident. It is also used in determining the set-point of alarms or interlocks in vessels or enclosures.	ASTM E2079 EN 14756
MIE	MIE is the minimum energy of an ignition source (such as spark) that is capable of igniting a fuel-oxidant mixture. The MIE data are primarily used to assess the vulnerability of flammable gases and vapors to ignition by electrostatic discharges.	ASTM E582
Explosion Severity (P_{max} and K_g)	Explosion severity is defined by the maximum explosion pressure (P_{max}) and the maximum rate of pressure rise $(dP/dt)_{max}$ for a flammable gas or vapor. The value of $(dP/dt)_{max}$ is used to determine the deflagration index, K_g. The P_{max} value is used for designing vessels to contain explosions, and the K_g value is used for designing protection for vessels, such as relief venting or suppression.	EN 13673-1 EN 13673-2 NFPA 68 Guidelines

Notes
[(1)] FP – Flash Point, LTL – Lower Temperature Limit, LFL – Lower Flammable Limit, UFL – Upper Flammable Limit, AIT – Auto-ignition Temperature, LOC – Limiting Oxidant (oxygen) Concentration, MIE – Minimum Ignition Energy, Explosion Severity (P_{max} – Maximum Explosion Pressure, $(dP/dt)_{max}$ – Maximum Rate of Pressure Rise, K_g – Deflagration Index), NFPA – National Fire Protection Association publications
[(2)] This listing of test methods is not a complete listing of all available methods

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of 47ºC (117ºF) [1]. The filtration was conducted at ambient temperature, around 25 to 29ºC (77 to 84ºF). One question that needed to be addressed was why a flammable vapour-air mixture had formed at a temperature below the Flash Point of the process liquid. The Flash Point of a sample was measured at the actual process pressure of 0.67 atm (9.8 psia) using the ASTM E1232 test method[2].

"The intent of flammable-process design should be to use a layer-of-protection approach"

Although the sample tested was not the actual process liquid – and it had a Flash Point of 78ºC (172ºF), which was higher than the actual product involved in the incident – the measured Flash Point at 0.67 atm was determined to be 19.4ºC (67ºF), which is lower than the Flash Point of the liquid at 1 atm by 58ºC (105ºF). This clearly confirmed that the flash points of chemicals are generally lower at reduced pressure, and the flash point of the process liquid involved in the flash fire incident likely was reduced to below the operating temperature of 25 to 29ºC at the operating pressure of 0.67 atm.

- **The limiting oxygen concentration (LOC) is generally lower at elevated temperatures**

LOC experiments were conducted on a process sample to determine the effect of process temperature on the LOC value and to aid in the determination of a suitable set-point for a high-oxygen-concentration alarm for the process. Tests were conducted at various temperatures from 100 to 375ºC and at atmospheric pressure. Due to the elevated temperatures, a 2.25-liter cylindrical stainless steel vessel was used, and this set-up was in general accordance with the ASTM E2079 test methodology[3]. At 100ºC, the LOC was determined to be 12.5%-v and at 225ºC, the LOC was determined to be 11.0%-v. At temperatures above 275ºC, some thermal oxidation was noticed that masked or affected the actual LOC value[4]. The test results indicated that the LOC decreases with an increase in temperature.

Explosion Prevention and Protection Measures

Depending on the magnitude of the fire and/or explosion hazard, the consequences could be significant and range from injury to personnel, harm to the environment and damage to equipment. The intent of flammable-process design should be to use a layer-of-protection approach, with more than one safeguard to minimise the risk of a fire and explosion. An order of preference is provided below:

1. Prevent the formation of flammable mixtures by fuel control. This is the most desirable basis of safety, and it might be accomplished by controlling the fuel concentration such that the gas or vapour is not allowed to be within its flammable range, by operating below the flash point of a liquid or by diluting a flammable liquid with a non-flammable liquid.

2. Prevent the formation of flammable mixtures by oxidant control. This basis of safety might be accomplished by reducing the oxidant concentration to a point where combustion cannot occur by inerting.

3. Eliminate ignition sources. This secondary basis of safety involves identifying and controlling ignition sources that are capable of igniting the flammable atmosphere.

4. Provide fire and explosion protection. Protect personnel, equipment, and property against the consequences of fire and explosion by automatic sprinkler and deluge systems, explosion containment, explosion suppression, explosion venting, or barricading.

Notes:

(1) D. Kong, "Measurement of Flammability Properties of Chemicals under Representative Process Conditions", Chilworth Focus Article, 2006.

(2) ASTM E1232 – Standard Test Method for Temperature Limit of Flammability of Chemicals

(3) ASTM E2079 – Standard Test Method for Limiting Oxygen (oxidant) Concentration in Gases and Vapors

(4) A. Kenchenpur [Chilworth Technology, Inc.], "Limiting Oxidant Concentration Testing for Process and Pure Sample", Report No. DU13285AK (February, 2013)

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