

# Minimize the Risks of Flammable Materials

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Flammable materials can cause fires and explosions if they are not handled properly. Understanding these materials and the risks they pose is the first step to mitigating fire hazards.

Most chemical plants contain flammable materials and face hazards related to the combustion of these materials. Almost all of the 100 worst chemical plant accidents involved flammable materials (1). This demonstrates the need to manage the risk of fires and explosions related to flammable materials.

Managing these risks requires an understanding of three key concepts: the anatomy of the fire and explosion process; the properties that characterize flammable materials; and the procedures used to reduce fire and explosion hazards.

This article discusses gas and liquid flammability hazards. Solids, including dusts, are more difficult to characterize and are not covered here. Furthermore, this is an introduction, and additional references or expertise should be consulted for major flammability hazards (2-4).

## The anatomy of fire

The necessary ingredients of a fire are a fuel, an oxidant, and an ignition source (Figure 1). The fuel and oxidant must be present at certain relative concentrations for a fire to start, and the ignition source must be robust enough to initiate a fire. The oxygen found in air is the most common oxidant, but other materials, such as chlorine, fluorine, and nitrates, may also act as oxidants. Combustion always occurs in the vapor phase; liquids are volatilized and solids are decomposed prior to combustion.

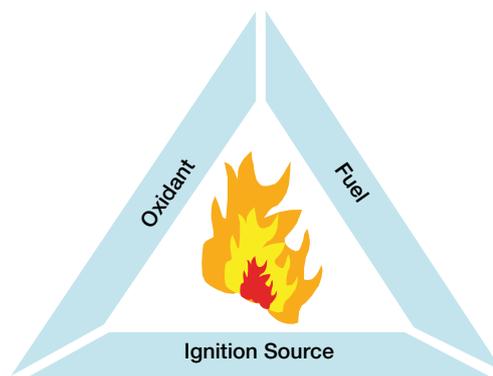
The difference between a fire and an explosion is the time frame of the event. Fires occur over a very long time frame and have a relatively low energy release rate. Explosions occur over a very short time frame — usually milliseconds or microseconds — and the energy release rate is very high.

## Characterizing flammable materials

Flammable gases and liquids can be characterized based on several properties (Table 1). These are not fundamental properties, but rather each is a function of particular experimental apparatuses and procedures. Thus, there is wide variability in these properties. In addition, these properties do not define rigid boundaries between safe and unsafe operation. All of these nuances must be carefully considered when handling flammable materials.

*Flammability limits.* The two most important properties of flammable gases are the upper flammability limit (UFL) and the lower flammability limit (LFL). These are frequently called the upper and lower explosion limits (UEL and LEL).

The LFL is the concentration of fuel vapor in air below which combustion is not possible; the mixture is considered too lean. The UFL is the fuel vapor concentration above



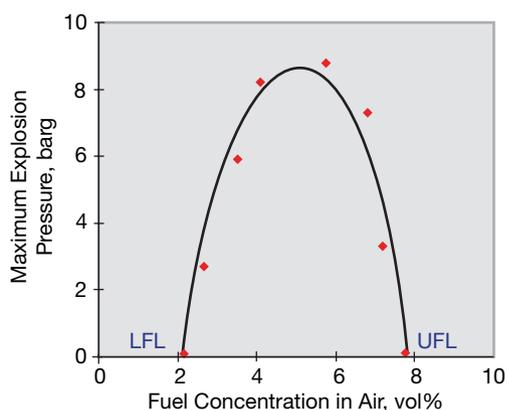
▲ **Figure 1.** A fire can only occur when a fuel, an oxidant, and an ignition source are present.

Table 1. Flammability properties are useful for determining whether flammable mixtures will form (13).

	Species	LFL, vol% fuel	UFL, vol% fuel	Flashpoint, °C	LOC, vol% oxygen	MIE, mJ	AIT, °C
Vapors	Methane	5.0	15.0	-188	12	0.28	600
	Ethane	3.0	12.5	-135	11	0.24	515
	Propane	2.1	9.5	-104	11.5	0.25	450
	Hydrogen	4.0	75.0		5	0.018	400
	Ammonia	16.0	25.0				651
	Carbon Monoxide	12.5	74.0		5.5		609
	Hydrogen Sulfide	4.3	45.0		7.5		260
	Acetylene	2.5	80.0	-18		0.020	305
Liquids	Hexane	1.2	7.5	-23	12	0.248	234
	Ethylene	2.7	36.0	-136	10		450
	Benzene	1.4	7.1	-11	11.4	0.225	562
	Ethanol	4.3	19.0	13	10.5		422
	Methanol	7.5	36.0	11	10	0.140	463
	Formaldehyde	7.0	73.0	-53			430
	Acetone	2.6	12.8	-18	11.5		538
	Styrene	1.1	6.1	32	9.0		490
	Gasoline	1.4	7.6	-43	12		

which combustion is not possible; in this case, the fuel is too rich. Both the LFL and UFL have units of volume-percent fuel in air.

The LFL and UFL are typically determined by mixing the flammable gas in a closed vessel with an oxidant and other gases, such as nitrogen, and then attempting to ignite it. If the ignition is successful, the pressure inside the vessel will first increase rapidly to a maximum pressure and then decrease as the gases are quenched and cooled on the vessel wall. The percent pressure increase is determined by subtracting the initial starting pressure from the maximum pressure, dividing by the initial starting pressure, and multiplying



▲ Figure 2. The maximum explosion pressure during combustion changes with fuel concentration.

by 100. The flammability limits are based on an arbitrary pressure increase. In the U.S., this is a 7% pressure increase, as specified by ASTM E918-83 (5). Standards organizations in other countries have used 5% and even 10%. Figure 2 is a typical plot of the maximum pressure vs. fuel concentration determined by this method. The maximum pressure changes as a function of fuel concentration. Other methods for defining these limits can be found in Ref. 6.

LFL and UFL values are typically reported at room temperature and pressure. In general, the LFL decreases and the UFL increases with increasing temperature. Increasing pressure generally increases the UFL, but the LFL is mostly unaffected. The quantitative estimation of the effects of pressure and temperature on flammability limits is poorly understood.

LeChatelier's rule can be used to provide an initial estimate of the flammability limits for mixtures of gases, although experimental verification is always advised:

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

where  $LFL_{mix}$  is the lower flammability limit of the mixture,  $n$  is the number of combustible species,  $y_i$  is the mole fraction of combustible species  $i$  computed on a combustible-species-basis only, and  $LFL_i$  is the lower flammability limit of the pure combustible species  $i$ .

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A similar expression can be written for the upper flammability limit.

LeChatelier's rule is empirical and contains many assumptions that may or may not be valid for a particular situation (7). It is known to be more accurate for calculating the LFL than the UFL.

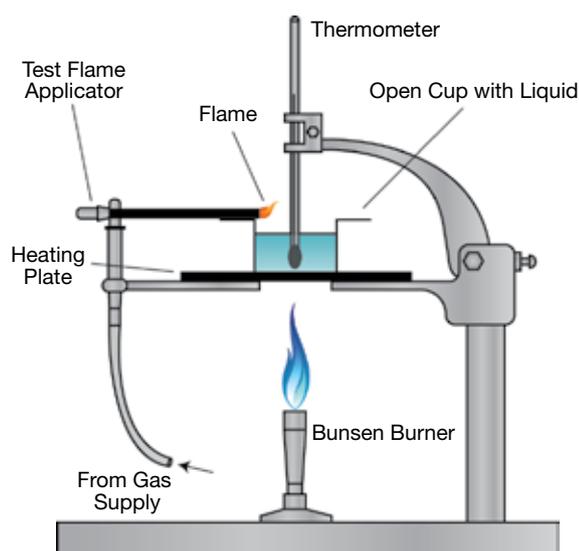
Other properties that can be used to characterize flammable gases include the limiting oxygen concentration (LOC), the minimum ignition energy (MIE), and the autoignition temperature (AIT).

**Limiting oxygen concentration.** The LOC is the oxygen concentration below which combustion is not possible at any fuel concentration. The LOC has units of volume-percent oxygen and is determined via the same closed-vessel apparatus used to determine the flammability limits.

**Minimum ignition energy.** The MIE is the minimum energy of an ignition source, such as a spark, required to ignite the vapor. This property varies widely. For flammable vapors, a nominal value of 0.025 mJ is frequently used. This is a very small amount of energy. In comparison, a small coin dropped from a height of less than 1 mm has more energy than this, and a spark that is just detectable to the touch contains about 20 mJ of energy. These low values indicate that ignition sources are plentiful. In fact, the elimination of ignition sources is not a robust method to prevent fires and explosions, although ignition source reduction is still essential.

Reference 8 provides a procedure for experimental determination of the MIE.

**Autoignition temperature.** The AIT is the temperature above which adequate energy is available in the environment



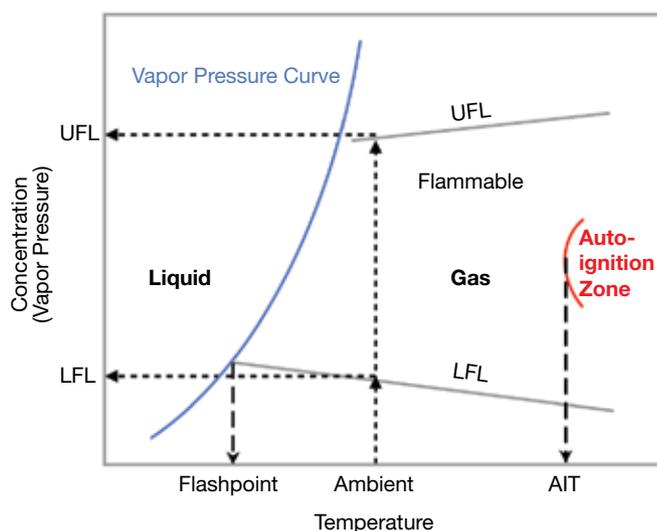
▲ **Figure 3.** The Cleveland open-cup tester is commonly used to determine flashpoint temperature (3).

to provide an ignition source. To determine the AIT, a small quantity of flammable liquid is injected into a preheated flask at a set temperature. The flask is observed over a fixed period of time for visible combustion behavior (9). If combustion is not observed, then the flask temperature is increased until combustion occurs.

**Flashpoint.** A liquid's vapor pressure is a measure of the relative concentration of vapor in equilibrium with the liquid. At high temperatures, flammable liquids will have higher evaporation rates and higher vapor pressures, often creating flammable mixtures above the surface of the liquid. The flashpoint is the lowest temperature at which this vapor forms an ignitable mixture with air. At the flashpoint, the vapor will burn only briefly. At a much higher temperature, called the fire-point temperature, the liquid will burn continuously. Since a fire or explosion can propagate from a flash, the flashpoint temperature is the primary property used to characterize liquid flammability.

Figure 3 is a schematic of the apparatus used to estimate the flashpoint temperature based on the Cleveland open-cup method (10). The liquid is placed in a small, open cup, which is heated with a Bunsen burner. A wand with a small flame at one end is moved back and forth above the liquid surface, and the temperature of the liquid is increased until a flash is observed. One problem with this method is that the open cup is vulnerable to drafts, which remove the flammable vapor. This problem can be avoided by using a closed-cup method (11).

Figure 4 depicts the relationships among the properties used to characterize combustion and how they relate to the saturation vapor pressure curve. The LFL intersects the



▲ **Figure 4.** The LFL, UFL, AIT, and flashpoint are functions of temperature and vapor pressure.

saturation vapor pressure curve at the flashpoint temperature. The AIT is the lowest temperature in an AIT zone. It is not known what happens to the UFL, LFL, and AIT zone boundary at high temperatures.

Many methods are available to estimate flammability properties (2, 3). These prediction methods should be used only for quick initial estimations and should not be used for engineering design. In addition, because the temperature and pressure effects are not well understood, experimental values should be obtained at conditions as close as possible to the actual process conditions.

For some partial oxidation reaction processes, the UFL is a key operating parameter. The conversion efficiency of the reactor and the safety of the process depend on the precision and accuracy of the UFL estimate. Typically, the process is operated at vapor fuel concentrations well above the UFL to prevent an explosion. However, as the fuel composition is reduced and approaches the UFL, the reaction conversion, and thus the yield, increases. In this case, there is an obvious tension between safety and production, and achieving the right balance requires a high degree of confidence in the flammability data.

Published LFL and UFL data are available only for air mixtures. However, situations that involve flammable non-air mixtures are frequently encountered, such as when an inert gas (e.g., nitrogen or carbon dioxide) is used to control flammable concentrations. A triangle flammability diagram is essential for these cases.

### Triangle diagrams

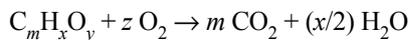
Figure 5 is a typical triangle diagram for a flammable mixture that contains nitrogen. The axes of the diagram represent the concentrations of each of the three components — fuel, oxygen, and nitrogen. At any point on the figure, the concentrations must add up to 100%. Most flammable materials demonstrate a flammability zone (the shaded area in Figure 5) — that is, a region within which the mixture is flammable at all concentrations.

The line connecting point A and point B is the air line. This line runs from point A at the top of the triangle (i.e., 100% fuel) to the point on the diagram that corresponds to a concentration of 79% nitrogen and 21% oxygen (i.e., pure air, point B) and represents all possible concentrations of a fuel and air mixture.

The line connecting point C and point D is the stoichiometric line. This line runs from the point on the diagram corresponding to a concentration of

100% nitrogen (point D) to the oxygen axis and represents all possible stoichiometric concentrations of a fuel and oxygen mixture. The point at which the stoichiometric line intersects the oxygen axis (point C) depends on the stoichiometry of the reaction.

Consider, for example, the following reaction:



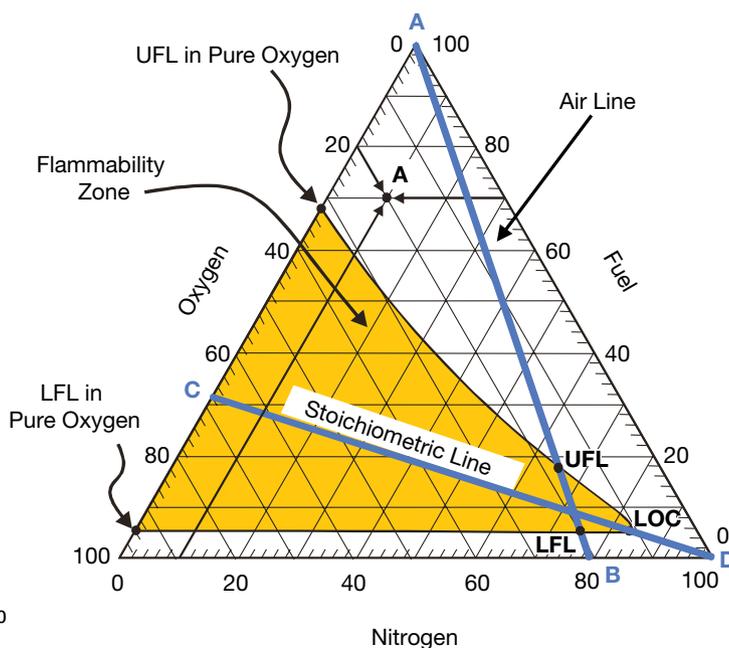
For this reaction, the stoichiometric line intersects the oxygen axis at:

$$100 \left( \frac{z}{1+z} \right) \quad (2)$$

The air line intersects the flammability zone at the flammability limits (i.e., LFL and UFL). The LOC is found at the point where a line parallel to the fuel axis just touches the flammability zone; its value is read from the oxygen axis.

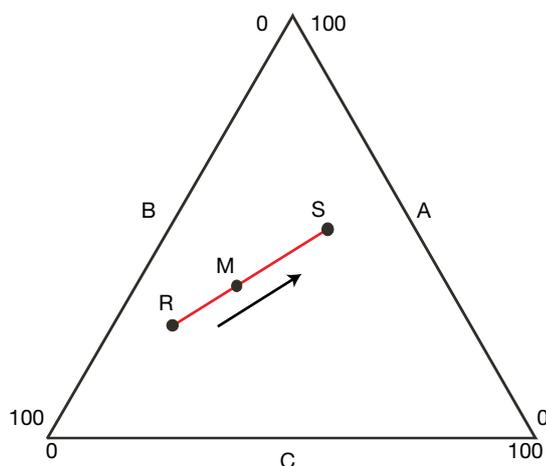
Triangle flammability diagrams are frequently used in industrial facilities to determine whether a flammable mixture will form during a procedure, such as inerting and purging, taking vessels and equipment in and out of service, and other common operations. Unfortunately, only a few complete triangle flammability diagrams have been experimentally determined, including methane and ethylene (12). Triangle diagrams differ depending on the fuel and the inert gas used. A triangle flammability diagram can be approximated (2, 3) using a limited amount of experimental data.

The following rules of thumb exist to help engineers use

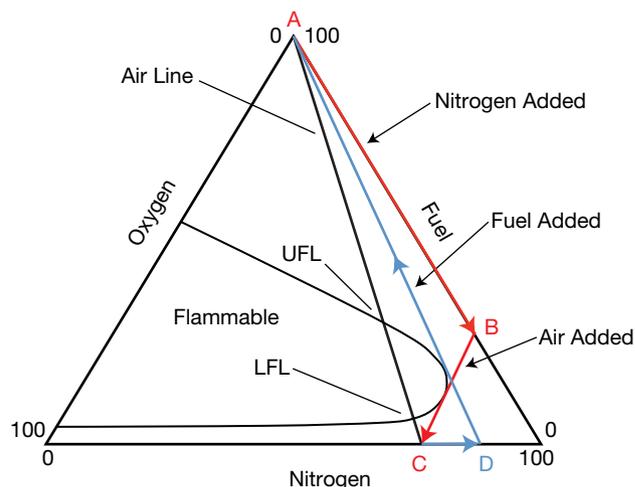


► **Figure 5.** A triangle flammability diagram can be used to determine flammable compositions for a non-air mixture.

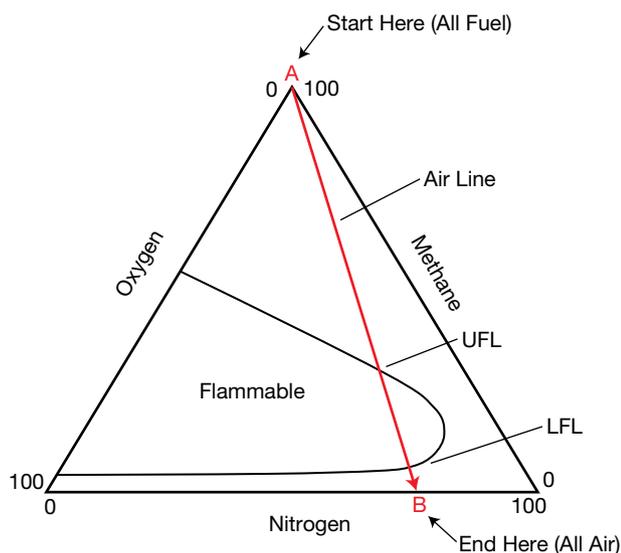
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▲ **Figure 6.** As mixture R is diluted with mixture S, the concentration of the combined mixture M follows a straight line between the compositions of the two original mixtures.



▲ **Figure 8.** To avoid the flammability zone, nitrogen is added to the pure fuel. When the vessel is vented with air, the system does not form a flammable mixture.



▲ **Figure 7.** Taking a vessel that contains methane under pressure out of service can form a flammable mixture if the proper procedure is not used. In this case, the vessel is initially depressurized to atmospheric pressure and then vented to the air. This procedure creates a flammable mixture.

triangle flammability diagrams for chemical plant operations. Equations for these rules can be found in Refs. 2 and 3.

1. If two gas mixtures R and S are combined, the composition of the resulting mixture (M) will lie on a line connecting points R and S on the triangle flammability diagram (Figure 6). The location of point M depends on the relative molar content of R and S; if the molar content of S in mixture M is higher than that of R, the composition of the final mixture will be closer to point S.

2. If mixture R is continuously diluted with mixture S,

the mixture composition will move closer and closer to point S along a straight line (as indicated by the arrow in Figure 6). Eventually, at infinite dilution, the mixture composition will be at point S.

3. For systems with composition points that fall on a straight line that passes through an apex corresponding to one pure component, the other two components are present in a fixed molar ratio along the entire length of the line. This is shown by the air line on Figure 5, where the ratio of oxygen to nitrogen is always constant.

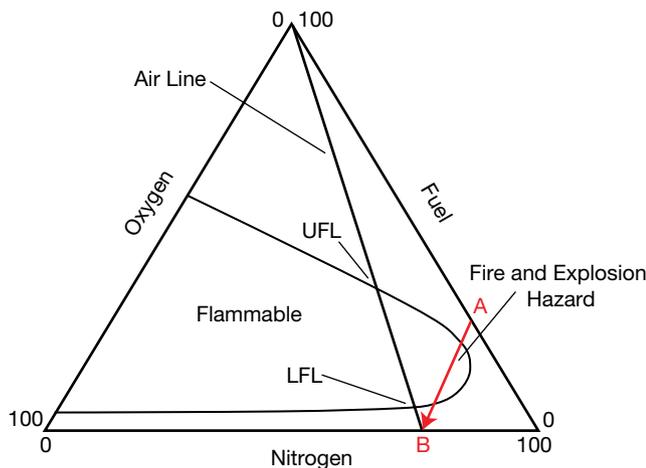
### Using the triangle flammability diagram

*Example 1.* A vessel contains methane gas under pressure. In preparation for a vessel-entry procedure, the engineers must remove the methane from the vessel and replace it with air in a way that does not produce a flammable mixture.

Figure 7 depicts what would occur if the vessel is opened, depressurized, and filled with air. The gas composition in the vessel has an initial value of 100% methane (point A), and then follows the air line until it reaches pure air (point B). This procedure creates a flammable mixture — as indicated by the concentration line entering the flammability zone — and poses a fire and explosion hazard.

Figure 8 is the triangle diagram for a procedure that removes the methane without forming a flammable mixture, avoiding the flammability zone. Starting with pure methane at point A, nitrogen is introduced into the vessel until the composition reaches point B. Then, air is added until the composition reaches point C. This procedure avoids the flammability zone. Equations are available to estimate the concentration at point B (3).

A similar procedure can be used before placing the



▲ **Figure 9.** Fuel vapors in a vessel that is inerted with nitrogen may become flammable when they escape and mix with air.

vessel back into service. In this case, the vessel initially contains 100% air (point C). The first step is to add nitrogen into the tank, shifting the concentration along the nitrogen axis to the right, eventually reaching point D. At point D, fuel can now be added following the blue line to point A, which is pure methane. This avoids the flammability zone.

*Example 2.* A storage vessel containing a fuel is inerted with pure nitrogen (*i.e.*, no oxygen is present in the vapor). A common misconception is that vapors in a storage vessel that have been inerted with nitrogen will not become flammable when the vapor escapes the vessel.

Figure 9 shows what happens when vapor escapes from an inerted vessel. Point A represents the vapor composition in the vapor space of the vessel, and point B represents pure air. The vapor space composition moves from point A to point B as vapor escapes and mixes with air — passing through the flammability zone. The use of an inert gas, such as nitrogen, carbon dioxide, or others, is a convenient way to control vapor concentrations to prevent flammable atmospheres. More details on inerting and purging methods are provided elsewhere (3).

### Wrapping up

Flammable materials have been used and handled for a long time, and a reasonable amount of data, mostly at room temperature and pressure for pure species, are available. Despite this, the fundamental basis for the properties that characterize flammable materials is not well understood and the effects of temperature, pressure, and composition on these properties cannot be adequately predicted. A better fundamental understanding would reduce the requirements for costly experimentation to obtain data, and result in an even better capability to handle these materials safely. **CEP**

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