

Hydrocarbon Fuels and their Properties

There are important properties of hydrocarbon fuels that need to be understood and considered to improve safety in upstream oil and gas operations. These include:

Flammability Limits

Auto-ignition Temperature

Minimum Ignition Energy

Other Considerations

The possible types of explosions and the effects of explosive overpressures also need to be taken into account.

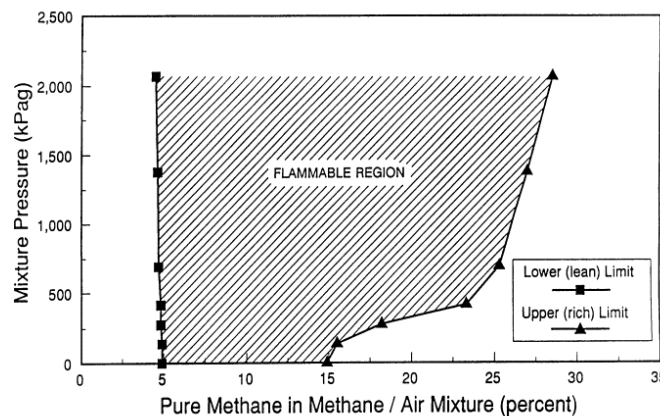
Types of Explosions

Explosive Overpressures

Flammability Limits

The upper (rich) and lower (lean) flammability limits define the range of concentrations of a gas or vapour in air that can be ignited and sustain combustion. Any composition outside of these limits cannot be ignited. The lower flammability limit decreases slightly as pressure is increased. However, the upper flammability limit can increase substantially as pressure increases.

The graph below shows the effect of pressure on the flammability range of methane in air. While these trends are consistent for all hydrocarbons, each fuel has a different flammability range.



**Effect of Pressure on Flammability Limits of a Methane/Air Mixture
for Upward Flame Propagation [10]**

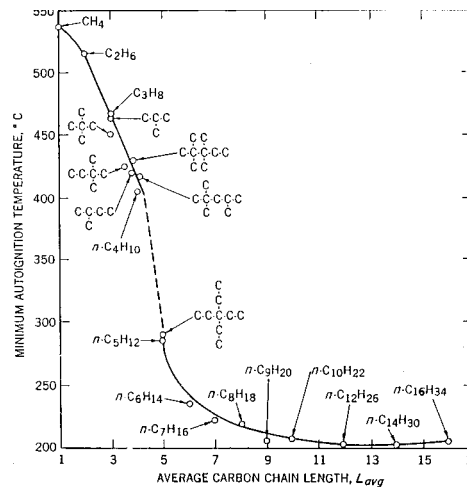
Other factors that widen the flammability range include:

- Increased temperatures
- Increased energy of the ignition source

- If pure oxygen, instead of air, mixes with a hydrocarbon
Moisture and other contaminants will also affect the flammability range.

Auto-ignition Temperature

A fuel - air mixture can ignite without the introduction of an ignition source. The minimum auto-ignition temperature is the lowest temperature at which the fuel vapours spontaneously ignite. Hydrocarbons that have been heated can ignite if they are exposed to air. The figure below shows the auto-ignition temperatures of hydrocarbons at atmospheric pressure.



Minimum Auto-ignition Temperature of Hydrocarbons [14]

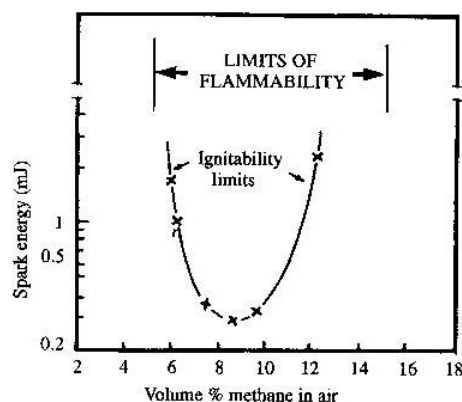
Methane has the highest auto-ignition temperature. As the number of carbon atoms in the hydrocarbon increases, the auto-ignition temperature decreases. In other words, heavier hydrocarbons tend to auto-ignite before lighter hydrocarbons. Increased pressures can also reduce the auto-ignition temperature.

Minimum Ignition Energy

The minimum amount of energy supplied that is needed for combustion is the minimum ignition energy. Every different fuel – air mixture will have different minimum ignition energies. Factors that affect the minimum ignition energy are:

- The temperature
- The total energy supplied
- The rate at which energy is supplied, or time period over which it is delivered
- The area over which energy is delivered

The minimum ignition energy values are usually given as the energy required to ignite the most reactive mixture of fuel and air. A flammable mixture that is close to either the upper or lower limits may require a higher amount of energy than the minimum ignition energy to ignite as shown in the figure below.



Ignitability limits of flammability for methane/air mixtures at atmospheric pressure and 26°C [13]

Other Relevant Hydrocarbon Considerations

With the exception of a few reactive or unstable substances, liquids do not ignite. It is the vapours given off from the surface of the liquids that ignite. Liquids will give off vapours at a rate that is proportional to their temperature. The ability to give off vapours and the rate at which this occurs defines the volatility of the liquid.

The flash point of a liquid is defined as the lowest temperature at which that liquid gives off vapours at a sufficient rate to support a momentary flame across its surface. The flash point is also related to the vapour pressure of the liquid. A low vapour pressure corresponds to a high flash point, and a high vapour pressure corresponds to a low flash point. [16] **It is important to remember that flash points are measured at atmospheric pressure; if the pressure is higher, the information relevant at atmospheric pressure is no longer accurate.**

The flash point should only be used as an approximate reference because the liquid may behave differently in the field than in laboratory tests performed to determine flash points. It is possible for an explosive atmosphere to exist even if the temperature of the environment is below the flash point of the liquid. The auto-ignition temperature for the liquid vapours is similar to that of gases.

A very fine mist from a hydrocarbon liquid may act as a pure gaseous substance. These aerosols may become an explosive mixture at temperatures that are far below the liquid's flash point. The droplets have to become vapourized but because of the small volume of the drops the energy required to do this is lowered significantly.

Specialized hydrocarbon fluids such as 'frac' fluids or 'lean oils' used in processing facilities readily absorb other hydrocarbons. Their properties will, therefore, change dramatically when they come in contact with other hydrocarbons such as formation fluids. As a result, the potential hazards associated with these fluids may be altered significantly. Any fluid being reused must be tested to confirm that its properties are still appropriate for the intended use.

The chemicals and hydrocarbon-based liquids typically used by the oil and gas industry also have the potential for creating explosive mixtures including:

- Chemicals used for well servicing and stimulations
- Solvents and cleaning agents
- Specially formulated hydraulic fluids and lubricants

In unique circumstances, some ‘solids’ used by the oil and gas industry may create explosive mixtures. As the solid is heated it can undergo pyrolysis, a chemical degrading that occurs resulting in a release of vapours. The vapours released have the ability to form an explosive atmosphere and can ignite. These solids can include:

- Lubricants
- Sealants
- Packings, “O” rings, diaphragms and valve seats
- Paints and Coatings

Types of Explosions

“An explosion is a rapid transformation of potential physical or chemical energy into mechanical energy and involves the expansion of gases [1:494].” Explosions are classified as follows:

Physical explosions occur, for example, when vessels are pressurized beyond their limits and rupture. A flammable vapour-air mixture explosion is an example of this. When a liquid contained in a vessel is heated above its atmospheric boiling point a BLEVE, or boiling liquid expanding vapour explosion, can occur. A BLEVE involves shock waves, a fireball, flying vessel fragments, and powerful heat radiation [2].

Chemical explosions are due to reactions between chemical species. Chemical explosions are more violent at or near the *stoichiometric* levels. A methane/oxygen is stoichiometric when the molar ratios are $1\text{CH}_4 + 2\text{O}_2 \rightarrow 1\text{CO}_2 + 2\text{H}_2\text{O}$. For every one molecule of methane the reaction requires two molecules of oxygen to be in a stoichiometric proportion.

A chemical explosion within a tank may induce a physical explosion if the pressure increase is sufficient.

Explosions are also characterized by the speed at which the flame front travels. A *deflagration* is defined as “a combustion reaction in which the velocity of the reaction front through the unreacted fuel medium is less than the speed of sound [3:1.3.31]”. Because the velocity is lower than the speed of sound, shock waves are not formed.

Detonations differ from deflagrations in that the velocity of the flame front in a detonation is equal to or greater than the speed of sound. Shock waves are formed, and they help to maintain the reaction [1]. Detonations can travel in any direction, and, when occurring in a pipe, are not impeded or restricted by the direction of the gas flow [4]. In a

closed vessel, peak pressure due to a detonation can range up to 18 to 30 times the initial pressure depending on stoichiometry of the fuel/oxidant mixture.

Explosive Overpressures

The overpressure created during an explosion depends on the ability of the flame front to accelerate and achieve high speeds. Obstacles, equipment, and congestion cause the flame to accelerate [1; 3; 5; 6; 7]. Turbulence formed by obstacles creates a positive feedback process; turbulence increases the flame speed, and as the flame moves faster, more intense turbulence is generated [6].

The rate at which a flame front moves through a stationary flammable mixture is known as its burning velocity. Higher burning velocities result in the generation of overpressures. Air-hydrocarbon mixtures have a maximum burning velocity when the concentration of fuel is slightly above stoichiometric. [3; 5]

Ignition location, ignition strength, fuel type, and fuel concentration are important parameters that influence the severity of explosions [5]. If a vapour cloud is ignited at its end, the flame front has the entire length of the cloud to accelerate. If ignition takes place in the middle of the cloud, the flame fronts have only half the distance to accelerate in both directions. Therefore, the areas that are affected by the greatest overpressure can be a considerable distance away from where the substance was released and ignited [7]. Unconfined vapour cloud explosions can produce damaging overpressures when large amounts of fuel are involved [3]. In contrast, an explosion in a confined volume results in a large rise in pressure because of the high temperature of the combustion products and the restricted ability of gases to expand. [5].

A study concerning gas explosions in closed vessels found that the maximum pressure generated was not dependent on the vessel size or shape. Furthermore, the rate of pressure rise decreased as the vessel size increased, and the rate of pressure rise increased when turbulence was initially present. Changes in initial pressure produced proportional changes in the maximum pressure generated and the rate of pressure rise. [8]

When the rate of pressure rise in an explosion is relatively slow, pushing or bulging types of damage effects will be produced. When the rate of pressure rise is rapid, it is more likely for confining vessels or containers to shatter. Shrapnel and debris will be thrown vast distances. [3]