

**THE EFFECT OF NITROGEN DILUTION ON FLAMMABILITY LIMITS OF  
LPG**

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## ABSTRACT

Many manufacturing processes involve in handling of flammable chemicals, and an accident involving a fire or explosion can occur in storage or process equipment if a flammable chemical exist inside it or if a loss of containment of flammable chemicals occurs. The aims of this study are to determine the flammability limits of LPG/ air mixture and to investigate the effect of nitrogen dilution on flammability limits of LPG/ air mixture at atmospheric pressure and ambient temperature. The experiments were performed in a 20 L closed explosion vessel. The mixtures were ignited by using spark permanent wire that placed at the centre of the vessel. The explosion pressure data is used to determine the flammability limits which flame propagation is considered occurred if explosion pressure greater than 0.1 bar. In this study, the result shows the flammability limits of LPG is from 2 % volume to 6 % volume of LPG and have revealed that the addition of nitrogen in LPG/air mixture reduce the upper flammability limit initially 6 % volume to 5 % volume of LPG.

## ABSTRAK

Kebanyakan proses pembuatan melibatkan bahan kimia yang mudah terbakar, dan kemalangan yang melibatkan kebakaran atau letupan boleh berlaku di dalam simpanan atau alat pemprosesan jika terdapat bahan kimia yang mudah terbakar. Objektif penyelidikan ini adalah untuk menentukan had pembakaran campuran LPG/udara dan juga untuk mengkaji kesan penambahan nitrogen ke atas had pembakaran campuran LPG/udara pada tekanan atmosfera dan suhu bilik. Eksperimen ini telah dijalankan di dalam bekas letupan tertutup yang berisipadu 20 L. Campuran LPG/udara dicucuh dengan wayar percikan tetap yang terletak di tengah bekas letupan. Data tekanan letupan digunakan untuk menentukan had pembakaran dimana pergerakan nyalaan dianggap berlaku sekiranya tekanan letupan lebih daripada 0.1 bar. Dalam penyelidikan ini, keputusan menunjukkan had pembakaran bagi campuran LPG/udara adalah daripada 2 % isipadu kepada 6 % isipadu LPG dan juga menunjukkan bahawa penambahan nitrogen ke dalam pembakaran LPG dan udara mengurangkan had pembakaran atas daripada 6 % isipadu kepada 5 % isipadu LPG.

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**LIST OF ABBREVIATIONS**

LOC	: Limiting Oxygen Concentration
BLEVE	: Boiling Liquid Expanding Vapor Explosion.
LPG	: Liquefied Petroleum Gas.
LFL	: Lower Flammability Limit.
UFL	: Upper Flammability Limit.
$P_{exp}$	: Explosion Pressure.
$P_{max}$	: Maximum Explosion Pressure.
$\Theta_{exp}$	: Explosion time.
IE	: Ignition Energy.
$P_{ci}$	: Pressure Due to Chemical Igniter.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

The 20<sup>th</sup> century has seen rapid increase of population and explosive growth in energy consumption. As more countries becoming industrialized, it is expected that more factories will be developed. Most of the factories that exist today are exposed to explosion accidents. The danger of explosion is difficult to avoid in processes where combustible chemicals are handled.

Many manufacturing processes involve flammable chemicals, and an accident involving a fire or an explosion can occur in storage or process equipment if a flammable chemical exist inside it or if a loss of containment of flammable chemicals occurs.

Because the gas mixture of a flammable substance could be ignited only if the concentration of the flammable substance lied within a given range known as the flammability limits, the flammability limits are one of the important features in the development of safe practices for handling a flammable vapor or gas.

Industry works with mixtures under many situations, for example, in a reactor or in a distillation column. For this reason, they constitute a crucial issue in research on processing and storing flammable chemicals safely.

## 1.2 Problem Statement

With the rapid increase of factories development, the explosion accident regarding to flammable chemical has been seen to be one of the most serious accidents that occur nowadays. This accidental explosion has been causing many serious damages in the industries. There were a lot of serious explosion that already occur and killed many peoples.

Most of combustible chemical can cause explosion when they are mixed with an oxidant like  $O_2$  and then ignite with an energy source such as electrical source. We can find a lot of these flammable chemicals in the Chemical Engineering Industries (natural gas storage and LPG storage for example). An explosion per day occurs as an average in France (**Petit, 1998**).

However, complex mixtures composed of flammable gases and nonflammable gases are also formed in process industries, for example, the inerting procedure. Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen below the limiting oxygen concentration (LOC) for the purpose of lowering the likelihood of explosion. In process industries, the inert gas is usually nitrogen or carbon dioxide, although sometimes steam may be used.

For a combustion process to occur, some oxidant is required. This is normally the oxygen in air but other oxidants such as chlorine or nitrogen dioxide may support combustion. Safety can be achieved by reducing the concentration below a level that will no longer support combustion with the addition of an inert gas. This is known as

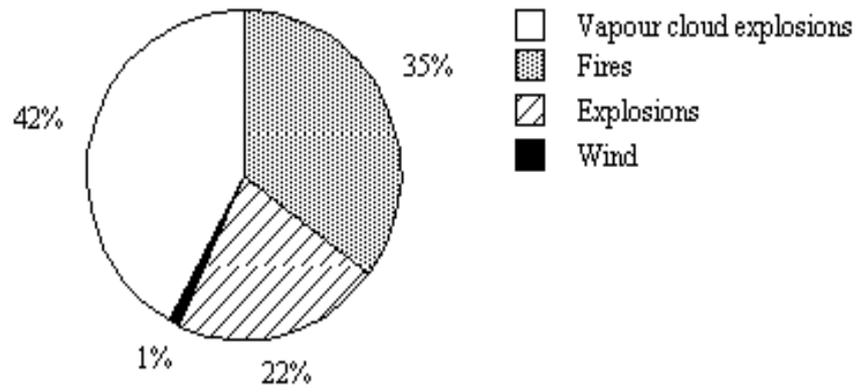
inerting process. Nitrogen gas is the most commonly used inert gas; however, argon and carbon dioxide can also be used.

The concentration of oxygen in air at which the atmosphere will no longer support combustion known as the Limiting Oxygen Concentration (LOC) for combustion. LOC values vary depending on the material involved and the inert gas used. LOC test is usually performed in the 20-liter sphere vessel. **(Ebadat, 2002)**

The inert atmosphere will need to be established before flammable atmospheres are present and should be maintained throughout the process. Once the inert atmosphere has been established the ingress of air should be prevented.

According to figure 1.1, we can see that, there are several types of losses regarding on explosion. When we look into the details of the individual accidental explosions that have happened, we will find a large variety in size of the explosion and loss experience. From accidental records we can learn that gas explosions have a tendency to repeat themselves in similar conditions. It is therefore important to investigate accidents, report the findings in open literature and take corrective actions.

Garrison (1988), has reviewed the hundred largest losses in the hydrocarbon process industry, from 1957 to 1986. He found that 42 % of these accidents were caused by vapor cloud explosions. In his classification vapor cloud explosions include gas explosions within buildings as well as outdoors (unconfined explosions). Events classified as explosions constitute 22 %. These explosions are probably run-away reactions, explosions in solids, BLEVE's, loss of containment, and gas explosions internally in process equipment. **(Garrison, 1988)**



**Figure 1.1:** Distribution of types of loss for the 100 largest losses in the hydrocarbon process industry from 1957 to 1986. (Garrison, 1988)

**Table 1.1:** Accidents that occur due to gas explosion. (Dr. Ingar O. Moen, 1986)

Place	Killed	Injured	Cause
Nypro plant at Flixborough on June 1, 1974	28	36	A release of about 50 tons of cyclohexane, probably due to failure of a temporary pipe. The flammable cloud was ignited about 1 minute or so after the release. A very violent explosion occurred.
On March 3, 1983 there was a hydrogen explosion in an open street in Stockholm	-	16	The event occurred when gas cylinders were unloaded from a lorry and hydrogen suddenly started to leak out. The hydrogen was stored in a bank of 18 cylinders which contained about 10 kg. of hydrogen. The blast wave from the explosion broke windows in a range of about 90 meters.
Piper Alpha is the "Flixborough accident" in the off-shore industry.	167	-	At Piper Alpha a rather small gas explosion in a compressor module caused fires which subsequently resulted in rupture of the riser.
The incident at Rafnes, Norway, in 1988	-	-	Known as a large fire. The persons sitting in the blast resistant control room felt that the whole building was shaking.
Port Hudson, Missouri, 1970	-	-	In this incident, liquid propane was released from a pipeline. The gas cloud flowed into a valley and about 20 min after the release started, the gas cloud exploded violently.

### **1.3 Objectives of Study**

The objectives of this study are:

1. To determine the flammability limits of premixed gas – air mixture in a gas fire explosion at atmospheric pressure and ambient temperature.
2. To study the effect of Nitrogen dilution on flammability limit of LPG.

### **1.4 Scope of Study**

This study is conducted to determine the effect of nitrogen dilution on flammability limit of LPG in a constant volume spherical vessel with a volume of 20 L by using conventional spark ignition system which is located at the centre of the vessel.

In this study, the study of the flammability limit will concentrate on the effect when nitrogen gas was added. The experiment will be run in constant pressure and temperature. The performance will be analyzed by comparing and analyzing the explosion that occurs from the various percent volume of nitrogen.

In this study, Liquefied Petroleum Gas (LPG) will be used as the fuel. The experiment was run four times with different volume of nitrogen. The Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) of LPG – air (normal nitrogen/oxygen ratio) were determined at concentration from 2 % volume to 6 % volume.

## 1.5 Significant of Study

In this study, the effect of nitrogen dilution in conventional combustion of LPG was investigated. Addition of nitrogen is said can reduce the flammability limit of LPG-air mixture.

It is significant to determine the leaner flammability limit of LPG since the concerns about safety in LPG storage and lack of fossil fuels have become increasingly greater these days.

Inerting process, which is adding an inert gas to a combustible mixture, can reduce the concentration of oxygen for the purpose of lowering the likelihood explosion. The characteristics of nitrogen which are inert gas can reduce the concentration of oxygen in air by dilute it into the mixture.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Explosion

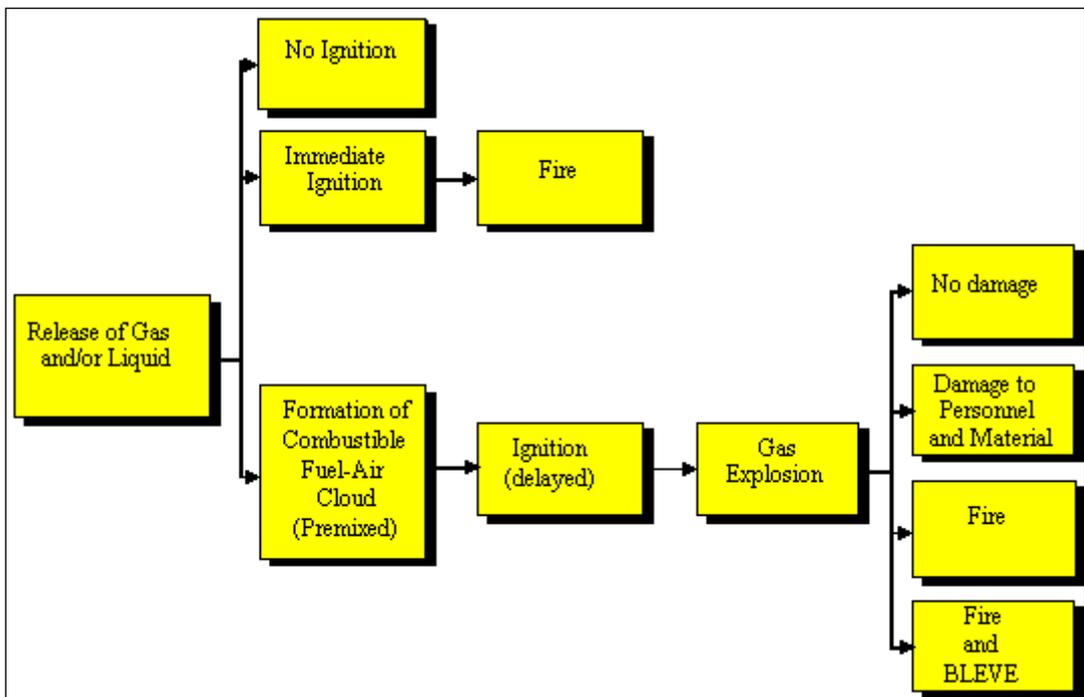
An explosion is a rapid increase in volume and release of energy in an extreme manner, usually with the generation of high temperatures and the release of gases. An explosion creates a shock wave. If the shock wave is a supersonic detonation, then the source of the blast is called a "high explosive". Subsonic shock waves are created by low explosives through the slower burning process known as deflagration.

An explosion is a chemical reaction or change of state affected in an exceedingly short period of time with the generation of a high temperature and generally a large quantity of gas. An explosion produces a shock wave in the surrounding medium. **(Rudolf Meyer, 2002)**

We define an explosion as an event leading to a rapid increase of pressure. This pressure increase can be caused by: nuclear reactions, loss of containment in high pressure vessels, high explosives, metal water vapor explosions, run-a-way reactions, and combustion of dust, mist or gas (incl. vapors) in air or in other oxidizers. **(Anon., 1975)**

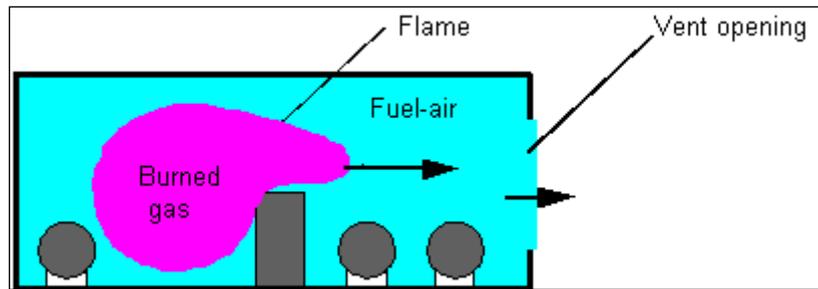
We define a gas explosion as a process where combustion of a premixed gas cloud, i.e. fuel-air or fuel/oxidizer is causing rapid increase of pressure. Gas explosions can occur inside process equipment or pipes, in buildings or off-shore modules, in open process areas or in unconfined areas. **(Dr. Ingar O. Moen, 1986)**

When we are talking about a gas explosion as an event, it is a more general term. It is then common to include the events both before and after the gas explosion process, see the figure 2.1 below.



**Figure 2.1:** An event tree showing typical consequences of accidental releases of combustible gas or evaporating liquid into the atmosphere.

**(Experimental Study of Fire and Gas Explosion Characteristic Properties)**



**Figure 2.2:** Gas explosion in a partly confined area with process equipment. (Dr. Ingar O. Moen, 1986)

Figure 2.1 and figure 2.2 show what can happen if combustible gas or evaporating liquid is accidentally released into the atmosphere. If the gas cloud, formed from the release, is not within the flammability limits or if the ignition source is lacking, the gas cloud may be diluted and disappear. Ignition may occur immediately, or may be delayed by up to tens of minutes, all depending on the circumstances. In case of an immediate ignition (i.e. before mixing with air or oxidizer has occurred) a fire will occur.

The consequences of a gas explosion will depend on:

- type of fuel and oxidizer
- size and fuel concentration of the combustible cloud
- location of ignition point
- strength of ignition source
- size, location and type of explosion vent areas
- location and size of structural elements and equipment
- mitigation schemes

Gas explosions may be very sensitive to changes in these factors. Therefore it is not a simple task to estimate the consequences of a gas explosion.

## 2.2 Characteristic of Nitrogen

Appearance colorless gas, liquid or solid of nitrogen



**Figure 2.3:** Appearance of nitrogen.

**Table 2.1:** Characteristics of Nitrogen.

<b>General properties</b>	
Name, symbol, number	nitrogen, N, 7
Pronunciation	/ˈnɑːtrədʒɪn/, NYE-tro-jin
Element category	Nonmetal
Group, period, block	15, 2, p
Standard atomic weight	14.0067(2) g•mol <sup>-1</sup>
Electron configuration	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>
Electrons per shell	2, 5
<b>Physical properties</b>	
Phase	Gas
Density	(0 °C, 101.325 kPa) 1.251 g/L
Melting point	63.153 K, -210.00 ° C, -346.00 ° F
Boiling point	77.36 K, -195.79 ° C, -320.3342 ° F
Triple point	63.1526 K (-210°C), 12.53 kPa
Critical point	126.19 K, 3.3978 MPa
Heat of fusion	(N <sub>2</sub> ) 0.72 kJ•mol <sup>-1</sup>

Heat of vaporization	(N <sub>2</sub> ) 5.56 kJ•mol <sup>-1</sup>					
Specific heat capacity	(25 °C) (N <sub>2</sub> ) 29.124 J•mol <sup>-1</sup> •K <sup>-1</sup>					
<b>Vapor pressure</b>						
<i>P</i> /Pa	1	10	100	1 k	10 k	100 k
at <i>T</i> /K	37	41	46	53	62	77
<b>Atomic properties</b>						
Oxidation states	5, 4, 3, 2, 1, -1, -2, -3 (strongly acidic oxide)					
Electronegativity	3.04 (Pauling scale)					
Ionization energies	1st: 1402.3 kJ•mol <sup>-1</sup> 2nd: 2856 kJ•mol <sup>-1</sup> 3rd: 4578.1 kJ•mol <sup>-1</sup>					

### 2.2.1 Nitrogen as an Inert Gas

In chemistry, the term inert is used to describe something that is not chemically active. The noble gases were described as being inert because they did not react with the other elements or themselves. It is now understood that the reason that inert gases are completely inert to basic chemical reactions (such as combustion, for example) is that their outer valence shell is completely filled with electrons. With a filled outer valence shell, an inert atom is not easily able to acquire or lose an electron, and is therefore not able to participate in any chemical reactions. For inert substances, a lot of energy is required before they can combine with other elements to form compounds. High temperatures and pressure are usually necessary, sometimes requiring the presence of a catalyst.

Elemental nitrogen is inert under standard room conditions and exists as a diatomic molecule, N<sub>2</sub>. The inertness of nitrogen is due to the presence of the very strong triple covalent bond in the N<sub>2</sub> molecule; nitrogen gas can, however, react to

form compounds such as lithium nitride ( $\text{Li}_3\text{N}$ ) under standard conditions. Inert atmospheres of gases such as nitrogen and argon are routinely used in chemical reactions where air sensitive and water sensitive compounds are handled.

### 2.3 Characteristics of LPG

LPG stands for “Liquefied Petroleum Gas”. The name describes a family of light hydrocarbon gases called "Natural Gas Liquids" (NGLs): Propane ( $\text{C}_3\text{H}_8$ ) and Butane ( $\text{C}_4\text{H}_{10}$ ) which exists as vapors under ambient conditions of temperature and pressure. LPG at normal temperature and pressure is a gas. It changes to a liquid when subjected to modest pressure or cooling.

**Table 2.2:** Characteristics of LPG

	<b>Commercial Butane</b>	<b>Commercial Propane</b>
Formula	$\text{C}_4\text{H}_{10}$	$\text{C}_3\text{H}_8$
Boiling point at 1.013 bars, °C	-0.5	-42
Relative density of liquid at 15.6 °C (Water = 1.00)	2.07	1.55
Relative density of gas (air = 1.00) at 1.013 bars at 15.6 °C	0.584	0.508
Volume of gas (liters) per kg of liquid at 15.6 °C and 1.013 bars	406 to 431	537 to 543
Liter/tonne at 15.6 °C	1 723 to 1 760	1 965 to 2 019
Ratio of gas volume to liquid volume at 15.6 °C	233	274
Vapor pressure for products at their maximum specified vapor pressure (gauge): Temperature °C	Bar	Bar
-40	*	0,5
-18	0,9	2,3
		4,5

0	1,93	6,9
15	4,83	14,5
38	5,86	17,6
45		
Sulphur content - % weight	Negligible to 0.02	Negligible to 0.02
Limits of flammability (percentage by volume of gas in a gas-air mixture to form a combustible mixture)	Upper 9.0 Lower 1.8	Upper 10.0 Lower 2.2
Calorific Values:		
Gross:		
(MJ/m <sup>3</sup> ) dry	121.8	93.1
(Btu/ft <sup>3</sup> ) dry	3 270	2 500
(MJ/kg)	49.3	50.0
(Btu/lb)	21 200	21 500
Nett:		
(MJ/m <sup>3</sup> ) dry	112.9	86.1
(Btu/ft <sup>3</sup> ) dry	3 030	2 310
(MJ/kg)	45.8	46.3
(Btu/lb)	19 700	19 900
Air required for combustion (m <sup>3</sup> to burn 1 m <sup>3</sup> of gas)	30	24

Note: LP Gas itself is odorless and colorless. To enable leaks to be detected an odorant usually Tetra Hydro Thiophane or Ethyl Mercaptan is added at a concentration of 20 ppm giving LP Gas its characteristic smell. (**National Gas Company, 2008**)

## 2.4 Flammability Limits

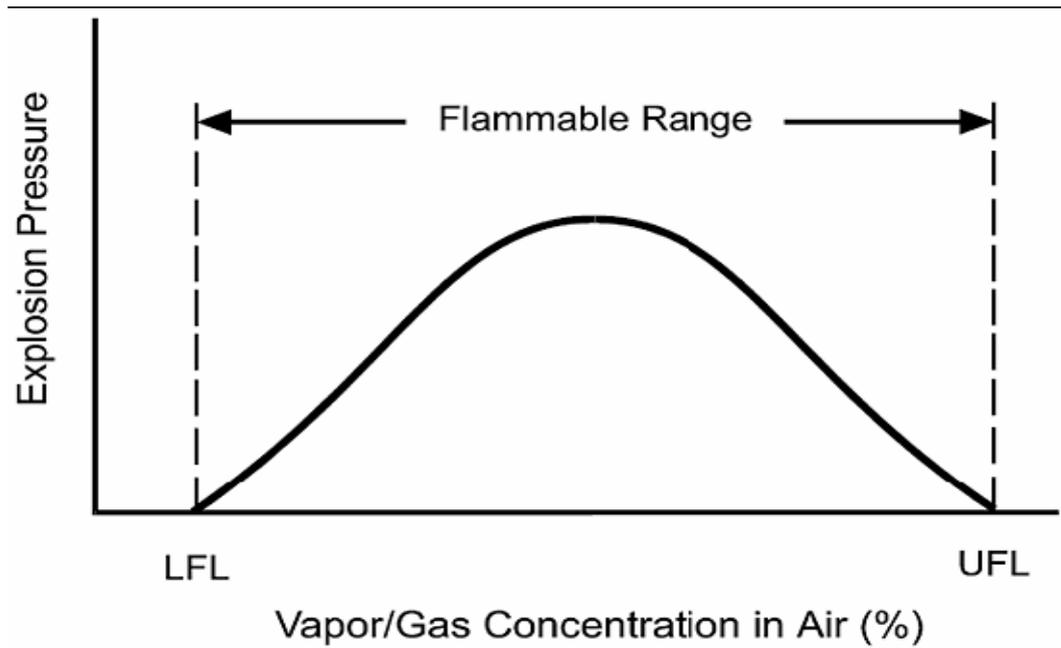
Knowledge of the flammability limits of gaseous mixtures is important for the safe and economic operation of many industrial and domestic applications that produce or use flammable mixtures.

Flammable limits apply generally to vapors and are defined as the concentration range in which a flammable substance can produce a fire or explosion when an ignition source (such as a spark or open flame) is present. The concentration is generally expressed as percent fuel by volume. When the combustion of the fuel is not controlled within the confines of a burner system, the limits of flammability can be called the explosive limits.

There are two distinct separate flammability limits for a mixture which are lean limit or lower flammability limit (LFL) and rich limit or upper flammability limit (UFL).

- i. Above the upper flammable limit (UFL) the mixture of substance and air is too rich in fuel (deficient in oxygen) to burn. This is sometimes called the upper explosive limit (UEL).
- ii. Below the lower flammable limit (LFL) the mixture of substance and air lacks sufficient fuel (substance) to burn. This is sometimes called the lower explosive limit (LEL).

In other words, combustion or explosion will take place and be self-sustaining only if fuel and air are mixed within the upper and lower flammability limits.



**Figure 2.4:** Schematic represents flammability limits.

It is now acknowledged that flammability limits are physical–chemical parameters of flammable gases and vapors of flammable liquids, which are related to many factors including the heat losses from the flame by conduction, convection and radiation to the apparatus walls, instabilities in the flame front resulting from buoyant convection, selective diffusion and flame stretch, as well as radical loss or their generation on apparatus walls. (**Karl S. Willson, 1984**)