THE EFFECT OF NITROGEN DILUTION AND HYDROGEN ENRICHMENT ON THE EXPLOSIVE LIMITS OF LIQUEFIED PETROLEUM GAS (LPG)

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ABSTRACT

The aims of this study are to determine the explosive limits of LPG/ air and to investigate the effect on explosive limits of LPG/ air when addition of hydrogen and dilution of nitrogen at atmospheric pressure and ambient temperature. The purpose of diluting with nitrogen is to control the explosive limits range of LPG because hydrogen will extend the explosive limits of LPG. This is for safety to avoid the LPG become very flammable fuel but at the same time to get the best performance of fuel mixing. The experiments were performed in a 20 L closed explosion vessel. The mixtures were ignited by using a spark permanent wire that placed at the centre of the vessel. The pressure-time variations during explosions of LPG/air mixtures in explosion vessel were recorded. The explosion pressure data is used to determine the explosive limits which flame propagation is considered occurred if explosion pressure greater than 0.1 bar. From the explosion pressure data, the maximum explosion pressure is determined also. In this study, the result shows the explosive limits of LPG is from 2 vol% to 8 vol % of LPG. The addition of 2 and 8 vol% hydrogen in 7 vol% nitrogen reduce the lower explosive limit(LEL) initially 1 vol% to 0 vol% of LPG/air mixture. For safety aspect, the addition too much hydrogen seems very dangerous for application because the mixture is in very flammable condition. The dilution nitrogen seems not give effect in controlling the explosive limits in this case.

ABSTRAK

Tujuan penyelidikan ini adalah untuk menentukan had pembakaran campuran LPG/udara dan menkaji kesan terhadap had pembakaran campuran LPG/udara apabila ditambah hidrogen dan nitrogen pada tekanan atmosfera dan suhu bilik. Tujuan penambahan nitrogen adalah untuk mengawal had pembakaran LPG kerana penambahan hidrogen akan meluaskan had pembakaran LPG. Ini adalah untuk tujuan keselamatan untuk mengelakkan LPG menjadi terlalu mudah terbakar dan dalam masa yang sama mendapatkan campuran bahan api untuk prestasi terbaik. 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. Dari data tekanan letupan juga, tekanan letupan tertinggi ditentukan. Dalam penyelidikan ini, keputusan menunjukkan had pembakaran bagi campuran LPG/udara adalah daripada 2 %isipadu kepada 8 %isipadu LPG. Penambahan 2 dan 8 %isipadu hidrogen dalam 7 %isipadu nitrogen mengurangkan had pembakaran bawah daripada 1 %isipadu kepada 0 %isipadu campuran LPG/udara. Untuk tujuan keselamatan, penambahan terlalu banyak hidrogen adalah merbahaya kerana campuran dalam keadaan yang terlalu mudah terbakar. Penambahan nitrogen tidak menunjukkan kesan ketara dalam mengawal had pembakaran dalam kes ini.

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LIST OF ABBREVIATIONS

NOx	-	nitrogen oxide
Vol%	-	volume percent
H_2	-	Hydrogen
N_2	-	Nitrogen
O_2	-	Oxygen
LPG	-	Liquefied Petroleum Gas
Pexp	-	explosion pressure
Pmax	-	Maximum explosion overpressure
LFL	-	Lower Flammability Limit
UFL	-	Upper Flammability Limit
LEL	-	Lower Explosive Limit
UEL	-	Upper Explosive Limit
J	-	Joule
L	-	Liter
IE	-	Ignition energy
t1	-	Combustion duration
FL_{mix}	-	vol. % flammability limit (lower or upper) of the mixture in air
$FL_{mix.dil}$	-	vol. % flammability limit of the combustibles containing diluent in air
y_1, y_2..y_i	-	vol.% of combustibles in the fuel mixture
l_1, l_2…l_i	-	vol. % flammability limit (lower or upper) of pure combustible in air
y_{dil}	-	vol.% of diluent in the fuel mixture

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

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. Flammability limits indicates the region of fuel–air mixture ratios within which flame propagation can be possible while outside that flame cannot propagate. 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) (Liao et. al, 2005). So that, combustion will take place only within the upper and lower flammability limits.

Explosion is the combustion of mixed combustible (gas cloud) causing rapid increase in pressure. When the combustion of the fuel is not controlled within the confines of the burner system, the limits of flammability is called explosive limits. It is important to analyze the explosive limits because of the safety reason and increase the efficiency in operation of much industrial and domestic application that uses the explosion concept.

In recent times, the premixed modes of fuel burning are gaining popularity due to stringent emission standard of government worldwide. As a result, the liquefied petroleum gas (LPG) is increasingly used not only in domestic sector but also in transport sector. But the safe use of LPG/air mixture is great concern for the successful utilization of LPG as viable fuel. Moreover, a situation in internal combustion engine, the LPG engine has lower power than a gasoline engine because the fuel is supplied into the cylinder in vapor. Thus, it is less economical and more harmful emission is exhausted than in gasoline engines. Due to that, it is necessary to optimize both of fuel supply system and the combustion characteristics in order to develop a low emission LPG engine (Lee et. al, 2004).

One of the effective methods to improve its lean operation is to add fuels with faster burning velocity. Hydrogen seems to be the best candidate, which is difficult to be used directly by transport engines due to the safety, storage and economics reason. With respect to the safety issues, dilution with inert gas like nitrogen is a common procedure to ensuring safety in use of flammable gas like hydrogen enrichment natural gas. Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of the oxygen below the limiting oxygen concentration for the purpose of lowering the likelihood of explosion. Knowledge of the explosion hazard of LPG is importance to ensure the safety in industrial and domestic applications that produce or use flammable mixture like natural gas. Nitrogen dilution to the fuels reduces the burning velocity remarkably by reducing the thermal diffusivity and flame temperature of the mixture (Tahtouh et. al, 2000).

1.2 Problem Statement

The environment problems caused by vehicle exhaust emission become more serious nowadays and because of that the exhaust gas emission and fuel economy standards become more severe. Thus, an alternative-fuel engine technology is needed to cope with the new requirement and regulation.

LPG is one of the best candidates for an alternative fuel among other clean fuel such as CNG, LNG, DME (dimethyl-ether). It is because it can be liquefied in a low pressure range of 0.7-0.8 MPa at atmospheric temperature and it has a sufficient supply infrastructure. Beside that, LPG fuel also has a higher heating value compared with the other fuel.

Moreover, a situation in internal combustion engine, the LPG engine has lower power than a gasoline engine because the fuel is supplied into the cylinder as a vapor. Thus, it is less economical and more harmful emission is exhausted than in gasoline engines. Due to that, it is necessary to optimize both of fuel supply system and the combustion characteristics in order to develop a low emission LPG engine (Lee et. al, 2004).

To increase the power, the hydrogen is added due to it has high flame speed, faster burning velocity, lower flammability limit and more reactive compare to LPG. Because of that, hydrogen enrichment LPG has faster burning velocity. So, for ensuring the safety in use of flammable gas like LPG/hydrogen/air mixtures, dilution with nitrogen is a better solution. The process can reduce the concentration of oxygen below the limiting oxygen concentration for the purpose of lowering the likelihood of explosion.

Next situation is internal combustion engine manufactures are faced with stricter anti-pollution regulations. An interesting way to reduce pollutant emissions is to work with lean or diluted mixtures. In this case, the mixture is diluted with nitrogen gas. Thanks to lean or diluted mixtures, combustion temperatures are decreased inducing lower NO_x emission according to the thermal Zeldovich mechanism (Halter et. al, 2007).

However, close to the lean flammability limits, the stability of the flame decreases and extinction phenomena may occur. A solution to control this phenomenon could be the addition of hydrogen to the mixture. It is because of the high reactivity of hydrogen, it may counterbalance the dilution effect. Moreover, its strong molecular diffusivity allows a better mixing inside the cylinder or inside the ducts, thus guaranteeing homogeneous mixtures.

1.3 Objectives

1. This study is to determine the explosive limits mixture of LPG-air in a combustion bomb at atmospheric pressure and ambient temperature.

2. To investigate the effect of nitrogen dilution and hydrogen enrichment on explosive limits of LPG-air mixture.

1.4 Scope of Study

A study of explosive limits mixture of fuel/air mixture is conducted 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 Liquefied Petroleum Gas (LPG) is used as the fuel. Then, the addition of hydrogen and dilution of nitrogen are added to investigate their effect. These gases are blend with the fuel.

The lower explosive limit (LEL) and upper explosive limit (UEL) of LPG-air mixture were determined at concentration from 1 vol% to 8 vol%. The parameter needs to be evaluated are hydrogen addition with concentration 2 vol% and 8 vol%. The addition of nitrogen is constant at 7 vol%.

1.5 Significant Of Study

In this study, the effect of dilution nitrogen and hydrogen enrichment in convectional combustion of LPG is investigated. Addition of hydrogen is said can extend the flammability limit of LPG-air mixture. Addition of hydrogen can increase the engine power. But, hydrogen enrichment in LPG is very easy to flame and explode if we do not take an action to control the hydrogen ratio. Dilution with inert gas like nitrogen is a common procedure to ensuring safety in use of flammable gas like LPG.

It is significant to know the effect when hydrogen and nitrogen are added to the LPG-air mixture for safety and performance aspects. By the well mixing the percentage of the fuel, high performance fuel plus the safety can be obtained.

CHAPTER 2

LITERATURE REVIEW

2.1 Explosion

An explosion is defined as a process whereby a pressure wave is generated in air by a rapid release of energy. This definition encompasses widely differing events ranging from the trivial example of a spark discharge through sudden release of stored energy in a compressed gas to the extreme of chemical detonations and nuclear explosions. Explosion can be measured by the explosion limits (Zalosh,2002)

Figure 2.1 shows the explosion pressure curve in order for the explosion to occur. The figure shows that at normal process pressure (1), explosion started to develop in the centre of ignition. By the end of the process which was estimated around pressure of 8 bar (3), the explosion is already at the final stage and it started to expand rapidly causes a blasting effect.

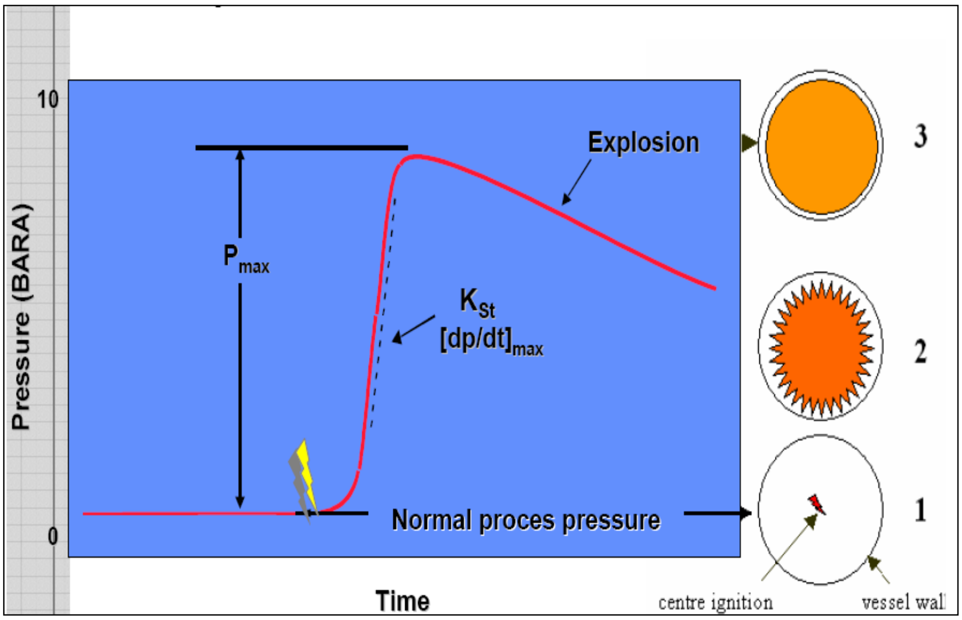

Figure 2.1: Explosion Pressure Curve (Raymondee, 2010)

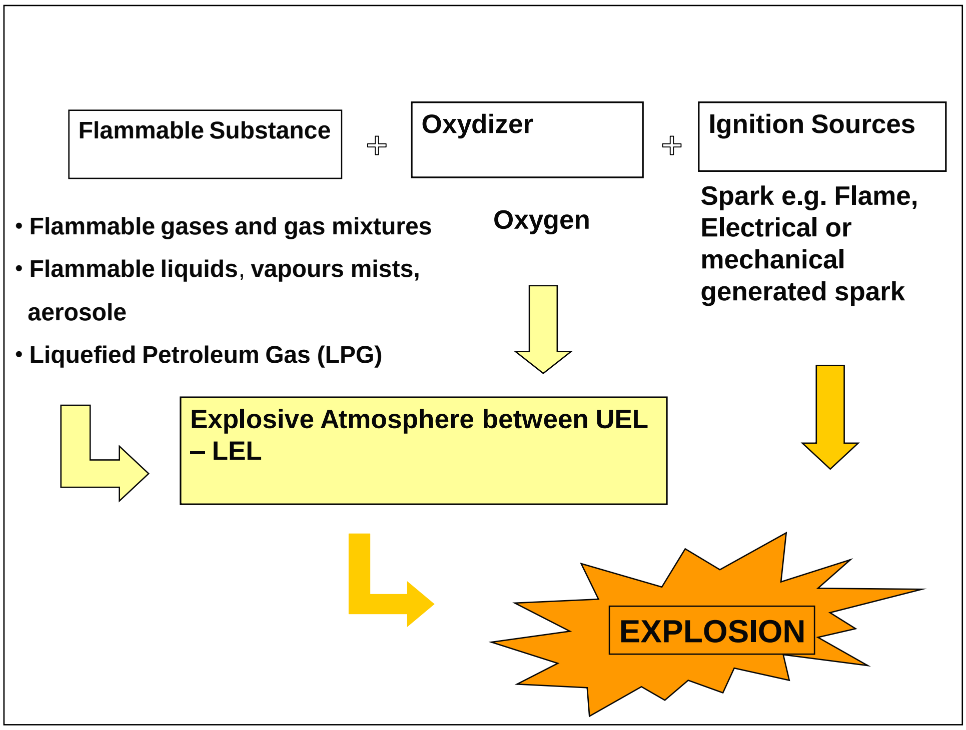

Figure 2.2: Characteristics of Explosion Event (Raymondee, 2010)

Figure 2.2 shows the characteristics of explosion event where in the presence of flammable substances, oxidizer and ignition sources, so that an explosion can occur. Without one of that, explosion cannot be occurring.

2.2 Flammability Limits/Explosive 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. 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 exists 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 sustance lied within a given range known as the flammability limits or explosive limits (Chen et. al, 2008).

There are two distinct separate flammability limits of a fuel/air mixture as shown in Figure 2.3. The lowest fuel lean mixture (rich of oxygen) up to which the flame can propagate is termed as lower flammability limits (LFL), while highest fuel rich mixture (lack of oxygen) is known as upper flammability limit (UFL). That means, below the LFL and above the UFL, the combustion is not possible. The limits are quoted either as percentage of fuel in the mixture or in terms of equivalence ratio. The information of these limits is very much required for prevention of explosive hazards (Mishra et. al, 2003).

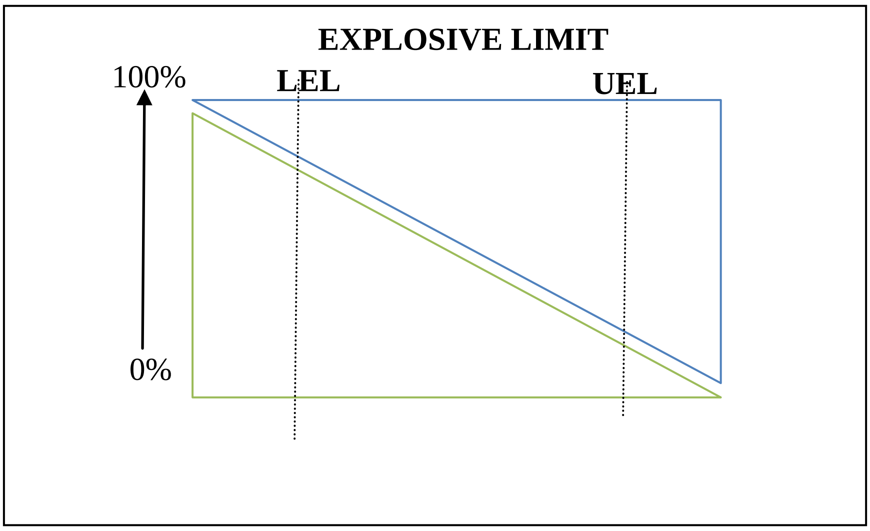

Figure 2.3: Diagram of explosive limits. (Andrew Furness,2007)

Flammability limits of mixtures of several combustible gases can be calculated using Equation 1 for combustibles without diluent and Equation 2 for combustible containing diluent.

$$FL_{mix} = \frac{100\%}{y_1/l_1 + y_2/l_2 + y_3/l_3 + \ldots\ldots.. y_i/l_i} \qquad \textbf{Equation 1}$$

Where,

FL_{mix}: vol. % flammability limit (lower or upper) of the mixture in air,
y_1, $y_2 \ldots y_i$: vol.% of combustibles in the fuel mixture,
l_1, $l_2 \ldots l_i$: vol. % flammability limit (lower or upper) of pure combustible in air.

$$FL_{mix,dil} = FL_{mix}\left(\frac{100}{100 - y_{dil}}\right) \qquad \textbf{Equation 2}$$

Where,

$FL_{mix.dil}$: vol. % flammability limit of the combustibles containing diluent in air,
FL_{mix}: vol. % flammability limit (lower or upper) of the pure combustibles in air,
y_{dil}: vol.% of diluent in the fuel mixture.

Table 2.1 shows the typical flammable range in air for methane, ethane, propane, butane, pentane, hexane, heptanes, LPG and heavier hydrocarbon as shown. In this table, lower explosive limit (LEL) and upper explosive limit (UEL) are given.

Table 2.1: Typical Flammable Range in Air

FUEL	**LEL(vol%)**	**UEL(vol%)**
Methane	5.0	15.0
Ethane	3.0	12.4
Propane	2.1	9.5
Butane	1.8	8.4
Pentane	1.4	7.8
Hexane	1.2	7.4
Heptane	1.05	6.7
Hexadecane	0.43	-
Paraffin	0.7	5.0
Ethylene	2.7	36.0
Hydrogen	4.0	75.0
Ammonia	15.0	28.0
LPG (30% Propane, 70% Butane)	2.0	10.0

2.3 Hydrogen Enrichment

Hydrogen gas is colourless, odourless, tasteless, non-toxic and undetectable for human senses. If released in a confined area, hydrogen can cause suffocation by dilution of the oxygen content. Gaseous hydrogen at its boiling point (20 K) is heavier than air. At a temperature > 22 K, it becomes buoyant and tends to rise in the ambient air.

In recent years, the addition of hydrogen to hydrocarbon-air mixtures has received considerable attention. Firstly and foremost, there is the introduction of hydrogen as an energy carrier to replace present-day fossil fuel energy carriers wherever possible. Secondly, hydrogen holds significant promise as supplemental fuel to improve the performance and emission of spark ignited and compression ignited engines. Next, the feasibility of NOx-reduction can be increased by operating at lower combustion temperatures (e.g. exhaust gas recirculation which relies on fuel-air dilution).

A major drawback of the latter is that the burning velocity is reduced and the flammability limit is approached so that the flame becomes less stable and more susceptible to extinction. One strategy to overcome these limitations is the addition of an amount of hydrogen because of its is high laminar burning velocity, low ignition energy and wide flammability limits (Tahtouh et. al, 2009). Hydrogen will burn at mixtures seven times leaner than gasoline and five times leaner than methane.

The wide flammability range of hydrogen enhances the lean burn capacity which would results in a low NOx emission level. The high burning velocity of hydrogen facilitates the constant volume combustion at top dead center and this may contribute to a relatively higher thermal efficiency. In addition, the low minimum ignition energy of initiation of hydrogen flame kernel could reduce the cycle by cycle variations.

However, one of the major problems associated with applying hydrogen is the combustion-induced disasters such as fires and explosion. The damages in fires are mainly caused by high heat flux from the flames and the toxic smoke from combustion. Explosion in confined spaces is a well recognized hazard due to the high explosion pressure and high rate of pressure rise (Tang et. al,2008).

2.4 Nitrogen Dilution

Nitrogen gas is colourless, odourless, tasteless, and mostly inert diatomic gas at standard condition, constituting 78.08% by volume of earth's atmosphere. Nitrogen dilution also can be called inerting process. In chemistry, the term inert is used to describe as being inert because they did not react with other elements or themselves. It appears that the potential of using partial inerting as an integral part of combined solutions to dust explosion protection has not been exploited in practice to the extent that one would perhaps anticipate. The purpose of the present paper is to draw further attention to the additional degree of freedom that this method offers. The essence of partial inerting is as follows: when the oxygen content of the atmosphere is reduced by mixing inert gas with the air, both the ignition sensitivity and the explosion violence of the dust cloud are reduced. In some cases, this can make it possible to implement one of the classical protective methods, i.e. full confinement, explosion venting, or automatic explosion suppression, and/or automatically triggered isolation systems, when this would otherwise have been unfeasible (Eckhoff et. al,2003).

In other words, the inert gas will reduce the concentration of oxygen below the limiting oxygen concentration (LOC). By reducing the oxygen concentration, it will narrow the flammability limits ranges of LPG. It is purpose of lowering the likelihood of explosion.

Other examples of inert gas that usually used in process inerting are carbon dioxide, steam and helium. The inert ability of these gases is different by each other. It depends on its mean molar heat capacity at the adiabatic temperature.

2.5 Liquefied Petroleum Gas (LPG)

LPG is odorless but a stench agent is added to assist in its detection in case of leakage. The odorant used in LPG is ethyl mercaptan, which possesses a distinctive and unpleasant odor. Ethyl mercaptan is selected because it is non-corrosive, has low sulphur content and possesses a boiling point very near that of LPG.

LPG is colorless whether in liquid or vapor form. The white cloud, which appears around a LPG leakage point, is not the product itself but chilled water vapor condensed from the surrounding air by the evaporating liquid or cooled vapors.

At ambient temperatures, LPG is highly volatile and flammable. Its vapor forms flammable and explosive mixtures with air. The vapor is heavier than air and can travel along the ground, into drains and conduits to a possible distant ignition source and can flash back explosively.

LPG consists almost entirely of carbon and hydrogen with negligible amounts of sulphur and other impurities. For practical purposes, therefore, stoichiometric air requirements and waste gas volumes can be determined by assuming complete combustion of the carbon and hydrogen contents.

LPG is a high performance fuel, but will only ignite if mixed with a quantity of air in roughly a gas:air ratio of between 1:50 and 1:10 (lower than the limits for mains gas). This low limit of flammability means that even small leaks could have serious results.

LPG is chemically reactive and will cause natural rubber and some plastics to deteriorate. Only equipment and fittings specifically designed for LPG should be used. Table 2.2 shows the physical and chemical properties of LPG from the Shell Company.

Table 2.2: Physical and chemical of LPG (Shell Company)

LPG	**Properties**
Form	Gas. May be liquefied by pressurization
Color	Colorless
Odor	Very faint petroleum odor 22,000 to 36,000 mg/m3
Specific gravity	0.5 @ 20ºC
Vapor density	1.55 (air = 1)
Vapor Pressure at ambient	500 kPa
Freezing point	-190^{o}C (-310^{o}F) (propane)
Boiling point	-40^{o}C to 80 ^{o}C (-40 to 176^{o}F)
Flash point	-104^{o}C (-156^{o}F)
Auto ignition	450^{o}C (842^{o}F)
Lower flammable limit	1.8% -1.9%
Upper flammable limit	9.5%
Hydrocarbon Composition (by Volume)	
Commercial Propane (C3H8)	30%
Commercial Butane (C4H10)	70%
Total Sulphur (stenched)	< 75 mg/kg
Calorific Value, gross	49.5 MJ/kg
Calorific Value, nett	45.7 MJ/kg

2.6 Experimental Methods

The standardized measurements of flammability limits are usually conducted in the flammability tubes or closed vessels. There are several criteria to determine the flammability limits. A successful attempt can be determined by one or a combination of the following criteria:

1. Inspection of the visualization of the flame kernel produced by the spark, namely visual criterion.
2. Measurements of pressure or temperature histories in the vessel and appropriate pressure or temperature rise criteria can be used to designate flammability rather than the purely visual observation of flame development.

A successful ignition would induce a rapid pressure increase and temperature rise within a short time as well as produce a propagating flame front that could be readily observed.

Previous gas flammability limit data were obtained mainly in flammability tubes which in those test a gas mixture in a vertical tube was ignited and flame propagation was inspected by visual criterion. However, the wall quenching has a significant effect on the flammability measurement in flammability tube.

Recently, the flammability measurements are conducted in closed chambers. This is because the larger size of combustion chamber can minimize wall effects and can allow potential use of stronger igniters to ensure the absence of ignition limitations (D.M Jiang et al, 2005).