

**THE EFFECT OF VACUUM PRESSURE ON THE FLAMMABILITY LIMITS
OF LIQUEFIED PETROLEUM GAS (LPG)**

NORAZMA BINTI MUKHTAR

**A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)**

**Faculty of Chemical & Natural Resources Engineering
University Malaysia Pahang**

November 2010

ABSTRACT

The Liquefied Petroleum Gas (LPG) is a flammable mixture of hydrocarbon gases. In transportation or handling the LPG gases, it is very important to know the flammability limits and the pressure of the gas to avoid any accident or explosion occurred. The pressure of LPG takes part in the flammability limits either Upper Flammability Limit (UFL) or Lower Flammability Limit (LFL). So, the aims of this research are to investigate the effect of vacuum pressure on the flammability limits of LPG/air. The experiments are performed in a 20 L spherical explosion vessel. The mixtures are ignited using spark permanent wire that place at the centre of the vessel. The pressures are used starting from 0.96 bar up to 1.0 bar. The pressure-time variations during explosions of LPG/air mixtures in explosion vessel are recorded. The explosion pressure data is used to determine the flammability limits which flame propagation is occurred if explosion pressure greater than 0.96 bar. In this experiment, the result shows the LFL is decrease when the pressure decreasing but, UFL is increasing with the increasing of pressure. The LFL for 0.98 bar is 2 volume % of LPG and for 0.96 bar is 1 volume % of LPG. The UFL for 0.98 bar and 0.96 bar are the same which is 8 volume % of LPG. But the P_m for UFL for 0.98 bar is 0.7 bar and P_m for UFL for 0.96 bar is 0.9 bar.

ABSTRAK

Gas Petroleum Cecair (LPG) adalah campuran gas hidrokarbon yang mudah terbakar. Dalam pengangkutan atau menangani gas LPG, sangat penting untuk mengetahui had mudah terbakar dan tekanan gas untuk mengelakkan kemalangan atau letupan berlaku. Tekanan LPG mengambil bahagian dalam had mudah terbakar baik UFL atau LFL. Jadi, tujuan dari penelitian ini adalah untuk mengetahui pengaruh tekanan vakum pada had mudah terbakar LPG / udara. Percubaan dilakukan dalam bekas letupan tertutup yang berisipadu 20 L. Campuran dicucuh dengan wayar percikan tetap yang terletak di tengah bekas letupan. Tekanan yang digunakan bermula daripada 0.96 bar sampai 1.0 bar. Variasi tekanan-masa selama letupan LPG campuran udara / letupan di dalam bekas letupan direkodkan. Data tekanan letupan digunakan untuk menentukan batas-batas yang mudah terbakar api propagasi berlaku apabila tekanan letupan lebih besar dari 0.96 bar. Dalam kajian ini, keputusan menunjukkan LFL yang menurun ketika tekanan rendah tetapi, UFL meningkat dengan meningkatnya tekanan. The LFL untuk 0.98 bar adalah 2 % isipadu LPG dan untuk 0.96 bar adalah 1 % isipadu LPG. UFL untuk 0.98, 0.96 dan 1.0 bar adalah sama iaitu 8 % isipadu LPG. Tetapi P_m untuk UFL untuk 0.98 bar adalah 0.7 bar dan P_m untuk UFL untuk 0.96 bar adalah 0.9 bar.

TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENT	vii
	LIST OF TABLES	ix
	LIST OF FIGURES	x
	LIST OF ABBREVIATIONS	xii
1.	INTRODUCTION	1
	1.1 Background of Study	1
	1.2 Problem Statement	2
	1.3 Objectives	2
	1.4 Research of Scope	3
	1.5 Rationale and Significance	3
2.	LITERATURE REVIEW	5
	2.1 Introduction	5
	2.2 Characteristic of LPG	6

2.3	Explosion	8
2.3.1	Explosion Pressure	11
2.4	Flammability Limits	12
2.4.1	Le Chatelier's Law	14
2.5	20-L Spherical Explosion Vessel	15
3.	METHODOLOGY	17
3.1	Experimental Apparatus	17
3.1.1	20 – L Spherical Explosion Vessel	18
3.1.2	Control Unit KSEP 310	19
3.1.3	Measurement and Control System KSEP 332	20
3.2	Experimental Condition	21
3.2.1	Pressure and Temperature	22
3.2.2	Ignition	22
3.2.3	Flammable Gases and Solvent Vapors	23
3.3	Experimental Procedures	23
4.	RESULTS AND DISCUSSION	28
4.1	Introduction	28
4.2	Experimental Results of LPG/Air Mixture for Pressure at 0.98 and 0.96 bar	29
4.3	Comparison from Previous Study	32
5.	CONCLUSION AND RECOMMENDATIONS	35
5.1	Conclusion	35
5.2	Recommendations	36
	REFERENCES	37
	APPENDICES	40
	Appendix A – D	41 - 55

LIST OF TABLES

TABLE NO	TITLE	PAGE
2.1	Physical and Chemical Properties of LPG	7
2.2	Categorizes of Explosion	9
3.1	Test Condition of Experiment	22
4.1	Graph of P_m versus Volume % of LPG at Pressure 0.98 Bar	29
4.2	Graph of P_m versus Volume % of LPG at Pressure 0.96 Bar	31
4.3	Graph of P_m versus Volume % of LPG at Pressure 0.96, 0.98 and 1.0 Bar	33

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
2.1	An Event Tree Showing Typical Consequences of Accidental Releases of Combustible Gas or Evaporating Liquid into the Atmosphere.	10
2.2	Explosion Pressure versus Initial Pressure for Stoichiometric Propane-Air in A 7 Litre Vessel	11
2.3	Schematic Represents Flammability Limits	13
2.4	20-L Spherical Explosion Vessel	15
2.5	Pressure/Time-Diagram of a Fuel Explosion	16
3.1	Schematic Diagram of Experimental Setup	18
3.2	Schematic Diagram of 20 – L – Spherical Explosion Vessel	19
3.3	Schematic of KSEP 310	20
3.4	Schematic of KSEP 332	21
3.5	Gas Fire Explosion Unit	23
3.6	Diagram of Igniter between the Electrode Rods	24
3.7	Test Condition Data for Pressure, Temperature and Ignition Energy	25
3.8	Pressure Signal Represents as Pressure versus Time	26
3.9	Experimental Work Flows	27

4.1	Graph of P_m vs. Volume % of LPG at Pressure 0.98 Bar	30
4.2	Graph of P_m vs. Volume % of LPG at Pressure 0.96 Bar	32
4.3	Graph of P_m vs. Volume % of LPG at 0.96, 0.98 and 1 Bar	34

LIST OF EQUATIONS

EQUATION NO	TITLE	PAGE
1	Le Chatelier's Law	14
2	Corrected Values of Explosion Overpressure, P_m	28

LIST OF ABBREVIATIONS

BLEVE	: Boiling Liquid Expanding Vapor Explosion.
LPG	: Liquefied Petroleum Gas.
LFL	: Lower Flammability Limit.
UFL	: Upper Flammability Limit.
P_m	: Corrected Explosion Overpressure
P_{exp}	: Explosion Pressure.
P_{max}	: Maximum Explosion Pressure.
Θ_{exp}	: Explosion time.
IE	: Ignition Energy.
P_{ci}	: Pressure Due to Chemical Igniter.
C	: The Proportion of Each Gas in the Fuel Mixture without Air.
dp/dt_{max}	: Maximum Rate of Pressure Rise in the Sphere.
t_1	: Duration of Combustion

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The liquefied petroleum gas (LPG) is widely used in domestic, leisure, industrial, commercial and agricultural sectors, especially where natural gas supplies are not easily available or accessible. It is mainly used for thermal applications.

The safety part in transportation of LPG gas by knowing the pressure and the flammability limits. Flammability limits indicate 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) (S.Y.Liao, 2005). In other words, combustion will take place and be self-sustaining only if fuel and air are mixed within the upper and lower flammability limits.

During the transportation of LPG, the high safety is needed to avoid any gas explosion occurred. Gas explosion is a process where combustion of a premixed gas cloud (fuel-air) 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 (Dag Bjerketvedt *et al*, 1987).

1.2 Problem Statement

The Liquefied Petroleum Gas (LPG) is widely used for both home and commercial nowadays. So, LPG has high demand from the customers. When the high demand exists, the transportation of the LPG also increases. So, the safety problem in the transportation and handling must be improved so that any hazardous event will be prevented.

The safety problem is very dangerous thing that must be avoided. During the transportation, the pressure will affect the flammability limits which is the range of explosion occurred.

When the LFL of the flammability limits decrease, the gas explosion tends to occurred shortly. So, it will make a big problem to the company (industry), human and also environments.

1.3 Objectives

The objective of this research is:

1. To study the effect of correlation of vacuum pressure with explosion pressure.
2. To study the effect of correlation of vacuum pressure with the UFL and LFL.

1.4 Research of Scope

This research is conducted to determine the effect used of vacuum pressures 0.96 and 0.98 bar on the flammability limits of LPG/air mixture 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 LPG gas cylinder is used.

The LFL and UFL of LPG/air mixture were determined at the pressure at 0.96 and 0.98 bar. This study is to determine if the flammability limits increase or decrease when the pressure at the vacuum pressure which is below 1.0 bar. So, the accident or explosion can be prevented.

1.5 Rationale and Significance

In this study, the effect of vacuum pressure on the flammability limits of LPG is investigated. Since the pressure at below atmospheric pressure, the range of flammability limits will increase.

It is significant to determine the LFL since the LFL is actually the time when the explosion will start. The initial pressure has effect on the LFL except at very low pressure (below 0.1 atm) where flames do not propagate.

During transportation of LPG, safety is the most important thing. So, the rationale of this research is to increase the safety during the transportation of LPG gases. By knowing the pressure used and the flammability limits of LPG, the explosion and hazardous during the transportation will not be swiftly occurred.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Liquefied petroleum gases (LPG) are substances such as propane and butane, which are transported and stored in the liquid phase in tanks under sufficiently high pressure. It is generated as a by-product either of oil and gas production or refining. At normal temperatures and pressures, but which turn liquid at moderate pressures; its main constituent is propane, and it is sometimes referred to by that name. The composition components of LPG are much simpler than that of gasoline. LPG is thought to be a cleaner fuel because it has less impact on air quality.

LPG is a mixture of hydrocarbon gases used as a fuel in heating appliances, a transportation fuel, and as an aerosol propellant and a refrigerant to reduce damage to the ozone layer by replacing chlorofluorocarbons. This group of products includes saturated hydrocarbons - propane (C_3H_8) and butane (C_4H_{10}), which can be stored/ transported separately or as a mixture. They exist as gases at normal room temperature and atmospheric pressure. They are described as "liquefied" because they liquefy at moderate

pressures, readily vaporizing upon release of pressure. It is this property that permits transportation of and storage of LPG in concentrated liquid form.

2.2 Characteristic of LPG

At normal temperatures and pressures LPG is a gas but as supplied it is a liquid under pressure. When this pressure is reduced, e.g. the control valve is opened, the liquid starts to boil and gas is evolved: 1 litre of liquid will provide about 250 litres of gas. Butane has a much lower vapour pressure than propane (it is less volatile) and propane is used more frequently in construction.

LPG is colourless and its liquid weight is about half that of water; however, propane vapour is at least 1 1/2 times heavier than air (butane 2 times) and because of this it tends to flow along the ground, often for a considerable distance, and collect in cellars, drains, excavations and other low-lying places. The vapour can remain for some time if the air is relatively still, and if ignition occurs at a remote point the resulting flame may travel back to the sources of the leak.

Small quantities of LPG can give rise to large volumes of gas/air mixture as approximately 2 % of the vapour in air will form a flammable mixture; if this situation occurs in a confined space and the mixture ignites, an explosion will result. Table 2.1 below shows the physical and chemical properties of LPG from Shell Company.

Table 2.1: Physical and chemical properties 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/m ³
Specific Gravity	0.5 @ 20°C
Vapor density	1.55 (air = 1)
Vapor Pressure at ambient	500 kPa
Boiling point	-40°C to 80 °C (-40 to 176 °F)
Freezing point	-190 °C (-310 °F) (propane)
Coefficient of water/oil	2.36 [log P]
Flash point	-104 °C (-156 °F)
Auto ignition	450 °C (842 °F)
Lower flammable limit	1.8% -1.9%
Upper flammable limit	9.5%
Hydrocarbon Composition (by Volume)	
Commercial Propane (C ₃ H ₈)	30%
Commercial Butane (C ₄ H ₁₀)	70%
Total Sulphur (stenches)	< 75 mg/kg
Free Water (Visual Inspection)	none
Relative density (compared to dry air)	1.85
Copper Corrosion Strip	1
Calorific Value, gross	49.5 MJ/kg 21,300 Btu/lb
Calorific Value, nett	45.7 MJ/kg 19,600 Btu/lb

2.3 Explosion

An explosion is a rapid expansion of gases resulting in a rapidly moving pressure or shock wave. The expansion can be mechanical (via the sudden rupture of a pressure vessel) or it can be the result of a rapid chemical reaction. Explosion damage is caused by the pressure or shock wave. (Crowl, D.A. and J.F. Louvar, 2002)

In general, an explosion occurred in the atmosphere if energy is released over a sufficiently small volume so as to generate a pressure wave of finite amplitude travelling away from the source. This energy may have originally been stored in the system in a variety of forms these include:

- a. Nuclear energy
- b. Chemical energy
- c. Electrical energy
- d. Pressure energy

However, the release is not considered to be explosive unless it is rapid enough and concentrated enough to produce a pressure wave that one can hear. Even though many explosions damage their surroundings, it is not necessary that external damage be produced by the explosion. All that is necessary is that the explosion is capable of being heard. Actually, explosions can be categorized into: (Dr. Kris Chatrathi, 1998)

- a. Physical explosions
- b. Chemical explosions

Table 2.2: Categorizes of the explosions (Dr. Kris Chatrathi, 1998)

Physical Explosions	Chemical Explosions
<ul style="list-style-type: none"> · The bursting of a vessel containing high pressures (pressures above atmosphere pressure). The vessels could contain compressed liquids. · Vapor or steam explosions. · Introduction of molten material into cooling liquids. The rapid mixing of materials at drastically different temperatures. 	<ul style="list-style-type: none"> · Gas and dust explosions · Unconfined vapor cloud explosions · Condensed material explosions · Runaway chemical reactions · Boiling liquid expanding vapor explosions (BLEVEs) · All of the explosions (both

Table 2.2 above shows the category of the explosion which is divided into two types which are physical explosion and chemical explosion.

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.

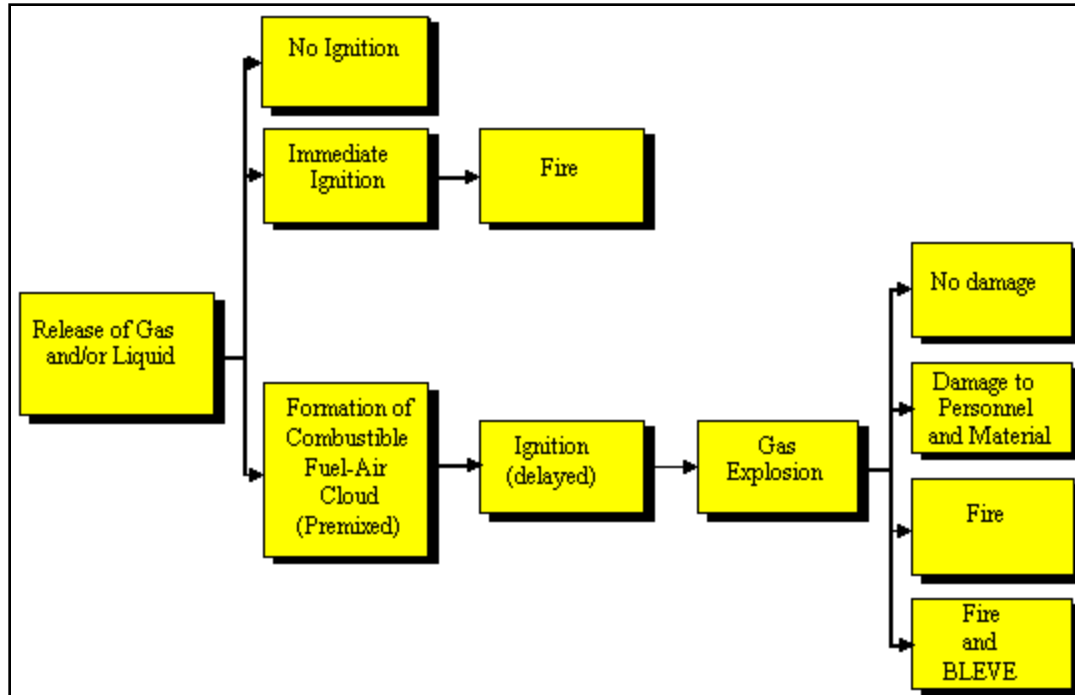


Figure 2.1 : An event tree showing typical consequences of accidental releases of combustible gas or evaporating liquid into the atmosphere. (Dag Bjerketvedt *et al*, 1987)

Figure 2.1 shows 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 (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.

2.3.1 Explosion Pressure

The initial pressure is a parameter which influences the explosion pressure at constant volume conditions. By increasing the initial pressure, the energy content, i.e. heat of combustion, per unit volume will increase. (Bartknecht, 1981) has given some measurements of explosion pressure for slow deflagration for propane in a 7 litre spherical vessel. (Bartknecht, 1981) These results are shown in figure 2.2. There is a nearly linear relation between initial pressure and explosion pressure. For stoichiometric fuel-air the pressure increase at constant volume will be approximately 8 times the initial pressure. To estimate constant volume explosion pressure for specific fuel-air or fuel/oxidiser mixtures at given initial conditions.

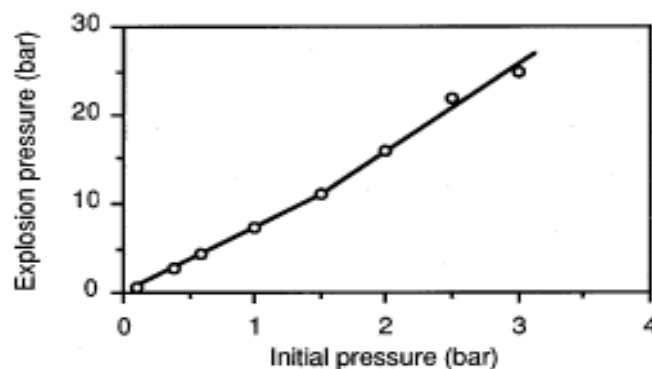


Figure 2.2: Explosion pressure versus initial pressure for stoichiometric propane-air in a 7 litre vessel (Bartknecht, 1981)

The characteristic parameters of a closed vessel explosion are the explosion pressure, the explosion time and the maximum rate of pressure rise. The explosion

pressure and explosion time were recently defined in the European standard on maximum explosion pressure determination:

- i. The explosion pressure, P_{exp} is the highest pressure reached during the explosion in a closed volume at a given fuel concentration.
- ii. The maximum explosion pressure, P_{max} is the highest pressure reached during a series of explosions of mixtures with varying fuel concentration.
- iii. The explosion time, θ_{exp} is the time interval between ignition time and the moment when the explosion pressure attained.

2.4 Flammability Limits

Flammability limits represent the extreme concentration limits of a combustible (gaseous or liquid vapors) in an oxidant through which a flame, once ignited, will continue to propagate at the specified temperature and pressure. The lower concentration value or the lean limit is often denoted by the symbol LFL which is Lower Flammability Limit while the upper or fuel rich limit is given the symbol UFL which is Upper Flammability Limit.

Fuel/air mixtures within these limits are said to be within their flammable or explosive range. Ignitions are much more intense within this range than if they were close to either the LFL or UFL. It should be emphasized that outside of the flammability limits i.e., either below the fuel lean or above the fuel rich limit one cannot effect ignition of a fuel/air mixture regardless of the intensity of the ignition source. Figure 2.3 above shows the schematic represents flammability limits.

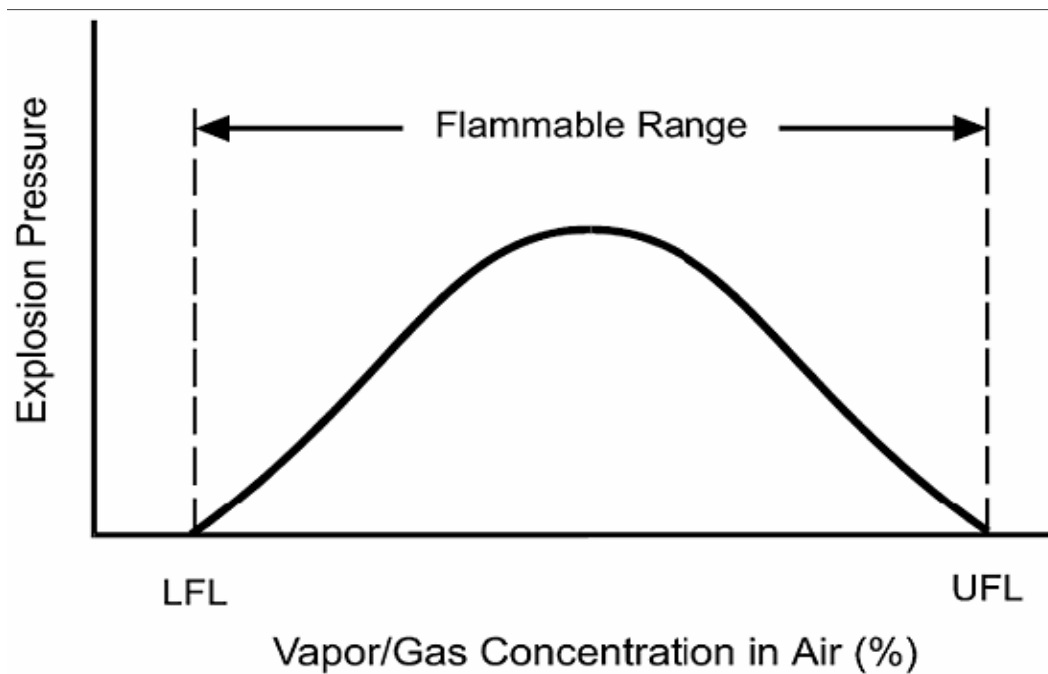


Figure 2.3: Schematic represents flammability limits.

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)

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

A fuel/air mixture is considered to be flammable if, when ignited, it produces a flame that can propagate throughout the available mixture. A flammable mixture might fail to ignite if the ignition source is too weak. However, successful ignition does not guarantee successful flame propagation. In some cases, the ignition source is strong

enough to initiate a small flame, but the flame is extinguished as it moves away from the ignition source. In such cases, only a portion of the available mixture is burned, and the mixture is not, therefore, considered flammable.

Actually, flames in gas mixtures of fuel and oxidizer can be ignited and propagate only under certain conditions. Ignition and propagation depend on many factors but there are pretty clear boundaries in composition, the flammability limits, outside of which is extremely difficult to get combustion. Flammability limits are sometimes referred to as “explosive limits” and are extensively used in hazard analysis and regulations to define the existence of a hazardous condition. There are related tests and limits for liquid fuels, the flash point, the fire point, and a concept known as auto ignition that is important in hazard analysis.

2.4.1 Le Chatelier’s Law

As to the lower flammability limit of multiple component fuel mixture in air, the LFL value of the mixture can also be estimated by following formula,

According to Le Chatelier’s law:

$$LFL_{mix} = \frac{100}{C_1/LFL_1 + C_2/LFL_2 + \dots + C_i/LFL_i} \quad \text{Equation 1}$$

Where;

$C_1 C_2 \dots C_i$ (vol %) is the proportion of each gas in the fuel mixture without air. (Kuchta, 1985)

2.5 20-L Spherical Explosion Vessel

A 20-L spherical explosion vessel was used for the explosion test as shown in figure 2.4 below. This apparatus was manufactured by Kühner AG of Switzerland. The parameters measured are the maximum pressure P_{\max} and the maximum rate of pressure rise in the sphere, $(dP/dt)_{\max}$.

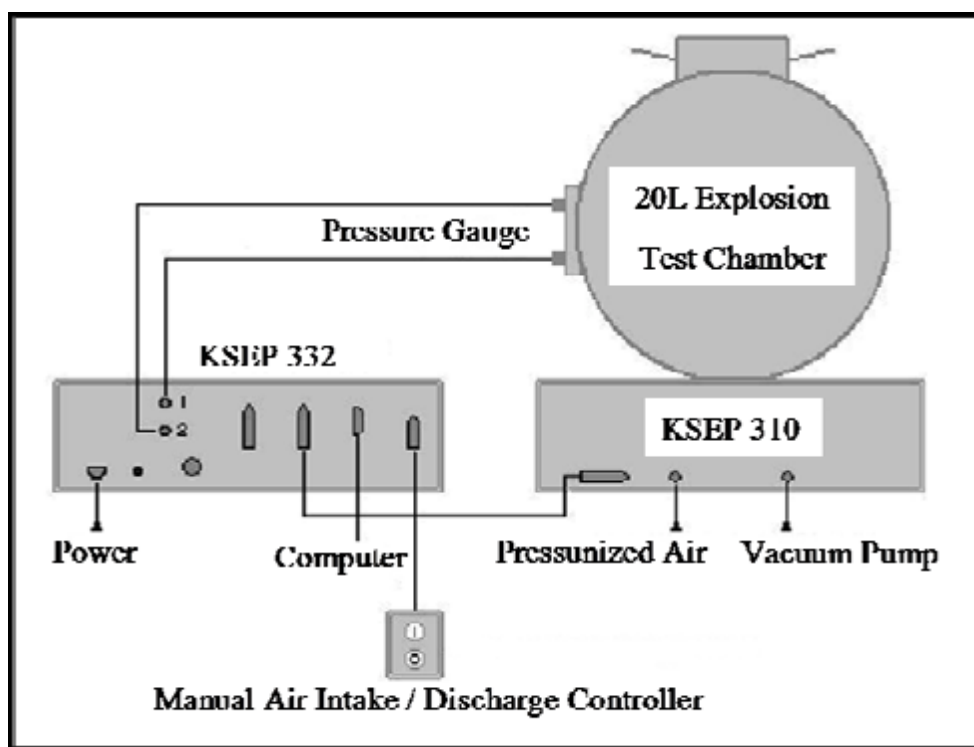


Figure 2.4: 20-L Spherical Explosion Vessel (Cesana and Siwek, 2003)