

EFFECTS OF CARBON DIOXIDE GAS ON
FLAMMABILITY LIMITS OF LPG

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EFFECTS OF CARBON DIOXIDE GAS ON FLAMMABILITY LIMITS OF
LPG

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A thesis submitted in fulfillment
of the requirements for the award of the degree in
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SUPERVISOR’S DECLARATION

“I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Degree in Bachelor of Chemical Engineering (Gas Technology)”

Signature :

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Date : 20 JANUARY 2012

STUDENTS'S DECLARATION

I declare that this thesis entitled “Effect of Carbon Dioxide Gas on Flammability Limits of LPG” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

Signature :

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Date : 20 JANUARY 2012

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ABSTRACT

Liquefied petroleum gas or LPG has well acknowledged as an attractive source of fuel in these centuries as it has provided us evidence to be the most effective and environmental friendly among all other fuel existed. However, like the other fuel, LPG also has its own benefits and drawbacks at when it is inadequately treated can be destructive to us. After knowing the characteristics of LPG and recognizing suitable ways of reducing risks in storage, handling and transportation of it, an appropriately planned experiment has been carried out. Specifically, this study is conducted to study the effect of carbon dioxide (CO_2) to the Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) of LPG. LFL and UFL create a range at which explosion may occur to any flammable substance. By adding diluents (in this case is CO_2) to the LPG-air mixture, the range was predicted to be narrowed down because the role of diluents to the mixture is to reduce the concentration of oxygen (O_2) existed in the mixture to a level where explosion can be stopped. The most proper equipment to be used in order to achieve the objective of the study is the 20-L-Explosion Vessel. Only by using this high-tech equipment- the experiments, which involving explosion, can be safely performed. In the experiment, different volume percentage of CO_2 was added in the pre-mixed LPG - air mixture. Three sets of experiments were done in order to compare the effect of CO_2 addition in the pre-mixed LPG - air mixture towards its flammability limit respectively. Fortunately, the results were moderately following the theories where the range of flammability limit of LPG - air mixture was fruitfully reduced from 4.2 % vol. To 3 % vol. of LPG.

ABSTRAK

Gas petroleum cecair atau LPG telah diperakui sebagai sumber bahan api yang menarik dalam abad ini kerana ia telah membuktikan keberkesannya selain lebih mesra alam melampaui semua bahan api lain. Walau bagaimanapun, seperti bahan api lain, LPG juga mempunyai kebaikan dan keburukan di mana ia mampu merosakkan dan membahayakan kita jika tidak digunakan dengan baik. Setelah mengetahui ciri-ciri LPG dan mengenalpasti cara yang sesuai untuk mengurangkan risiko dalam penyimpanan, pengendalian dan pengangkutannya, eksperimen yang bersesuaian telah dijalankan. Secara khususnya, kajian ini dijalankan untuk mengkaji kesan karbon dioksida (CO_2) terhadap Had Kemudahbakaran Bawah (LFL) dan Had Kemudahbakaran Atas (UFL) LPG. LFL dan UFL mewujudkan julat di mana letupan boleh berlaku kepada apa-apa bahan yang mudah terbakar. Dengan menambah perencat (dalam kes ini adalah CO_2) ke dalam campuran LPG dan udara, julat ini diramalkan akan menjadi semakin mengecil kerana peranan perencat ialah untuk mengurangkan kepekatan oksigen (O_2) yang wujud di dalam campuran hingga ke tahap di mana letupan boleh dihentikan. Peralatan yang sesuai digunakan untuk mencapai objektif kajian ini ialah '20-L-Explosion Vessel'. Hanya dengan menggunakan peralatan berteknologi tinggi ini, eksperimen yang melibatkan letupan, boleh dilaksanakan dengan selamat. Dalam eksperimen ini, peratusan isipadu CO_2 yang ditambah ke dalam pra-campuran LPG dan udara telah ditetapkan. Tiga set eksperimen telah dilakukan untuk membandingkan kesan tambahan CO_2 dalam pra-campuran LPG dan udara yang mampu membawanya ke arah had kemudahbakaran masing-masing. Keputusan daripada eksperimen yang telah dijalankan adalah sederhana mengikut teori-teori mengenai had kemudahbakaran campuran LPG dan udara di mana had kemudahbakarannya dapat dikurangkan dari 4 % isipadu kepada 3 % isipadu LPG.

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LIST OF ABBREVIATIONS

Ar	-	Argon
CH ₄	-	Methane
CO	-	Carbon Monoxide
CO ₂	-	Carbon Dioxide
LEL	-	Lower Explosive Limit
LFL	-	Lower Flammability Limit
LPG	-	Liquefied Petroleum Gas
MS	-	Malaysia Standard
Ne	-	Neon
NO _x	-	Nitrogen Oxide
N ₂	-	Nitrogen
O ₂	-	Oxygen
P _{ex}	-	Explosion Overpressure
P _m	-	Corrected Explosion Overpressure
P _{max}	-	Pressures Generated by The Closed Gas
t _d	-	Time-Delay Of the Outlet Valve
t _v	-	Ignition Delay Time
UEL	-	Upper Explosive Limit
UFL	-	Upper Flammability Limit
Xe	-	Xenon

LIST OF SYMBOLS

°C	-	Degree celcius
barg	-	Bar gauge
kL	-	Kilo litre
kg	-	Kilo gram
kPa	-	Kilo pascal
L	-	Litre
ppm	-	Part per million
Re	-	Reynold's number

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

When mentioning about Liquefied Petroleum Gas (LPG), one must have imagined the usage of this fuel as a power source to everyday transportations such as cars, motorcycles and buses. Less realized by public, LPG has also been used primarily in empowering industrial sectors. For instance, in Ceramic and Glass Industry, LPG has been a far better-quality and extra clean fuel in eliminating obstacles during the melting process. Glass melting in this industry is a huge operation and involves numerous chemical reactions which occur during the process where LPG is the best choice of fuel because it enhances the product quality thereby reducing technical problems related to the manufacturing activity. Additionally, LPG is also the most idyllic fuel for production of food by Agriculture and Animal Husbandry. Drying of crops and other farm products require a clean and sulphur free fuel for drying activity to avoid any transfer of bad taste or smell to the dried crops. LPG in the farming industry can be used for examples in cereal drying, flame cultivation, soil conditioning and livestock farming (“LPG Application: Farming Industry”,n.d).

Above all the spectacular uses of LPG, it is actually quite a risky fuel to deal with. Accidents involving LPG is sometimes unpredictable. LPG in cylinder vessel may leak as a gas or a liquid. If the liquid leaks it will rapidly evaporate and form a rather large cloud of gas which will drop to the ground, as it is heavier than air. LPG vapors

can run for long distances along the ground and can assemble in drains or basements. When the gas meets a source of ignition it can burn or worse, explode. As liquid LPG is a fast evaporates substance, it can cause cold burns to the skin and it can act as an asphyxiant at high concentrations (Health and Safety Authority, 2011).

Realizing on how LPG can bring many unforeseen hazards to human, some initiatives should be taken to help reducing the risk of handling, processing and storing of it. One of the methods that is quite reliable and attract the engineers' interests to study further on is the addition of inert gas in the LPG itself. This process is usually addressed as inerting. It is done basically to protect a storage system (usually tanks and cylinder vessels) from exploding by keeping the oxygen content low. Conceptually, inerting will result in an increment in the Lower Flammability Limit (LFL) and decrease in the Upper Flammability Limit (UFL) which in other words, reduce the range of flammability of a flammable gas ("Standard for Inert Gas Systems", 1984).

Nitrogen (N_2) and carbon dioxide (CO_2) are examples of inert gases typically used for this purpose. As for this study, CO_2 has been chosen. According to Li *et al.* (2010), the usage of CO_2 gas as diluents in any flammable gas was proved to be working out. It is believed that CO_2 gas may decrease the explosion area of a flammable gas after it is added into the mixture of that gas with air.

1.2 PROBLEM STATEMENT

In 28 September 2011, there was an explosion and fire involving LPG happened in one of the premier shopping malls in Subang Jaya. The incident was traced by the accidental escape of the LPG from one of the food retail outlets on the lower ground floor early in the morning at about 3.45 am on that very day. Flash fire was noticed during the explosion and it was reported that there were two persons who were on the ground floor had been thrown off and landed on their backs some distance away. It was also reported that another two security guards who were at the control room at the

level P1 car park were slightly injured by fallen debris (Department of Occupational Safety and Health, 2011).

The incident described is one of many other incidents happened involving LPG that leaved hideous impacts including deaths and injuries. Just like any other flammable gases, LPG explosions occur within the flammability limits of its substance. Diluents such as CO_2 and N_2 can help reducing the risks of an explosion of flammable substances by manipulating their flammability limits. This is why the flammability characteristics of LPG are very important when it comes to deal with storage, handling and transportation of this gas.

Thus, many studies and experiments have been performed in order to study and understand this special characteristic of LPG and how exploiting the usage of diluents may regulate its flammability limits. This continuing effort is very important to enhance safety.

1.3 OBJECTIVE OF STUDY

- a) To study the effect of CO_2 as a diluents to the LFL and UFL of LPG.

1.4 SCOPE OF STUDY

This study has been conducted based on three main variables:

- a) Manipulated Variables:-

Manipulated variables are the variables that have to be adjusted to obtain the desired results. In this research, the variable that has been manipulated was the percentage of CO_2 in the LPG-air mixture used. This percentage was based on volume of CO_2 over summation of CO_2 and LPG volume. This percentage must not exceed 15 % to avoid overloading of diluents and errors in results obtained.

b) Constant Variables:-

Constant variables are the parameters of the research. These variables must be fixed to avoid disturbances or errors during the experiment. The significant variables that have been decided to be the constant variables are the operating temperature and pressure. The temperature was constantly at 20 °C while pressure was maintained at 1 bar absolute.

c) Controlled Variables:-

Superior attention must be given to the controlled variables as they are the fundamentals for an experiment. They lead the experiment and showed how the manipulated variables should be varied in order to get desired results. In this case, the controlled variables were the UFL and LFL of LPG.

1.5 RATIONALE AND SIGNIFICANCE OF STUDY

As diluents, CO₂ may help to reduce the concentration of oxygen (O₂) in a fuel-air mixture. Theoretically, when the concentration of O₂ is reduced, the possibilities of explosion to occur are reducing too. In other words, the lower the O₂ concentration in fuel-air mixture, the fewer potential it has to be exploded. Besides that, exclusion of O₂ from spaces in storage tanks and vessels can also protect against the risks of unwanted chemical reactions with the stored liquid and corrosion of the storage container (BP Group Engineering Standards Forum, 1992).

Explosion, similar to combustion, may only be sustained if the heat released due to combustion is greater than that absorbed by the surroundings. It needs O₂, ignition source and flammable gas as the essential elements for the process. Exclusion of O₂ from spaces in storage tanks and vessels protects against the risks of fire and explosion, unwanted chemical reactions with the stored liquid, and corrosion of the storage container (Kasmani, 2011).

Therefore, the significance of this study was to reduce one of these elements (in this case O_2) by finding the most suitable amount of CO_2 to be added in the LPG-air mixture with the intention of changing its LFL and UFL to a safer level where possibilities of explosion to take place was minimum.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Storage, handling and transporting of Liquefied Petroleum Gas (LPG) can be very fussy because there are quite a number of procedures to be followed. No matter where these process take place, there are always a guide or a standard to be referred based on certain situations. But, above all this, proper procedures for the handling, storage and transportation process is very important to keep away from unwanted disaster such as explosion (BP Group Engineering Standards Forum, 1992).

LPG, as well known by us, is usually stored and transported in cylinder vessels to meet up with just about the entire of its end consumers. The pressure inside each vessel is the vapor pressure for propane and butane mix at surrounding temperature. By using Figure 2.1, the vapor pressure of LPG can be estimated at surroundings' temperature range of -40 °C to 60 °C. However, this figure is only valid for small scale LPG cylinder which usually used by domestic consumers.

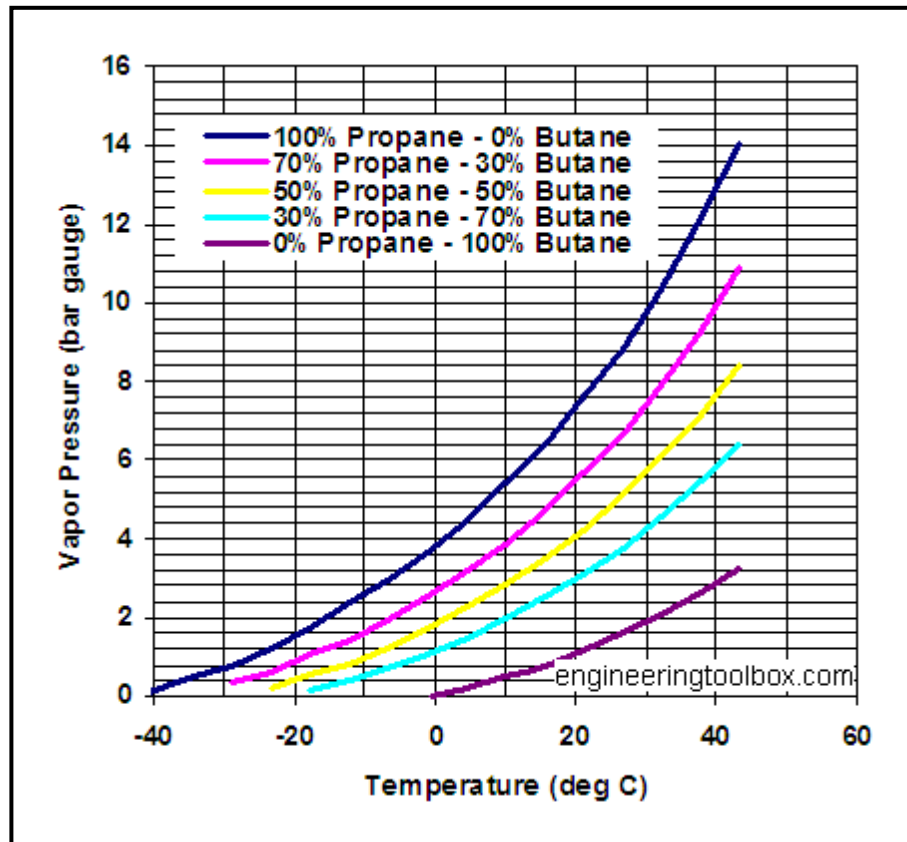


Figure 2.1 The Propane and Butane Mixture Diagram

Source: The Engineering Toolbox, 2012.

From Figure 2.1, vapor pressure of LPG with typical composition (30 % propane and 70 % butane) at surroundings' temperature of 20 °C is around 3 bar gauge (barg). If only this pressure is rapidly getting higher due to the escalating of surroundings' temperature, failure of the vessel might happen and possibilities of leaking to be happened are elevated.

Let's consider a worst case scenario where leakage of LPG took place. LPG in cylinder vessel may leak as a gas or a liquid. If the liquid leaks it will rapidly evaporate and form a quite large cloud of gas which will dive to the ground, as it is heavier than air. However, how much of LPG is considered necessary in order for an explosion to occur? A parameter called as flammability limit has helped to answer that question. Flammability limit is a range of percentage volume of any flammable gases where

combustion or explosion might occur. So, if the percentage volume of leaked LPG is within this range, possible explosion can happen if there is air or O₂ and ignition present (Michelsen, 1992).

For decades, many researchers had done studies on how to minimize the flammability limit. As a result, it is found that addition of diluents can narrow down the range of flammability limit and indirectly lessen the risk of explosion to happen. Diluents usually make use of the inert gases such as neon (Ne), argon (Ar), xenon (Xe), nitrogen (N₂) and CO₂ with the purpose of helping to reduce the concentration of O₂ present (“Standard for Inert Gas Systems”, 1984).

As for this study, CO₂ has been selected to be the diluents for LPG and air mixture because it is rather economical in cost if compared to other inert gases. Detail clarifications will be discussed in the becoming sub-section of this study (Bumgartner, n.d.).

2.2 LIQUEFIED PETROLEUM GAS (LPG)

In emergent world we are facing now, liquefied petroleum gas (LPG) is a practical source of energy as it emits less gases that can cause pollution such as nitrogen oxide (NO_x) and carbon monoxide (CO) (Razus *et al.*, 2009).

It can be categorized as a clean fuel as it also emits low percentage of CO₂ gas to the atmosphere and also has low sulphur contents that can be harmful to the environment. These facts thus providing a clean alternative energy in this age of rightful concern with environment safety and pollution control. It is a complete combustion fuel which reduces maintenance costs through the reduced plant and boiler downtime (Flogas, 2010).

2.2.1 Physical and Chemical Properties of LPG

LPG originally existed in gases form. It is then liquefied under certain pressure to be liquid form for storage and transportation purposes. This non-toxic fuel also carries many advantages to users such as minimal effect of corrosion towards equipments involved, environmental friendly as it consequences in clean burning as well as emits no contaminating gases and affect in low maintenance cost and time as it gives out no soot when burning and results to a longer life of equipments (TOTAL in India, n.d). Table 2.1 shows the list of some physical and chemical properties of LPG.

Table 2.1 Chemical and Physical Properties of LPG

PROPERTIES	DESCRIPTIONS	
Chemical Formula	C ₃ H ₈ ,	C ₄ H ₁₀
Molar Mass (gmoI ⁻¹)	44.0	58.0
Proportion (%)	30	70
Appearance	Colourless	
Odour	Pungent Odour – Ethyl Mercaptan (added)	
Solubility	Insoluble in water	
Boiling Point (°C)	-44.5	
Vapour Pressure (kPa)	380 – 830	
Flash Point (°C)	-104	
Auto Ignition Temperature (°C)	510	
Flammability Unit (% vol.)	UFL = 8.5 LFL = 1.9	

Source: Petronas Dagangan Berhad, 2004.

In addition to Table 2.1, LPG is also classified as non-toxic and non-carcinogen gas. However, if LPG is exposed to human, effect of overexposure might be asphyxiant and the target organs will be eye, skin and respiration system (Petronas Dagangan Berhad, 2004).

2.2.2 Storage, Handling and Transportation of LPG

In this sub-section, overall description is based on Malaysia Standard (MS) 830 which is the Code of Practice for The Storage, Handling and Transportation of Liquefied Petroleum Gases. According to MS 830, the domestic kind of LPG cylinder is classified as the 'portable container' which is designed to be readily moved, as distinguished from containers designed for stationary installations. Portable containers designed for transportation in such a manner that they can be safely transported in the filled or partly filled condition.

2.2.2.1 Storage

In specification of LPG storage cylinder, it shall be designed, fabricated and tested in accordance with MS 641 or MS 642 or other codes approved by the relevant authority. This scheme is also applied for the determination of its design pressure. In addition to this, marking must also be considered. Each container shall be conspicuously and permanently marked with the following information:

- a. Manufacturer's name or trade-mark, serial number and year of manufacture
- b. Pressure vessel code to which it is made
- c. The water capacity in litres (L) or kilolitres (kL)
- d. Class of vessel (e.g. Class 1)
- e. Design pressure in kilopascals (kPa)
- f. Date of initial hydrostatic test

- g. Date of hydrostatic retest
- h. The maximum safe working pressure in kilopascal (kPa)
- i. The tare mass in kilograms (kg) of container (for containers to be filled by mass)
- j. Official stamp of the inspecting authority

It is also specified that the containers of storage shall be equipped with openings suitable for the service for which the container is to be used. Such openings may be either in the container proper or in the manhole cover or part in one and part in the other. Connections for safety relief valves shall be located and installed in such a way in order to have direct communication with the vapour space whether the container is in storage or in use. If the containers located in a well inside the container with piping to the vapour space, the design of the well and piping shall permit sufficient safety relief valve discharge capacity. On the other hand, if they are located in a protecting enclosure, the enclosure shall be designed to protect against corrosion and allow inspection (MS 830, 2003).

In the installation requirement, LPG storage containers within a group shall be located so that their longitudinal axes are parallel to each other and preferably are directed away from any nearby storage of hazardous gases or flammable or combustible liquids. Cylindrical storage containers may be placed end to end with that the distance between the ends is not less than 3 meter or twice the diameter of the larger container, whichever is the greater. It is must also realized that storage containers shall not be installed one above the other as covered by MS 830 (2003).

Other than that, MS 830 (2003) has also stressed that the safety distance for LPG storage container must also be considered. Safety distances are intended to protect the LPG facilities from the radiation effects of fires involving other facilities as well as to minimize the risk of escaping LPG being ignited before being dispersed or diluted.

2.3 CARBON DIOXIDE (CO₂)

2.3.1 Physical and Chemical Properties of CO₂

Carbon dioxide (CO₂) was first discovered by a Scottish chemist and physician, Joseph Black, in 1750s. The linear molecule consists of a carbon atom that is doubly bonded to two oxygen atoms, O=C=O. It is an odourless and colourless gas which is slightly acidic and non-flammable (Lenntech Water Treatment and Purification, 2009).

Even though CO₂ mainly found in the gaseous form, it also has a solid and a liquid form. It can only be solid when temperatures are below -78 °C. Liquid CO₂ mainly exists when it is dissolved in water. CO₂ is only water-soluble, when pressure is maintained. After pressure drops, the CO₂ gas will try to escape to air. This results in the bubbles' forming into water. CO₂ can be found mainly in air, but also in water as a part of the carbon cycle CO₂ is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm (Shakhashiri, 2008). Table 2.2 shows extra information on physical and chemical properties of CO₂.

Table 2.2 Physical and Chemical Properties of CO₂

PROPERTIES	DATA
Molecular formula	CO ₂
Molecular weight (g/mol)	44.01
Specific gravity (°C)	1.53 at 21
Critical density (kg/m ³)	468
Concentration in air (ppm)	370.3 x 10 ⁷
Stability	High

Liquid (kPa)	Pressure < 415.8
Solid (°C)	Temperature < -78

Source: Lenntech Water Treatment and Purification, 2009.

In addition of the properties shown in Table 2.2, CO₂ has been used in various ways such as an ingredient in a carbonated drink to make it fizzy, as a component in producing lasers, a part of fire extinguisher substances and so much more. It is naturally exists in our environment in gases form. CO₂ is also classified as a green house gas as it can cause the green house effect where it absorbs some of the heat and trap it near the earth's surface, so that the earth is warmed up (Bumgartner, n.d.).

2.4 EFFECTS OF CO₂ ON FLAMMABILITY LIMITS OF LPG

Diluents acted as an important part in inerting process. Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen for the purpose of lowering the likelihood of explosion (Chen, 2009).

When an inert gas is added to a hydrocarbon gas/air mixture, the result is an increase in the lower flammable limit concentration and a decrease in the upper flammable limit concentration (“Standard for Inert Gas Systems”, 1984). Figure 2.2 describes the effect of increasing in diluents in hydrocarbon gas-air mixture to flammability limit of hydrocarbon gases.

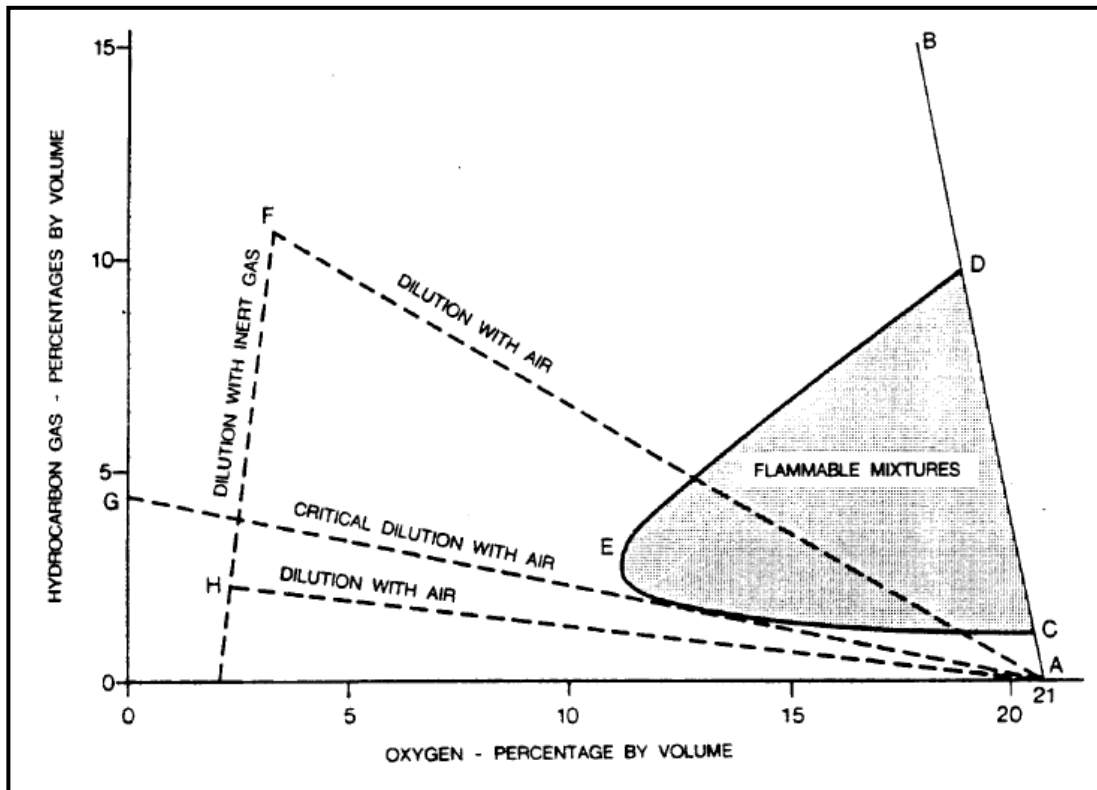


Figure 2.2 Hydrocarbon Gas/ Air/ Inert Gas Mixtures Effect on Flammability Limit

Source: “Standard for Inert Gas Systems”, 1984

From Figure 2.2, hydrocarbon/air mixtures, without inert gas, lie on the line AB, the slope of which shows the reduction in O_2 content as the hydrocarbon content increases. Points to the left of AB correspond to mixtures whose O_2 content is further reduced by the addition of inert gas. As inert gas is added to hydrocarbon/air mixtures, the flammable range gradually decreases, until the O_2 content reaches a level (normally taken to be about 11 % by volume) at which no mixture can burn (“Standard for Inert Gas Systems”, 1984).

From a study to predict the effects of the presence of diluents with methane on spark ignition engine performance conducted by Bade *et al.*, (2001), diluents were found especially good when the percentage of diluents in fuel is less than 50 %. The presence of a diluents with methane reduces the effective heating value of the fuel mixture when

the energy released by the oxidation reactions of the fuel component is shared with the diluents. The energy released by combustion taken up by the CO_2 component was amplified drastically with temperature since the specific heat of CO_2 increased with temperature at a much greater rate than that for N_2 or air. These will tend to modify the composition of the final products of combustion. The effects of the presence of CO_2 were more obvious than that of N_2 (Bade *et al.*, 2001).

A professor from Canada said that the presence of CO_2 and N_2 as diluents with methane had lower down its effective heating value. Besides that, it has also reduced the flame speed of the mixture (Karim, 2010). Figure 2.3 shows a clearer proof on this.

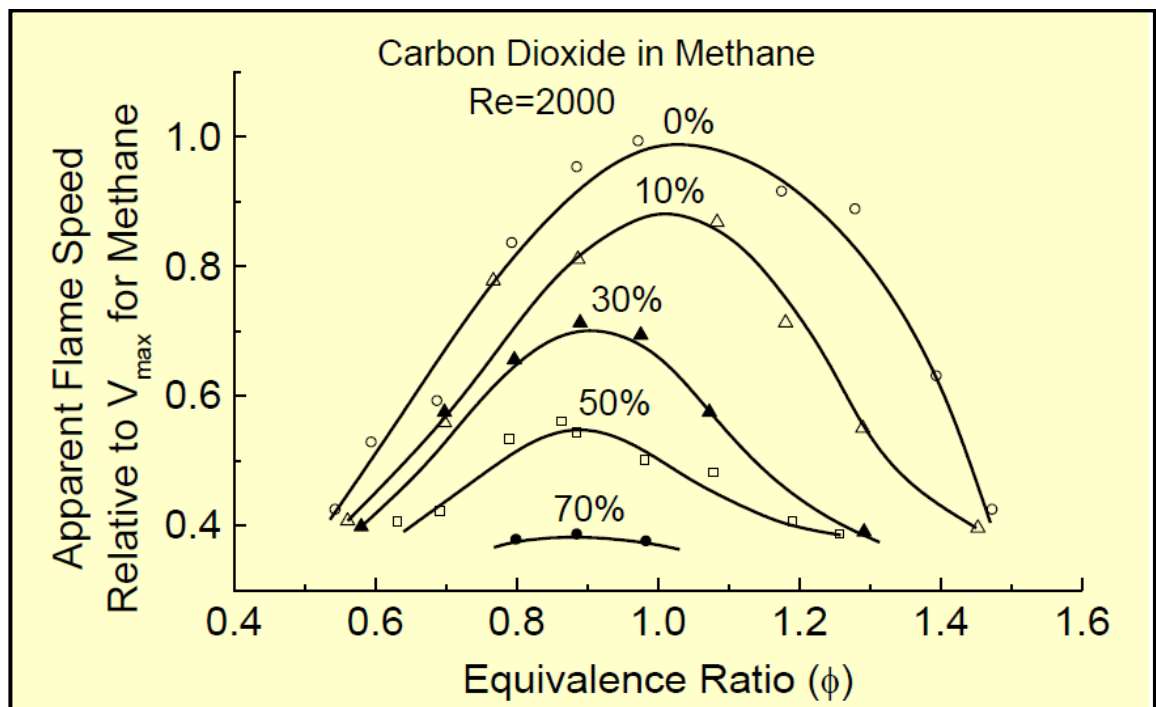


Figure 2.3 The Flame Propagation Rates within Flowing Mixtures Of Methane- CO_2 -Air for a Flow Reynolds Number of 2000 and Different Volumetric Concentrations of CO_2 -in the Methane.

Source: Karim, 2010

Figure 2.3 had clearly showed that the more the volumetric concentration of CO_2 added in the methane (CH_4)-air mixture, the smaller the graph's shape had been. These situations had indicated that the addition of CO_2 had somehow helped the flame speed of the fuel mixture to decrease and indirectly proposed that it can as well reduce the severity of an explosion.

Meanwhile, it is also believed that the area of the explosion limits of gas mixtures decreased after adding CO_2 into flammable gas mixture. In Figure 2.4, a graph had been constructed from a study on the effect of the explosion limits of the flammable gas mixture ratios of CH_4 and hydrogen (H_2) with CO_2 during the experiment and derived effective relations between the explosion limits of these flammable gas mixtures with CO_2 (Li *et al.*, 2010).

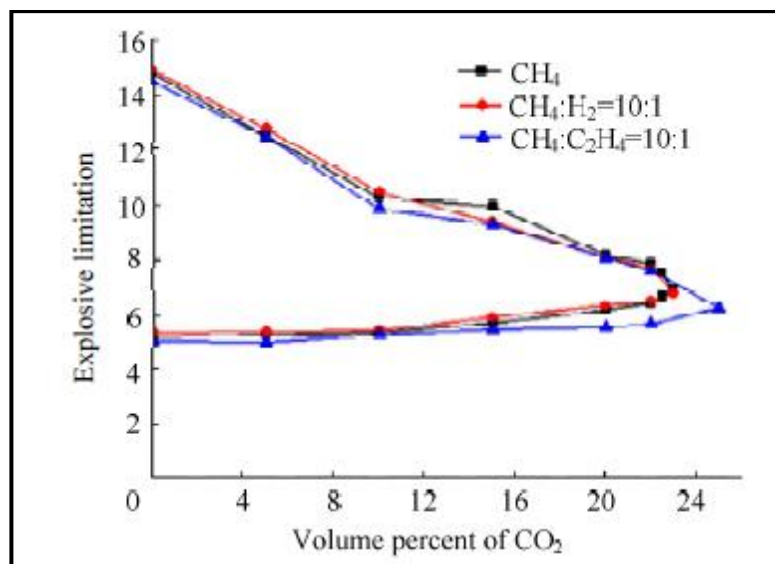


Figure 2.4 Effect of explosive limits of CH_4/H_2 and $\text{CH}_4/\text{C}_2\text{H}_4$ in ratio of 10/1 gas mixtures with CO_2

Source: Li *et al.*, 2010

As displayed in Figure 2.4, the explosive limitation of different gas mixtures, CH_4 and H_2 as well as CH_4 and ethane (C_2H_4), had shown changes once CO_2 was added into that mixture.

2.5 FLAMMABILITY LIMITS

Flammability limits can be divided into two which are the Lower Flammability Limits (LFL) and Upper Flammability Limits (UFL). LFL is the smallest quantity of combustible fuel when mixed with an air (or other oxidant) which will support a propagating flame. Whereas, UFL is the highest quantity of combustible fuel when mixed with air (or other oxidant) which will support a propagating flame. Both LFL and UFL are sometimes called as Lower Explosive Limits (LEL) and Upper Explosive Limits (UEL) (Kasmani, 2011). Figure 2.3 will give clarifications on the definition of flammability limit.

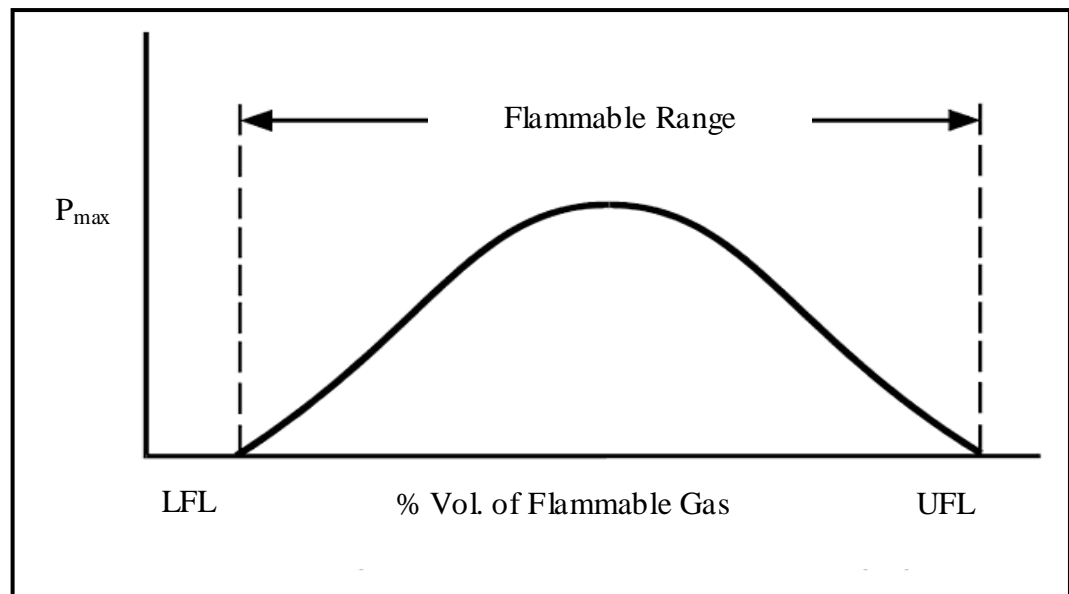


Figure 2.5 Flammable Range of a Flammable Substance

Source: U.S. Department of Labor, n.d.

The rich flammability limit is usually not as essential for explosion safety as the lean limit. This is because we are normally concerned with a leak of flammable material that comes into the flammable range from the lean side. For a rich limit

explosion air or oxygen has to leak into a pure fuel situation and this is regularly giving concern in hydrocarbon storage vessels. It can occur in vapour extraction systems such as common vacuum extraction lines (Kasmani, 2011).

2.6 20-L-SPHERICAL EXPLOSION VESSEL

The experiment relating to this study was using the 20-L-Explosion Vessel or also known as 20-L-Spherical Explosion Vessel or 20-L-Explosion Vessel. The equipment has been developed by Kühner (2001) and is shown in Figure 2.4. The pressure and temperature should be at 1 bar absolute and 20 °C.

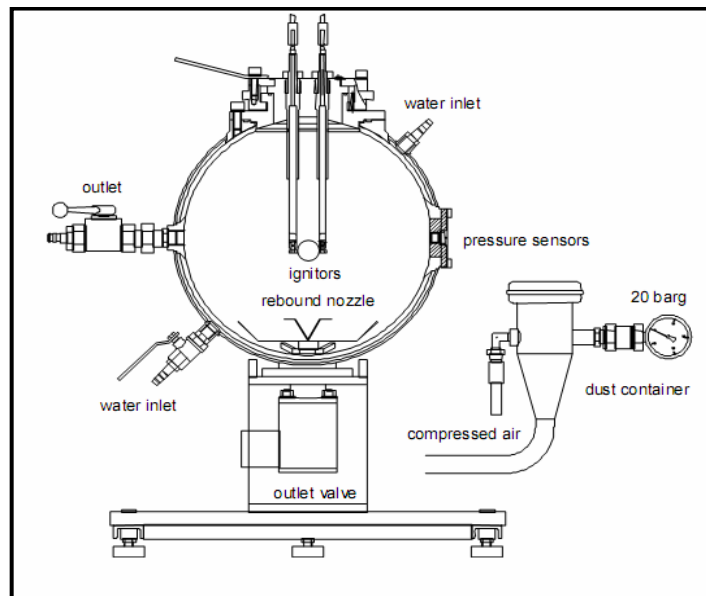


Figure 2.6 A 20-L-Spherical Explosion Vessel

Source: Cesana, 2001.

Due to the a lesser amount of favorable surface to volume ratio, the explosion pressure P_{ex} measured in the 20-L-Explosion Vessel is in general vaguely lower than the one measured in the 1 m³ vessel. This is caused by cooling effects as well as the pressure effects caused by the chemical igniters. Comparisons of pressure/time recordings also

show that the pressure drop after the explosion is much faster in the 20-L-Explosion Vessel. Consequently, a correction has to be made. With both (automatic) corrections, the P_{ex} value measured in the 20-L-Explosion Vessel agree excellent with those measured in the 1m^3 vessels. Figure 2.5 is a pressure/time diagram that linked a few terms used in using 20-L-Explosion Vessel.

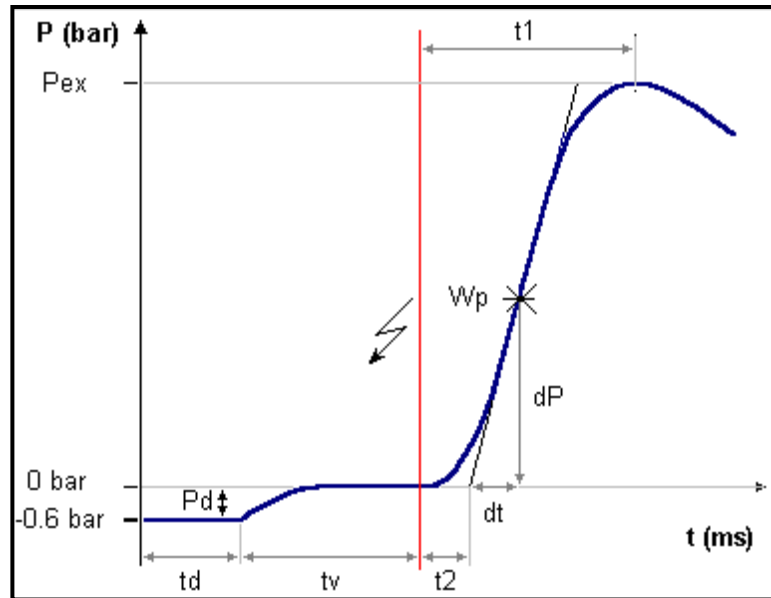


Figure 2.7 Pressure/ Time Diagram of a Fuel Explosion

Source: Cesana, 2001.

From Figure 2.5, P_{ex} is the explosion overpressure. It is the difference between the pressure at ignition time (normal pressure) and the pressure at the peak point. Because of this explosion vessel has a volume of 20 liter, the explosion overpressure, P_{ex} , must undergo some corrections in values. This is where P_m comes from. By definition, P_m is the corrected explosion overpressure due to cooling and pressure effects caused by the chemical igniters in the 20-L-Explosion Vessel (Cesana, 2001). On the other hand, P_{max} is the typical pressures generated by the closed gas. It helps to describe the explosion behavior of gases. P_{max} is very crucial in order to know the highest pressure to be expected, should a gas explosion occur within the equipment (Kasmani,

2011). We can see t_d and t_v in the figure too. t_d is time-delay of the outlet valve while t_v is the ignition delay time. t_d can also be defined as time between electrically activating the valve and beginning of pressure rise in the 20-L-Explosion Vessel. This time-delay has to be in the range of 30 to 50 ms; otherwise the valve and the dispersion device are probably dirty. On the other hand, t_v can influence the degree of turbulence. This is the most important control parameter. Apart from that, the minimum volume for the explosion testing of gas or solvent vapor / air mixtures is 1 liter. Therefore, the 20-L-Explosion Vessel is suitable for the explosion testing of gases and vapors (Cesana, 2001).

In an explosion, minimum ignition energy is a measure of sensitivity to ignition by electrostatic discharge. Minimum ignition energy is increasing with the reduction of pressure. It requires a large particle size, low volatile content substance and reducing values of K_{st} and P_{max} in purpose to increase the ignition energy. But, to minimize the ignition energy, amount of O_2 must be lowered down (Lewis *et al.*, 1968).

Besides ignition energy, another important term in dealing with explosion is the minimum ignition temperature. Minimum ignition temperature is a measure of sensitivity to ignition by hot surfaces, friction sparks and electrical equipment. The lowest temperature of the heated impact plate at which the gas inserted into the oven ignites producing flames or explosion in less or equal to 10 seconds (Kasmani, 2011).

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

Materials that have been used in this experiment were obviously gases of CO₂ and LPG. CO₂ which added into the vessel according to the percentages that have been agreed which were 5 %, 10 % and 15 %. The percentage, as stated before, is based on the volume of CO₂ per summation of fuel (in this case LPG) and CO₂ volume. However, the percentage then converted into partial pressure before it was inserted into the vessel.

Figure 3.1 is the general arrangement of overall set of the 20-L-Explosion Vessel including the vessel itself, computer and supplied gas as well as the KSEP 320 special tools.

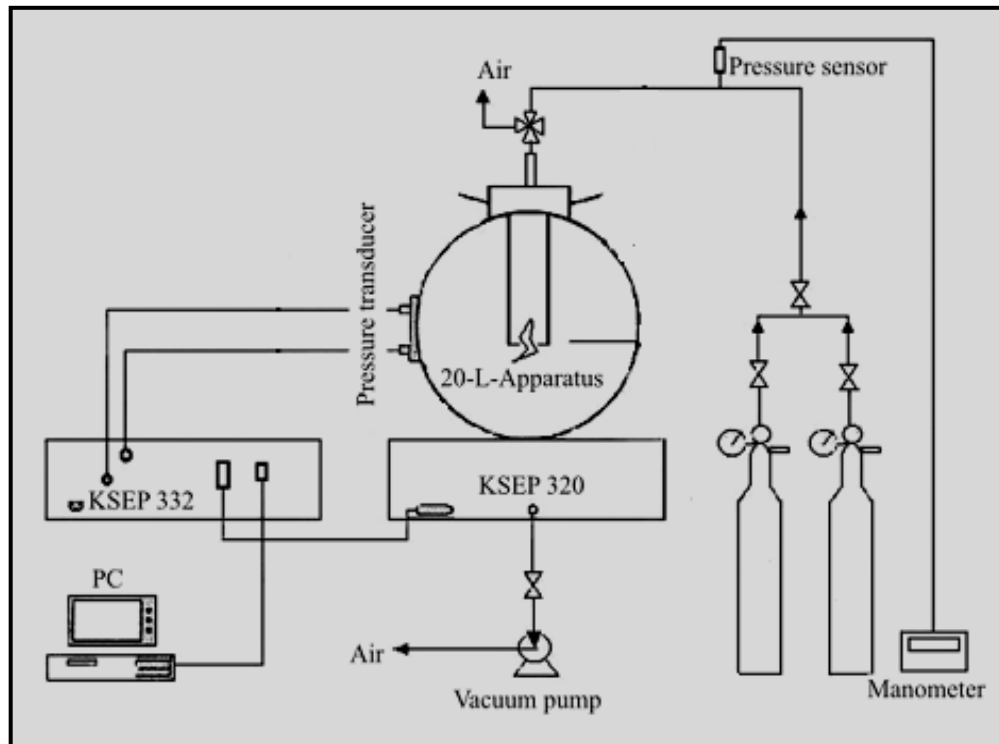


Figure 3.1 The Schematic Diagram of Experimental Set Up

Source: Cesana, 2001

From Figure 3.1, KSEP 320 unit has used piezoelectric pressure sensors to measure the pressure as a function of time and control the valves as well as the ignition system of the 20-L-Explosion Vessel. The measured values were processed by a personal computer which was digitized at high resolution. The use of two completely independent measuring channels had gives good security against erroneous measurements and allowed for self checking (Cesana, 2001).

3.2 EXPERIMENT PROCEDURES

In order to obtain the required results, proper procedures have been done while experimenting. The same things went to this study where the usage of 20-L-Explosion Vessel was applied. Figure 3.2 is the clearer view of the 20-L-Explosion Vessel.

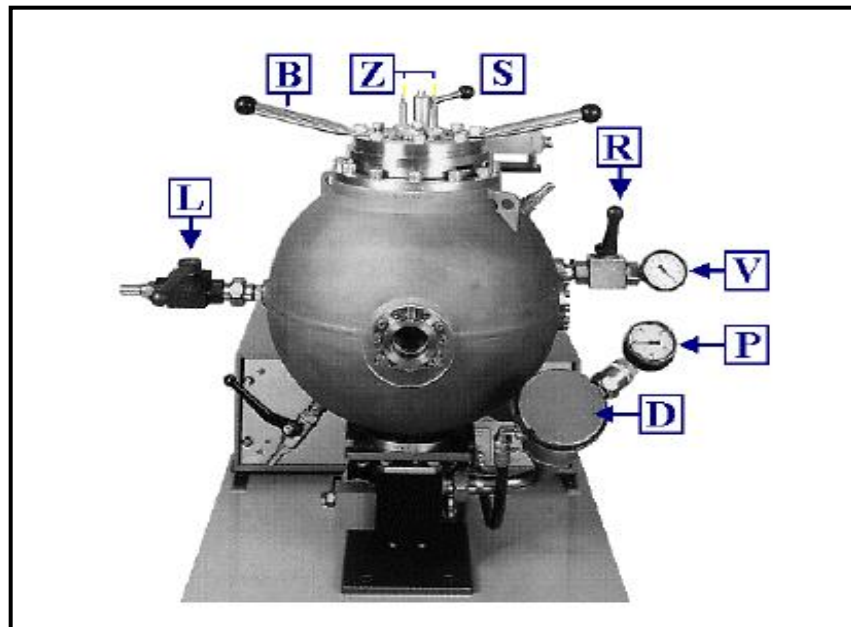


Figure 3.2 A 20-L-Explosion Vessel with Labels

Source: Cesana, 2001

From Figure 3.2, the labeled parts are:

- B = bayonet-ring
- S = safety switch
- R = valve to vacuum pump
- V = pressure indication in sphere
- P = pressure indication for air
- L = ball valve for ventilation

As for the procedures, the standard steps were following the guide prepared by Kühner (2001). Because the equipment was high-technology equipment, first step was surely by turning on all programs as well as the personal computers. Before any run was

carried out, cleaning of the inside of the vessel has been done. In order to do this, the cover of the explosion vessel was opened by making sure that the safety switch (S) was opened while the bayonet ring (B) was turned over following anti clock wise direction. Inside the vessel, a special section was prepared for entering igniters. After brief cleaning procedures, the igniters' area which situated parallel to the electrode rod that connected to the cover of the vessel was filled with a 10 J igniter. Figure 3.3 shows the specific position of igniters and electrode.

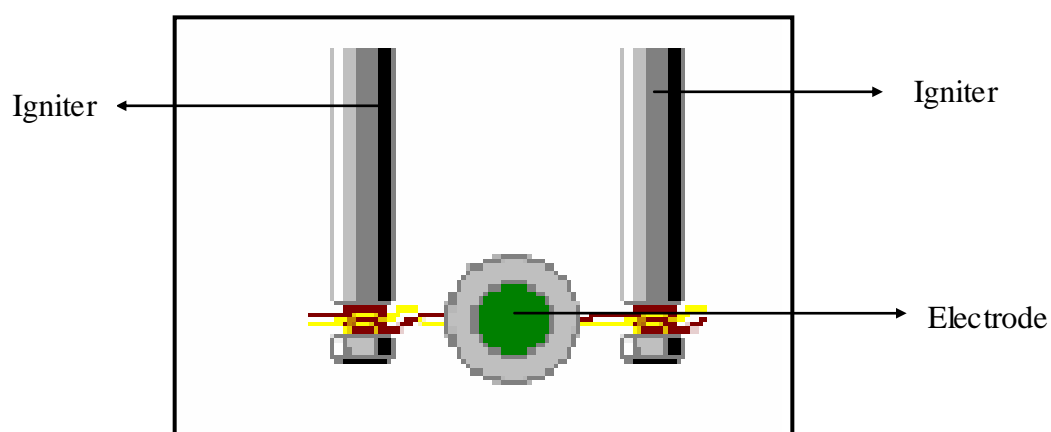


Figure 3.3 The Diagram of The Electrode Between The Two Igniters.

Source: Cesana, 2001

When the insertion of igniters was done, the cover then placed back on the vessel and the ignition line (Z) connected. After this process, the vessel must be vacuumed in order to give a more precise value of gas proportions inserted later. The ball valve (L) and ball valve (R) were opened before starting the vacuum pump before the vessel was evacuated to 0.1 bar absolute. The ball valve (R) was then closed.

After everything on the vessel was set up properly, the next steps was involving the computer. The software of KSEPT 6.0 was set up. The test conditions data were filled up in the software as shown in Figure 3.4.

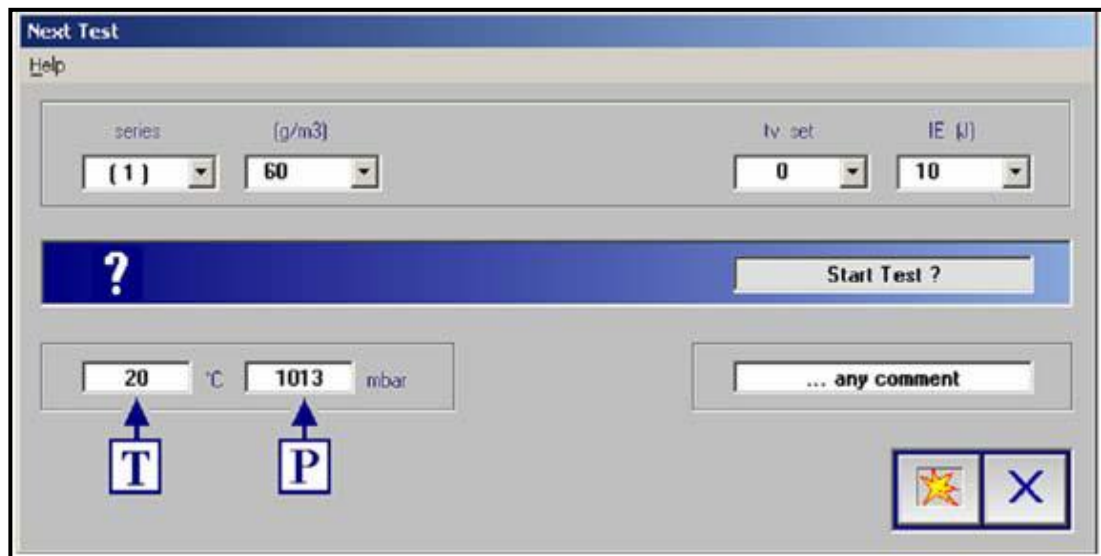


Figure 3.4 The Test Conditions Data that have been Filled Up in the KSEPT 6.0

Source: Cesana, 2001

In order to determine the effect of CO₂ gas to the LFL and UFL of LPG, the equipment was properly vacuumed to avoid any disturbances from foreign gases. The experiment set up was then key-in into the software before the LPG-air mixture ignited. The first combination of LPG-air mixture percentage was then fed in. The explosion was occurred shortly after that and the pressure-time variation during the explosion was recorded. After each explosion, the vessel was cleaned up before proceeding with the next combination of LPG-air mixture percentage. To understand the procedures better, Figure 3.5 shows the simplified procedures' sequence of the experiment.

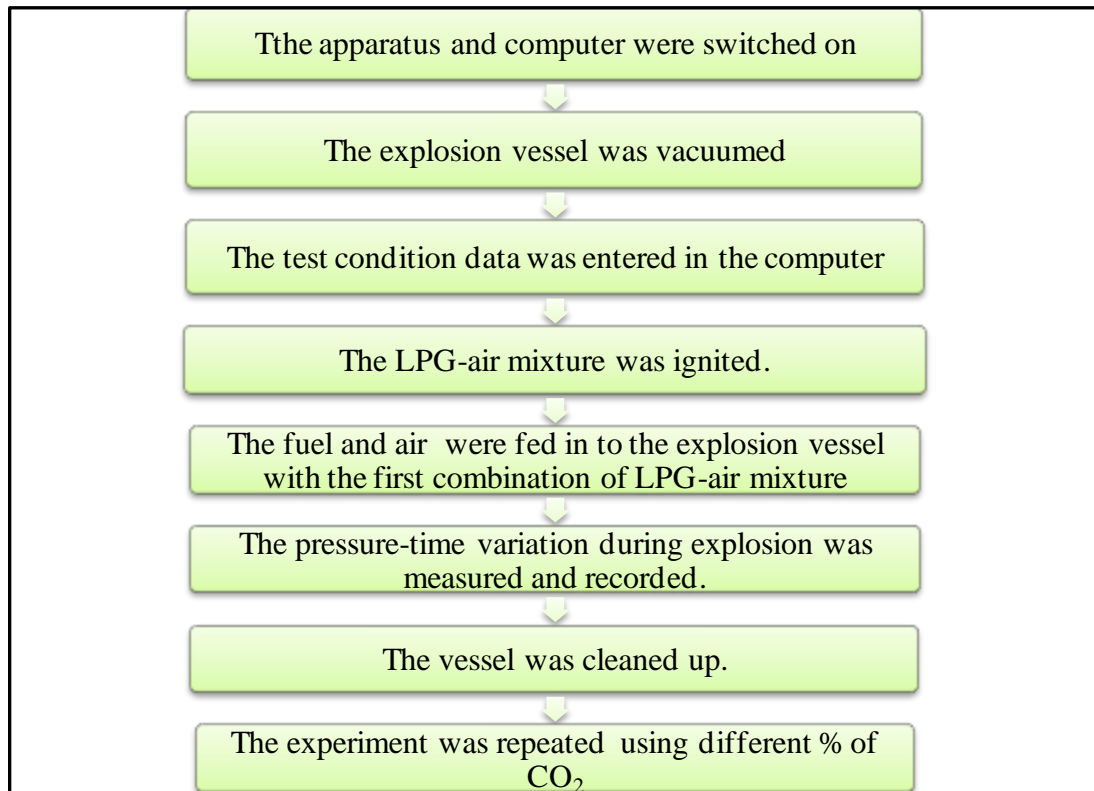


Figure 3.5 The Sequence of The Experimental Work

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

Essentially, the 20-L-Explosion-Vessel can give very little visual observation on result obtained from the experiment. Observation can only be visually done by looking from a small, round porthole on the outside body of the vessel. One can see quite clearly on magnitude for explosion in each run.

Yet, the 20-L-Explosion-Vessel was equipped by a modern, specialized computer program, KSEPT 6.0. The program was installed in the computer which has been programmed to be connected with the vessel. For each run, KSEPT 6.0 gave a set of table containing a few required data and also provided some graphs according to the data obtained. Figure 4.1 shows an example of the attained result transformed into graph by the program while Figure 4.2 is an example of summary table done automatically by the program after each set of experiment completed.

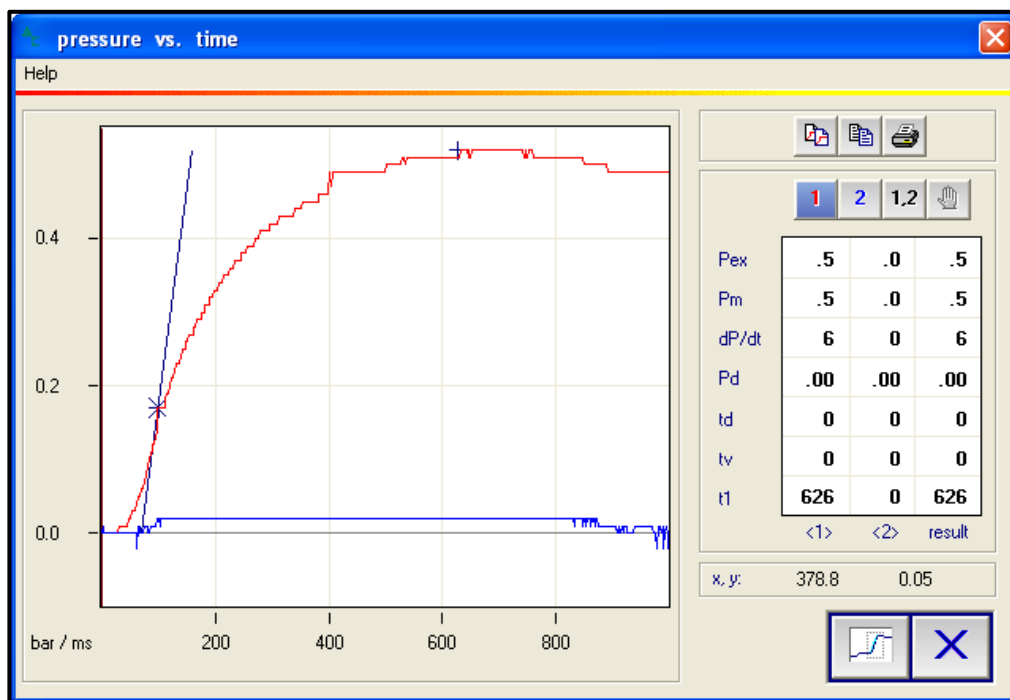


Figure 4.1 Example of Graph Constructed by KSEPT 6.0 for Each Run

test	conc.	Pm	dP/dt	t1	tv	IE	O2
1 (1)	1.0	.0	0	0	0	10J	
2 (1)	2.0	2.4	30	289	0	10J	
4 (1)	3.0	.3	6	625	0	10J	
5 (1)	4.0	.0	0	0	0	10J	

[series] vol% bar bar/s ms ms J %

Figure 4.2 Overall Summary Table Constructed by KSEPT 6.0 after Each Set of Experiment Done

For this result and discussion section, the average data for every run have been considered. This was intentionally done to ensure the precision of result utilized will be high. On top of that, one set of data used for this section was taken from previous research done by Kadir (2010). Table 4.1 provides the experimental result of LPG-air mixture with no addition of diluents.

Table 4.1 Experimental Results of LPG-Air Mixture with No Addition of Diluents

Run	Partial P of LPG in 1 bar Sphere	% Vol. of LPG	Partial P of CO ₂ in 1 bar sphere	% Vol. of CO ₂	Partial P of air in 1 bar sphere	P _m
1	0.012	1	0	0	0.776	0.0
2	0.024	2	0	0	0.752	0.0
3	0.036	3	0	0	0.728	2.3
4	0.048	4	0	0	0.704	2.8
5	0.060	5	0	0	0.760	1.4
6	0.072	6	0	0	0.728	0.1
7	0.084	7	0	0	0.716	0.0

Source: Kadir, 2010

From Table 4.1, the graph of flammability limit of LPG-air mixture with no addition of any diluents was plotted and shown in Figure 4.3. From the figure we can see that the flammability limit for pure LPG-air mixture is relatively small.

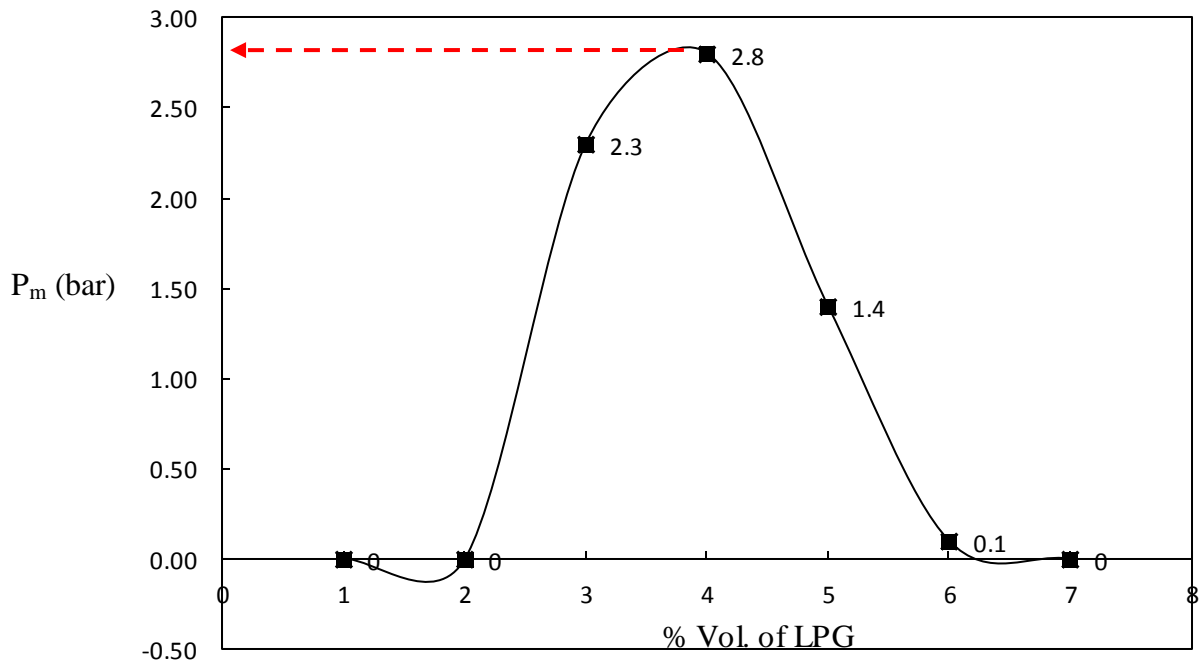


Figure 4.3 Graph of LPG-Air Mixture with No Addition of Diluents

Source: Kadir, 2010.

From Figure 4.3, it is clear that the LFL of LPG-air mixture is 2 % vol. and the UFL of LPG-air mixture is 6.2 % vol. P_{max} is happening at % vol. of 4 with the value of 2.8 bar. The range of flammability limit of this LPG-air mixture is 4.2 % vol.

4.2 EXPERIMENTAL RESULT OF LPG-AIR MIXTURE WITH CO₂ ADDITION

Intended for this research, there were three set of experiments done with three different amount of CO₂ added. The amount of CO₂ added was measured by volume percent of CO₂ in total mixture. It is believed that dilution involving the presence of CO₂ is better below 15 % range (Karim, 2010). So, the most suitable values for this need are 5 %, 10 % and 15 %.

4.2.1 Effect of 5 % CO₂ Addition to LFL and UFL of LPG-Air Mixture

Table 4.2 Experimental Results of LPG-Air Mixture with 5 % Addition of CO₂

Run	Partial P of LPG in 1 bar Sphere	% Vol. of LPG	Partial P of CO ₂ in 1 bar sphere	% Vol. of CO ₂	Partial P of air in 1 bar sphere	P _m
1	0.012	1	0.060	5	0.728	0.0
2	0.024	2	0.060	5	0.716	1.9
3	0.036	3	0.060	5	0.704	2.5
4	0.048	4	0.060	5	0.692	2.6
5	0.060	5	0.060	5	0.680	0.8
6	0.072	6	0.060	5	0.668	0

Table 4.2 shows the completed experimental values of 5 % vol. of CO₂ that have been added into the LPG-air mixture. A graph P_m versus % vol. of LPG was constructed and shown in Figure 4.4.

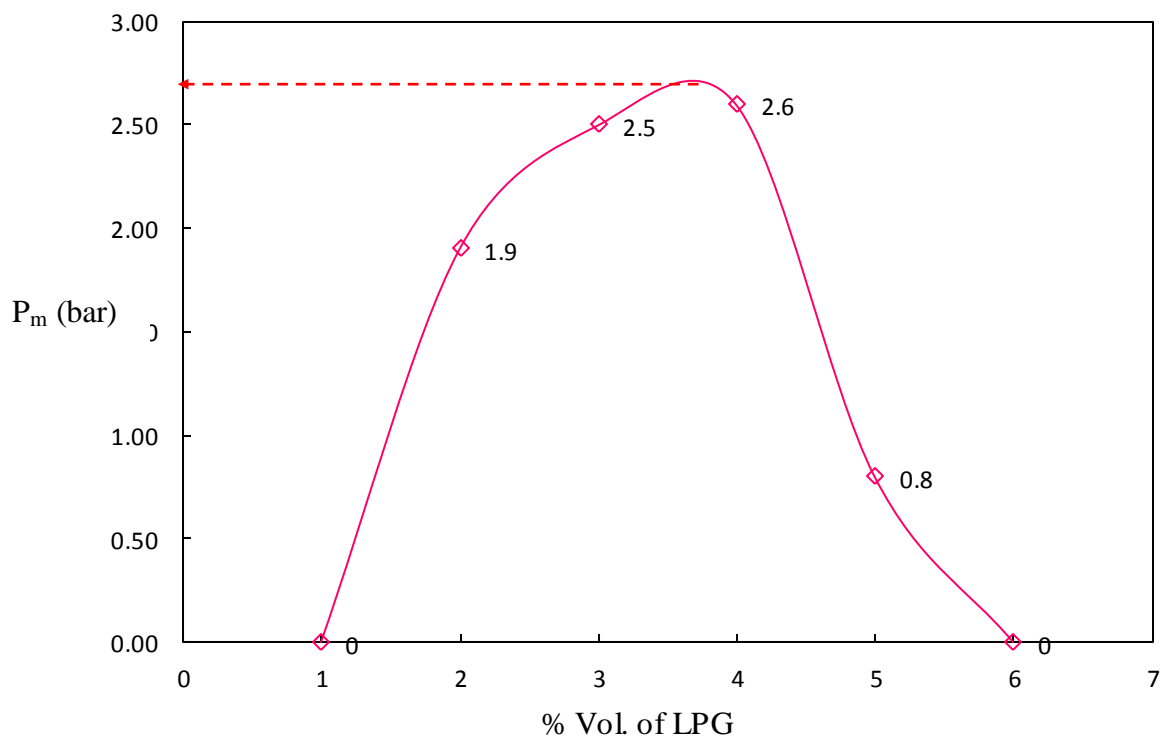


Figure 4.4 Graph of LPG-Air Mixture with 5 % Addition of CO_2

It can be seen that in Figure 4.4, after the addition of 5 % of CO_2 , the LFL of LPG-air mixture seemed to change its position from 2 % vol. (for no addition of CO_2) to 1 % vol. for the addition of 5 % vol. of CO_2 . On the other hand, the UFL of LPG-air mixture was decreased to 6 % vol. The value of P_{\max} for this set of experiment is 2.70 bar.

It was quite unexpected that the value of LFL was decreasing instead of increasing. Theoretically, LFL of LPG-air mixture was supposed to be increased with the addition of CO_2 while its UFL was supposed to decrease (“Standard for Inert Gas Systems”, 1984). The result obtained might be due to certain errors that occurred while the experimentation. Because of this new trend, the range of flammability limit of LPG-air mixture was increased to 5 % vol. However, still following theoretical suggestion, the value of P_{\max} of LPG-air mixture was reduced to 2.70 bar when 5 % of CO_2 gas was added.

4.2.2 Effects of 10 % CO₂ Addition to LFL and UFL of LPG-Air Mixture

Table 4.3 Experimental Results of LPG-Air Mixture with 10 % Addition of CO₂

Run	Partial P of LPG in 1 bar Sphere	% Vol. of LPG	Partial P of CO ₂ in 1 bar sphere	% Vol. of CO ₂	Partial P of air in 1 bar sphere	P _m
1	0.012	1	0.120	10	0.668	0.0
2	0.024	2	0.120	10	0.656	2.4
3	0.036	3	0.120	10	0.644	0.3
4	0.048	4	0.120	10	0.632	0.0

From Table 4.3, it can be seen that the pattern of the experimentation has changed where less explosions can be observed. It seems like the more percentage of CO₂ added, the lesser possibilities for LPG-air mixture to explode. A graph of P_m versus % vol. of LPG was plotted and can be seen in Figure 4.5.

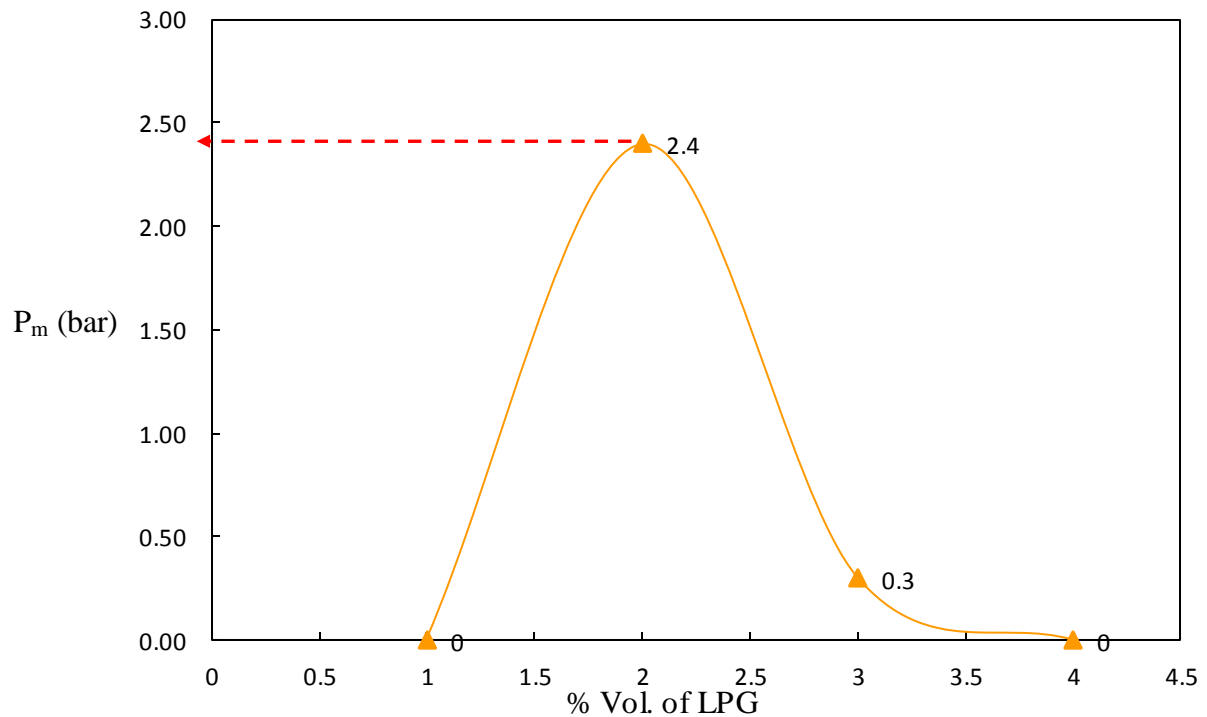


Figure 4.5 Graph of LPG-Air Mixture with 10 % Addition of CO₂

When 10 % of CO₂ was added, quite a significant change can be observed. The UFL of LPG-air mixture was drastically descending to 4.0 % vol. whereas; the LFL of this mixture was disappointingly unchanged from previous value with 1 % vol. However, the range of flammability limit of LPG-air mixture was finally following the theory of inerting. The range was reduced to 3.0 % vol. after the addition of 10 % CO₂.

Still on the exact track, the value of P_{max} for this set of experiment was gradually decreased to 2.40 bar from 2.70 bar for the previous data.

It was still blurry why the LFL of LPG-air mixture was still unaffected by the increment of CO₂ percentage. If compared from previous studies done by Chen *et al.* who had done the research by using different kind of diluents which is N₂, the results obtained by them was also gave minimal impacts towards the LFL values of their selected fuels. As for that study, they believed that the situations can be solved by doing their own kind of implicit differentiation. From the differentiation, they believed that it was quite common that diluents gave minimal effects to LFL values for any hydrocarbon gases. Although this bizarre behavior was observed, the overall flammability limit of LPG-air mixture was so far magnificently declining.

4.2.3 Effects of 15 % CO₂ Addition on LFL and UFL of LPG-Air Mixture

Table 4.4 Experimental Results of LPG-Air Mixture with 15 % Addition of CO₂

Run	Partial P of LPG in 1 bar Sphere	% Vol. of LPG	Partial P of CO ₂ in 1 bar sphere	% Vol. of CO ₂	Partial P of air in 1 bar sphere	P _m
1	0.012	1	0.180	15	0.608	0.0
2	0.024	2	0.180	15	0.596	1.5
3	0.036	3	0.180	15	0.584	1.1
4	0.048	4	0.180	15	0.572	0.0

In Table 4.4, the data that have been successfully obtained were quite similar from the previous set. To give clearer view, a graph of P_m versus % vol. of LPG was plotted and can be seen in Figure 4.6.

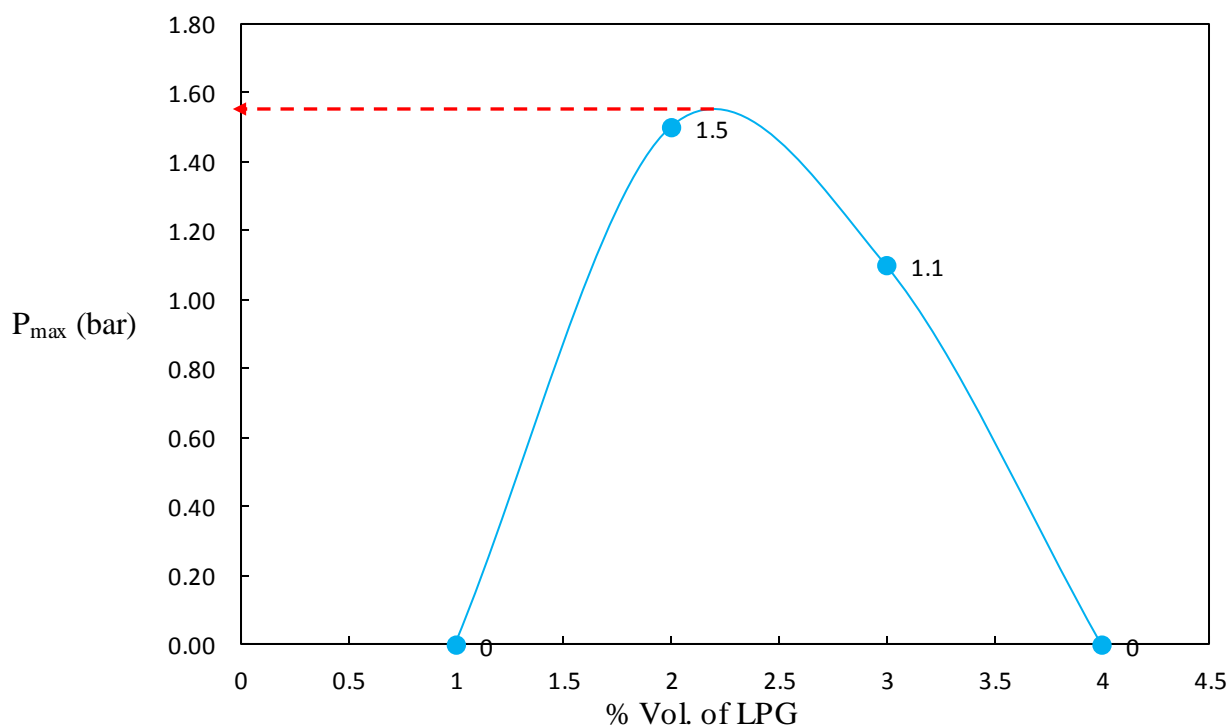


Figure 4.6 Graph of LPG-Air Mixture with 15 % Addition of CO_2

After the next set of experiment was conducted, the outcome was quite unsatisfactory when it was found that the range of flammability limit of LPG-air mixture was maintained at 3 % vol. The value of LFL of this mixture seemed to be motionless by maintaining its position at 1 % vol. while the UFL was unexpectedly static at 4 % vol.

The results were probably influenced by the inaccuracy of procedures taken while carrying out the experiment. As for the P_{max} value for this case, the value was kept on dropping to 1.56 bar at the addition of CO_2 is equal to 15 %.

So as to give a clearer view on how the effect of CO₂ affecting the whole set of experiments; Table 4.5 was constructed by using overall data from each set of experiments.

Table 4.5 Comparison Data for LPG-Air Mixture With and Without the Addition of CO₂

Run	% Vol. of LPG	P _m (bar)			
		LPG	LPG + 5 % CO ₂	LPG + 10 % CO ₂	LPG + 15 % CO ₂
1	1	0.0	0.0	0.0	0.0
2	2	0.0	1.9	2.4	1.5
3	3	2.3	2.5	0.3	1.1
4	4	2.8	2.6	0.0	0.0
5	5	1.4	0.8	0.0	0.0
6	6	0.1	0.0	0.0	0.0
7	7	0.0	0.0	0.0	0.0

From the table of combination of overall data (Table 4.5), it is quite obvious that results for 10 % and 15 % addition of CO₂ gave less readings if compared to the first data obtained. A graph in Figure 4.7 had been constructed so that it will be clear for us to see how the effects of CO₂ towards the LFL and UFL of LPG-air mixture.

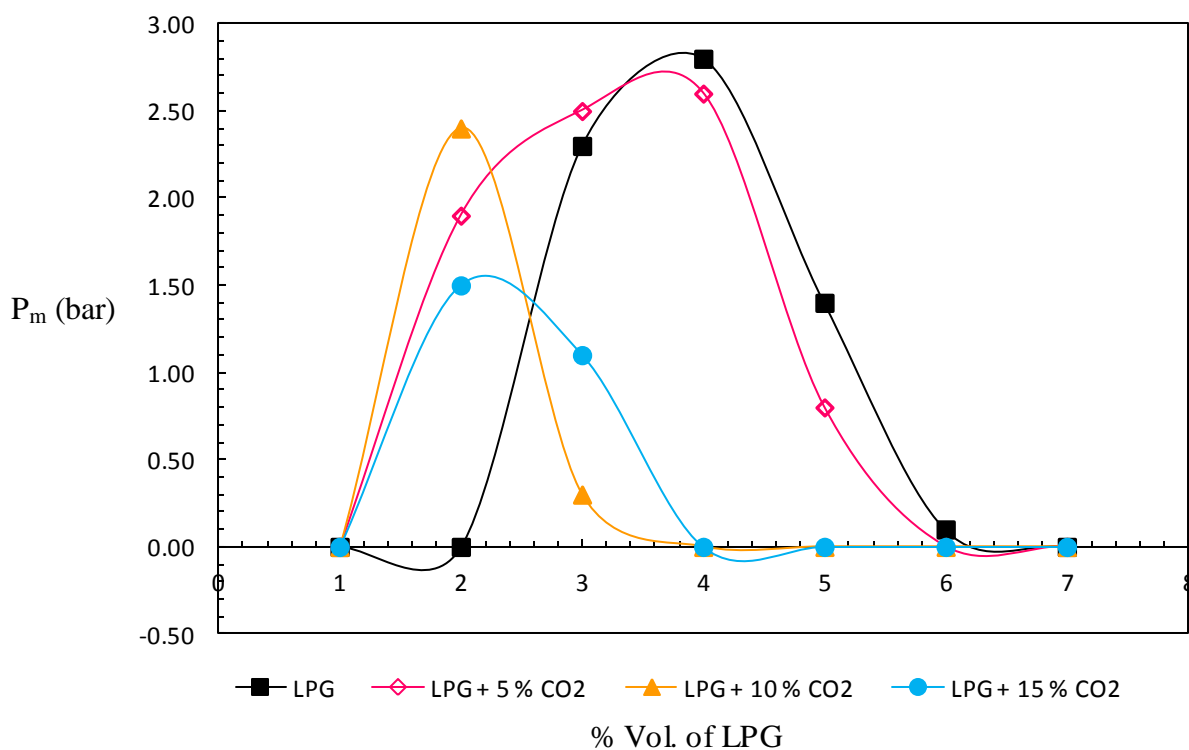


Figure 4.7 Graph of LPG-Air Mixture with Various Concentration of CO₂

As displayed in the Figure 4.7, it can be seen that different percentage of CO₂ had affect the results in different ways. From 0 % to 5 % to 10 % to 15 % of CO₂ addition, it was quite obvious that the overall flammability limit of LPG-air mixture was fairly reduced.

However, when the results were giving a closer look, there were some irregularities here and there. As an example, the value of LFL of LPG-air mixture was initially assumed to be increased in order to help narrowing down the range of flammability limit was proven decreased from one point of % vol. to another before statically unaffected for the rest of the experiments. Besides that, the value of UFL obtained in the beginning of these experiments was quite satisfying as it followed the theories of inerting well. Approaching the last set of the experiment, it was quite unexpected that the value of UFL was finally maintained which made it unparallel with

the result studied. Because of this, the range of flammability limit which at first algorithmically going down, was also affected.

For additional information, this study was still helped to prove that the addition of CO₂ can still reduce the hazards of explosion by deescalating the P_{max} of LPG-air mixture. A lower value of P_{max} indicated a slower magnitude of explosion of any exploded substances (Kasmani, 2011).

As the results obtained in this research were quite contrasting from theories suggested by the Standard for Inert Gas Systems” (1984), it must be some slip-ups in the experimentation. Possibilities of errors include; inaccuracy in inserting amount of gases into the explosion vessel due to inability to adjust the valve perfectly according to the pressure gauge scale, chemical interruptions to the explosion process due to imperfectly clean inner side of the vessel wall from previous run which may contain carbons and water droplets and also effects from surrounding temperature at which the experiments were carried out. Besides that, the difference in results obtained from previous studies done by researchers around the world might be caused by the different quality of LPG used based on which country they were originated. The different compositions of LPG used probably gave dissimilar outcomes in the result attained.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The improvement of technology in controlling the flammability limit of LPG-air mixture is expanding day by day. The applications of inert gases naturally existed in atmosphere have been wisely exploited. With proper studies and researches, probably there will be many other studies regarding the same technical purpose will be emerging.

As for this study, the results were concluded to be fairly tagged along with the theoretical assumptions. But still, the objective of the study which is to study the effect of CO₂ gas to the flammability limit of LPG was achieved after undergoing several procedures before collecting the results.

From there, it can be wrapped up that the existence of CO₂ gas in an LPG-air mixture will somehow reduce the width of flammability range of the mixture by only decreasing the value of UFL without disquieting the value of LFL of LPG-air mixture. The flammability limits range was successfully reduced from 4.2 % vol. to 3 % vol. of LPG. Besides that, the magnitude of explosion was also reduced, identified from the gradually decreased amount of P_{max} which had reduced from 2.80 bar to 1.56 bar.

5.2 RECOMMENDATIONS

After finishing the overall studies on this research, a few recommendations and suggestions need to be taken into consideration for any possibilities of further studies.

- i. The percentage of CO₂ used in this research should be varied more closely from one value to another. By doing this, enhanced observations on effects adding CO₂ into the LPG-air mixture can be obtained. The best range of CO₂ percentage to be considered is from 5 % vol. to 10 % vol.
- ii. The objective of this research supposed to be widened so that the effect of CO₂ gas to the P_{max} of LPG-air mixture can be investigated during the explosion of those mixtures. Once this is done, the significant of the study should be identified in order to give clearer view on the contributions of the research to the society.
- iii. Different types of diluents should be used in further studies such as nitrogen and steam in order to understand the pros and cons of each diluent. Hence, a better selection of inert gas system can be chosen and applied.

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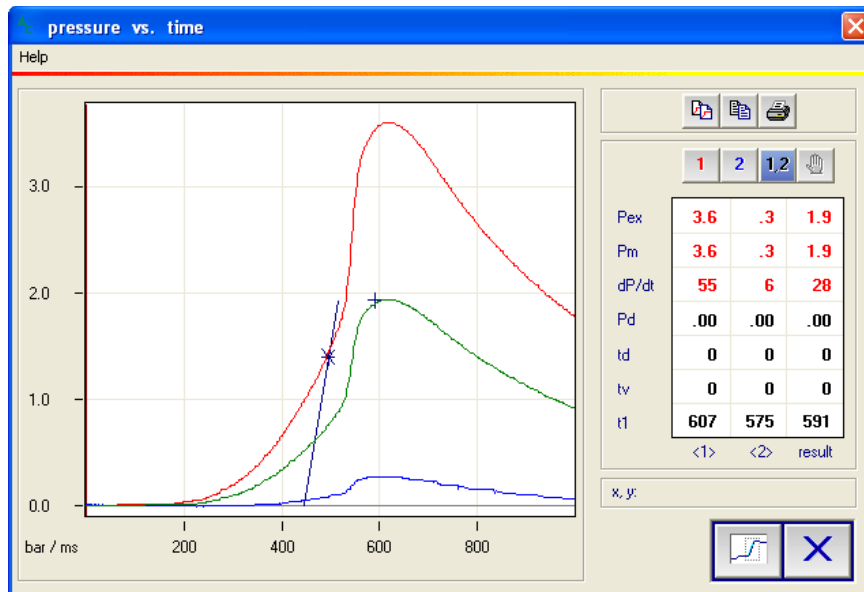
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APPENDIX A1

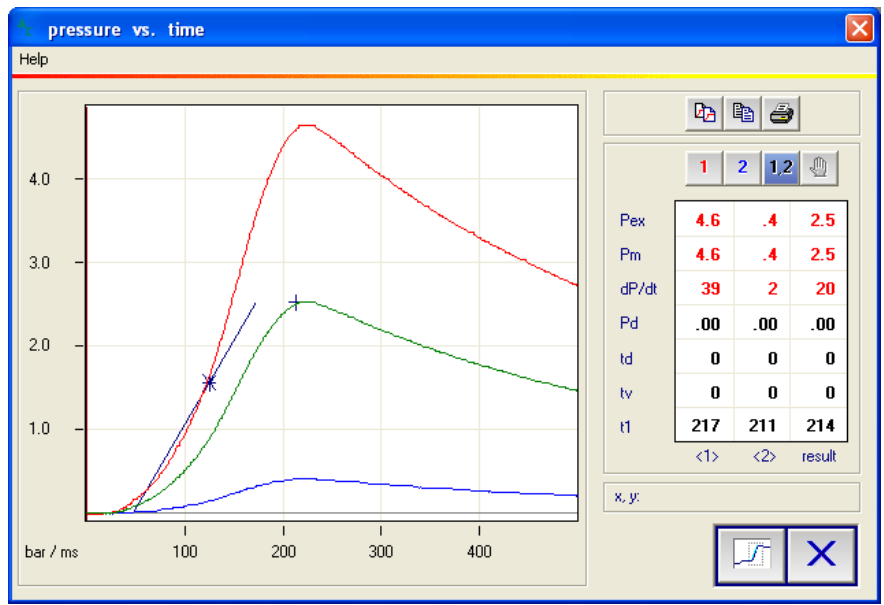
**RAW DATA USED FOR INTERPRETING THE EXPERIMENT INVOLVING
ADDITION OF 5 % OF CO₂**



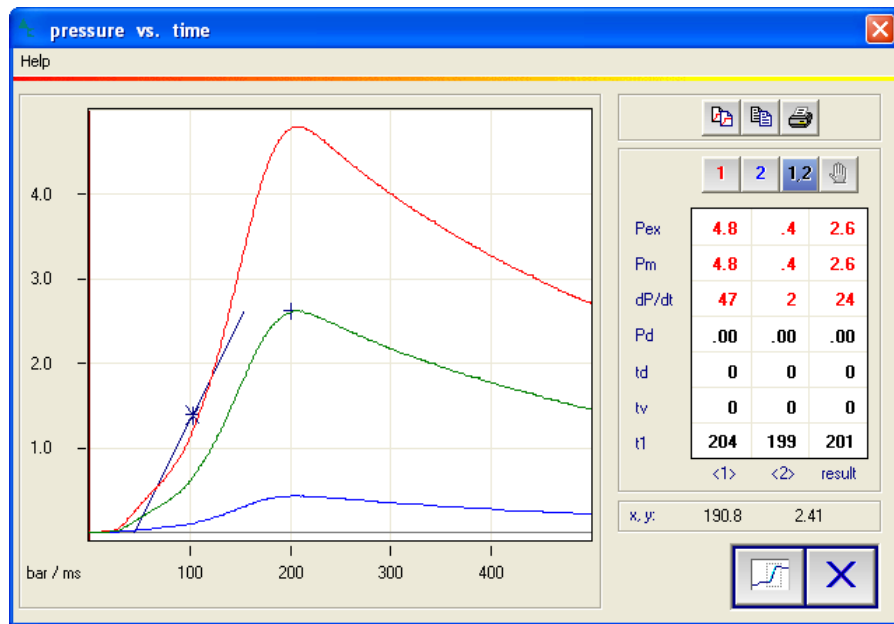
Data at 1 % Vol. of LPG



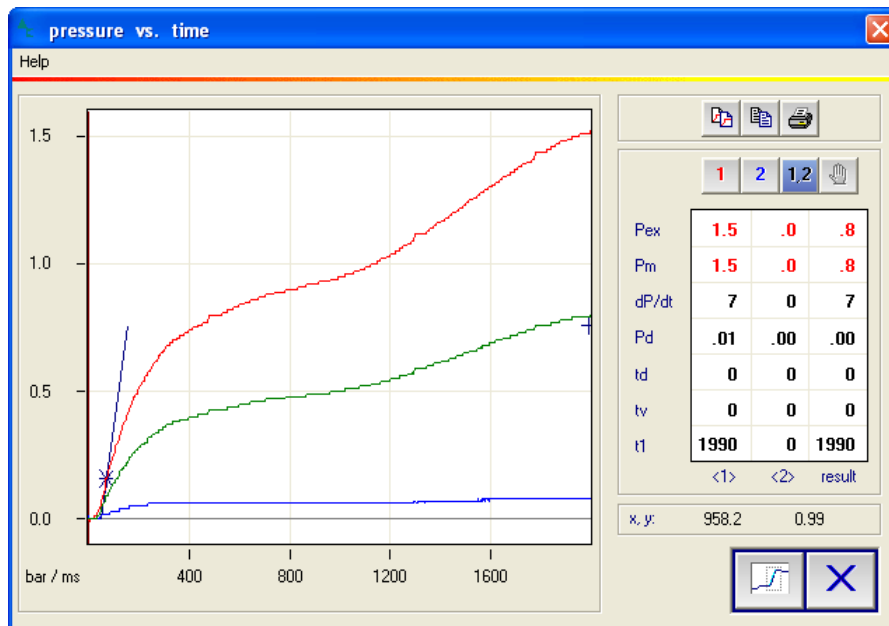
Data at 2 % Vol. of LPG



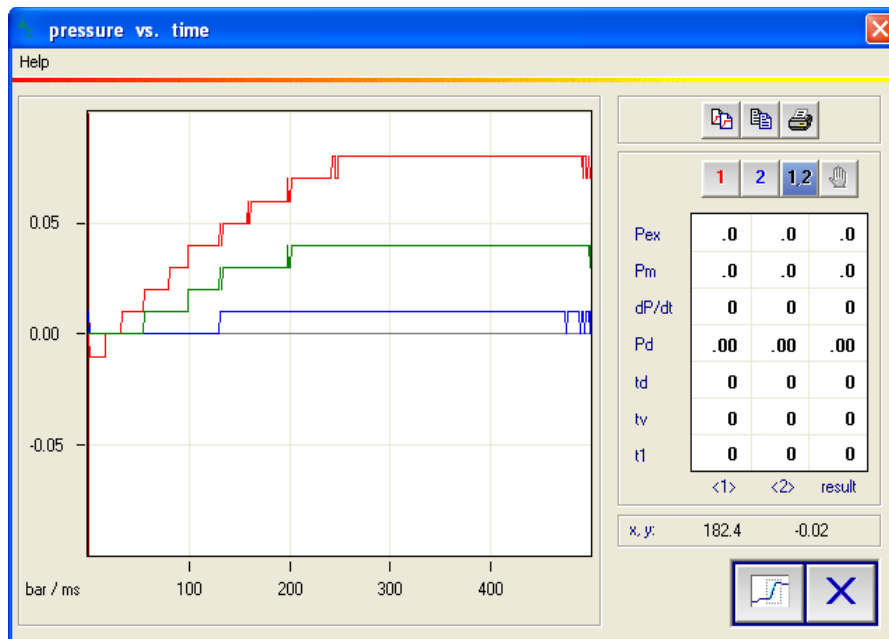
Data at 3 % Vol. of LPG



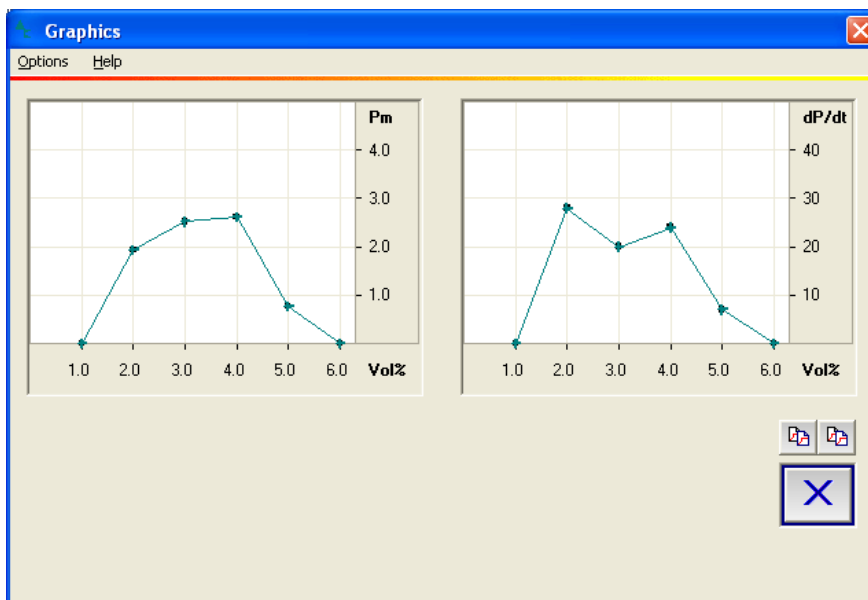
Data at 4 % Vol. of LPG



Data at 5 % Vol. of LPG



Data at 6 % Vol. of LPG



Overall Automated Plotted Graph

KSEP 6.0 f software window showing a summary table for 'LPG+5% CO2 Exp. Syilla'. The table has columns for test, conc., Pm, dP/dt, t1, tv, IE, and O2. The data is as follows:

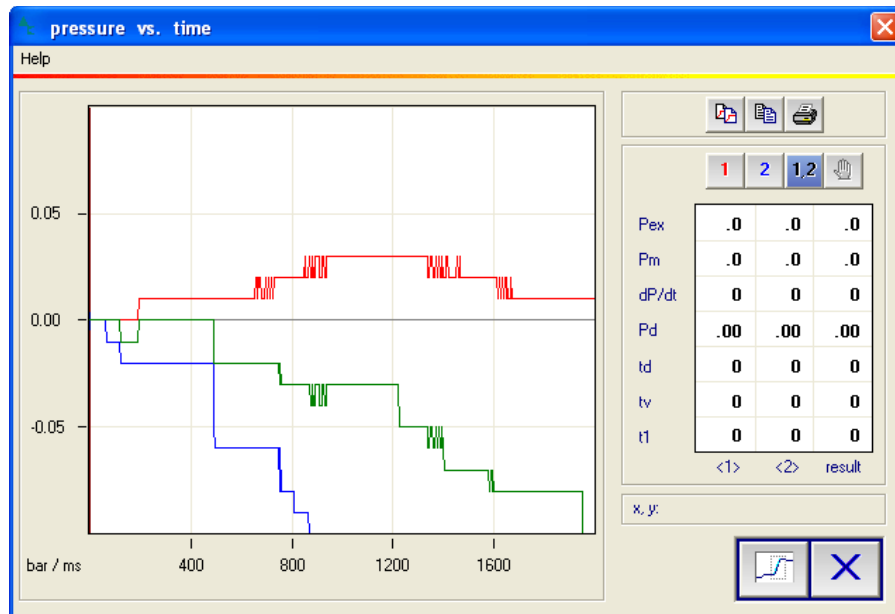
test	conc.	Pm	dP/dt	t1	tv	IE	O2
1 (1)	1.0	.0	0	0	0	10J	
2 (1)	2.0	1.9	28	591	0	10J	
3 (1)	3.0	2.5	20	213	0	10J	
4 (1)	4.0	2.6	24	201	0	10J	
5 (1)	5.0	.8	7	1990	0	10J	
6 (1)	6.0	.0	0	0	0	10J	

Units: (series) vol% bar bar/s ms ms J %

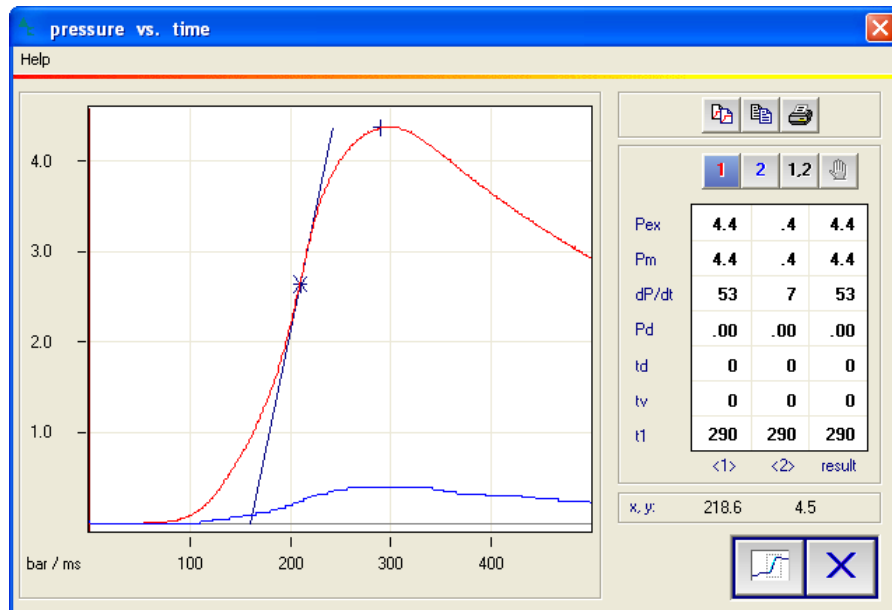
Overall Summary Table

APPENDIX A2

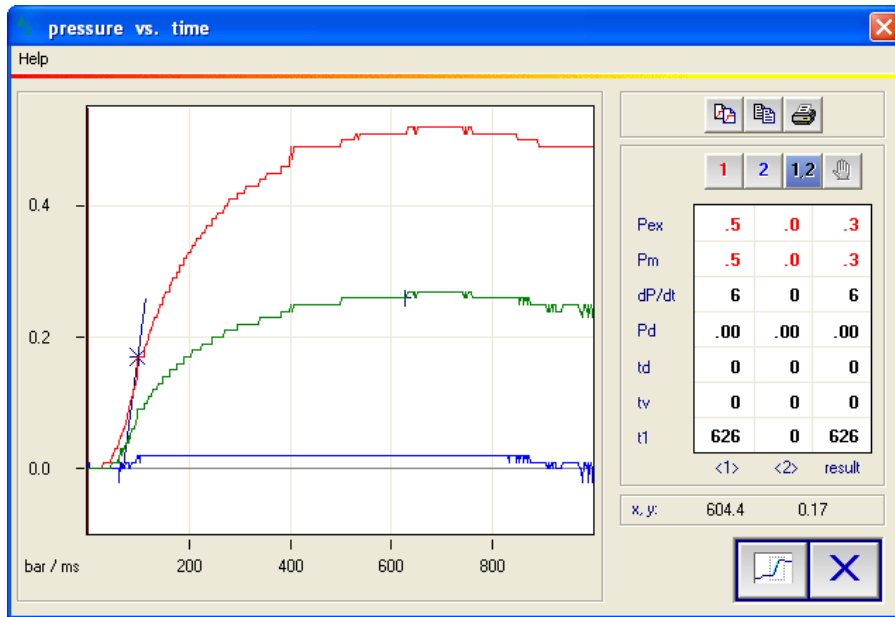
**RAW DATA USED FOR INTERPRETING THE EXPERIMENT INVOLVING
ADDITION OF 10 % OF CO₂**



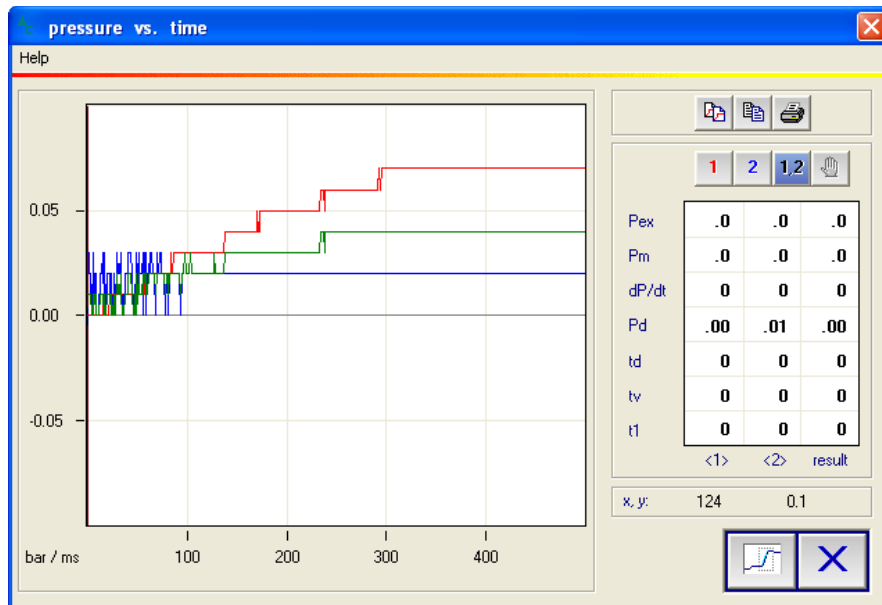
Data at 1 % Vol. of LPG



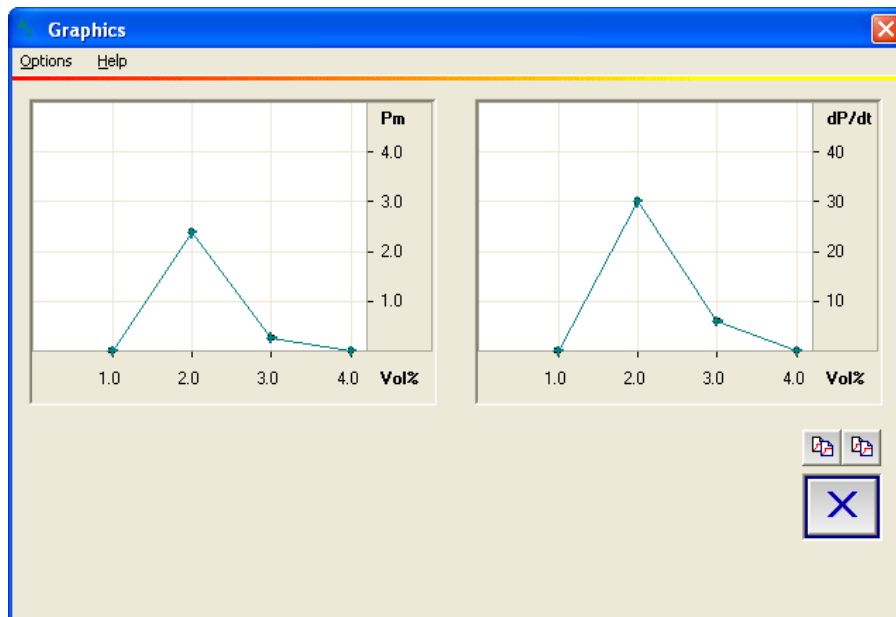
Data at 2 % Vol. of LPG



Data at 3 % Vol. of LPG



Data at 4 % Vol. of LPG



Overall Automated Plotted Graph

KSEP 6.0 f
File Report Tools Help Exit
LPG+CO2(10%) Syilla 2011 Gas, Solvent

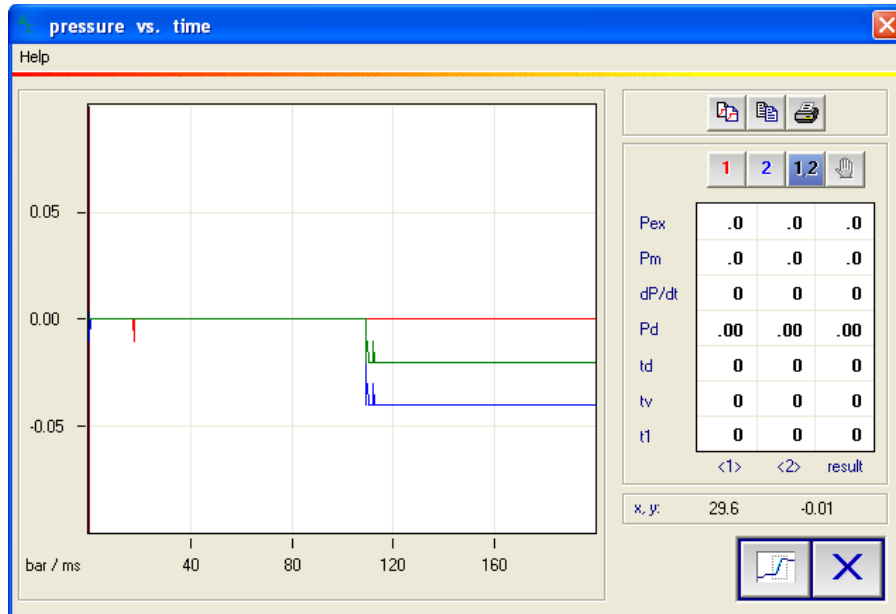
test	conc.	Pm	dP/dt	t1	tv	IE	O2
1 (1)	1.0	.0	0	0	0	10J	
2 (1)	2.0	2.4	30	289	0	10J	
4 (1)	3.0	.3	6	625	0	10J	
5 (1)	4.0	.0	0	0	0	10J	

(series) vol% bar bar/s ms ms J %

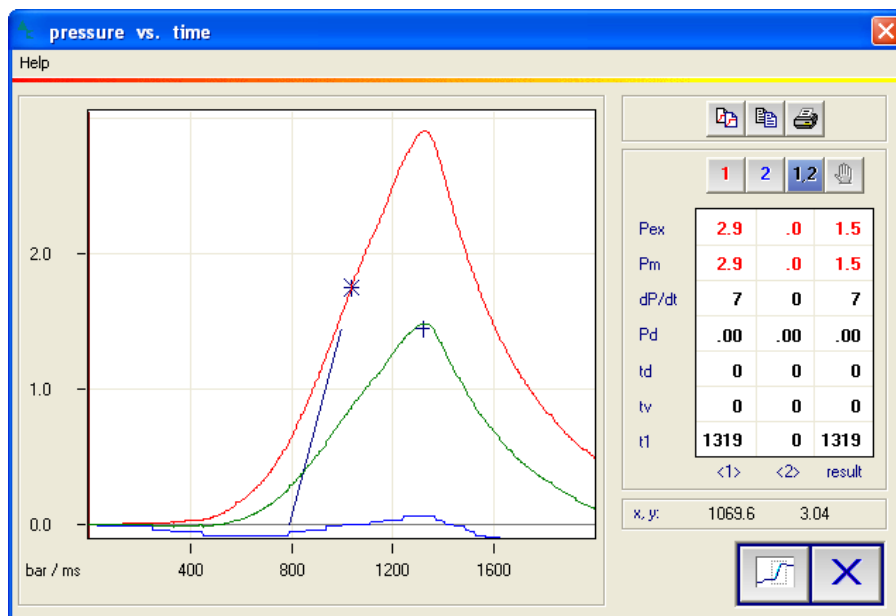
K332AN-9916

Overall Summary Table

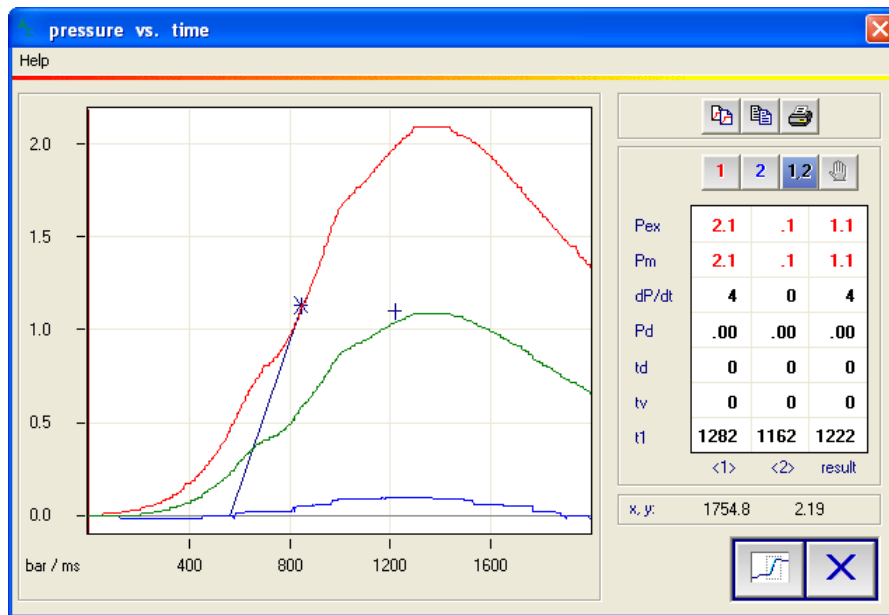
APPENDIX A3

RAW DATA USED FOR INTERPRETING THE EXPERIMENT INVOLVING
ADDITION OF 15 % OF CO₂

Data at 1 % Vol. of LPG



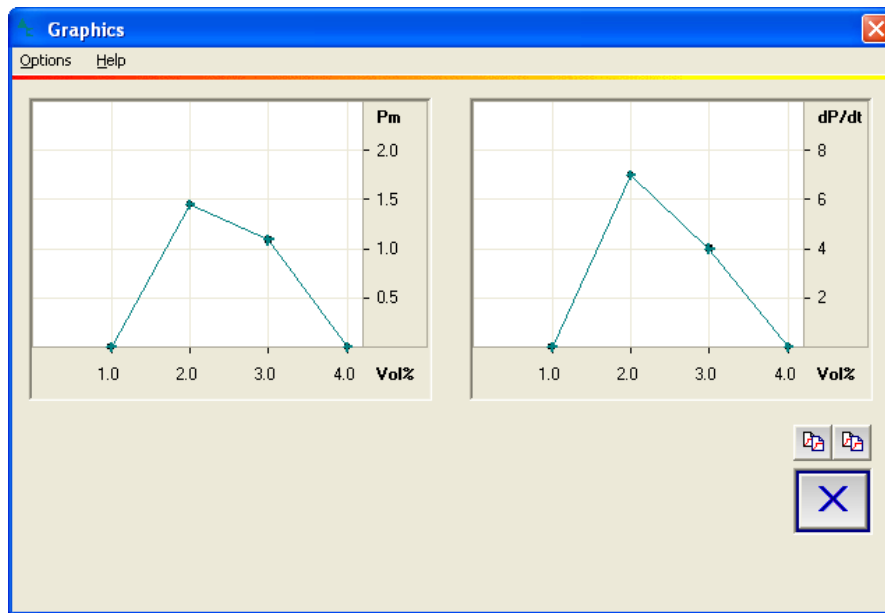
Data at 2 % Vol. of LPG



Data at 3 % Vol. of LPG



Data at 4 % Vol. of LPG



Overall Automated Plotted Graph

KSEP 6.0 f
File Report Tools Help Exit
LPG+CO2(15%) Syilla 2011 Gas, Solvent

test	conc.	Pm	dP/dt	t1	tv	IE	O2
1 (1)	1.0	.0	0	0	0	10J	
2 (1)	2.0	1.5	7	1318	0	10J	
4 (1)	3.0	1.1	4	1222	0	10J	
5 (1)	4.0	.0	0	0	0	10J	

(series) vol% bar bar/s ms ms J %

K332AN-9916

Overall Summary Table