THE EFFECT OF HYDROGEN ENRICHMENT ON EXPLOSIVE LIMITS IN LIQUEFIED PETROLEUM GAS

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ABSTRACT

The use of hydrogenated fuels shows considerable promise for applications in gas turbines and internal combustion engines. The aims of this study are to determine the explosive limits of liquefied petroleum gas/air mixture and to investigate the effect on explosive limits liquefied petroleum gas/air mixture enriched up to 8 vol % hydrogen by total volume at atmospheric pressure and ambient temperature. The experiments were performed in 20 Liter closed explosion vessel. The mixtures were ignited by using spark permanent wire that placed at the centre of the vessel. The pressure-time variations during explosion of liquefied petroleum gas/air mixture in explosion vessel were recorded. The explosion pressure data is used to determine the explosive limits which flame propagation is considered to occur if explosion pressure greater than 0.1 bar. In this study the result shows the explosive limits is from 2 to 8 vol % of liquefied petroleum gas/air mixture and have revealed that the addition of hydrogen in liquefied petroleum gas/air mixture decreases the lower explosive limits from 2 to 1 vol % and for the upper explosive limits, the limits is also decrease from 8 to 7 vol %.

ABSTRAK

Penggunaan bahan api campuran hidrogen boleh diaplikasikan pada gas turbin dan enjin pembakaran. Objektif penyelidikan ini adalah untuk menentukan had pembakaran campuran cecair petrolium gas/udara serta untuk menyiasat kesan penambahan hidrogen sebanyak 8 % daripada jumlah isipadu udara dan bahan api pada tekanan atmosfera dan suhu bilik. Eksperimen ini dilakukan di dalam bekas letupan 20 Liter yang tertutup. Campuran ini dicucuh dengan wayar percikan tetap yang terletak ditengah bekas letupan. Variasi tekanan-masa semasa letupan campuran cecair petrolium gas/udara direkodkan. Data tekanan letupan digunakan untuk menentukan had pembakaran dimana pergerakan nyalaan dianggap berlaku sekiranya tekanan letupan lebih daripada 0.1 bar. Dalam penyelidikan ini, keputusan menunjukkan had pembakaran adalah daripada 2 hingga 8 % daripada isipadu campuran cecair petrolium gas/udara dan penambahan hidrogen dalam pembakaran campuran cecair petrolium gas/udara menurunkan had bawah pembakaran daripada 2 kepada 1 % dan had atas pembakaran turut diturunkan daripada 8 ke 7 % isipadu campuran cecair petrolium gas/udara.

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LIST OF ABBREVIATIONS

ASTM - American Standard Testing Material
BMEP - brake mean effective pressure
CH_4 - methane
CI - compression ignition
CNG - compressed natural gas
CO - carbon monoxide
CO_2 - carbon dioxide
°C - Celsius
GPL - gas petroleum liquid
H_2 - hydrogen
IE - ignition energy
J - Joule
K - kelvin
Kg - vapour/gas deflagration index
L - liter
LPG - liquefied petroleum gas
LEL - lower explosion limit
LFL - Lower Flammability Limit
MOC - minimum oxygen concentration
MPa - megapascal
N_2 - nitrogen
NOx - nitrogen oxide
O_2 - oxygen
Pexp - explosion pressure

Pmax - maximum explosion overpressure

s - second

SI - spark ignition

tv - ignition delay time

t1 - combustion duration

UEL - upper explosion limit

UFL - Upper Flammability Limit

Vol % - - volume percent

THC - total hydrocarbon

CHAPTER 1

INTRODUCTION

1.1 Introduction

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

There are two categories of limits or range for the explosion of the mixture to occur, which are lean limit or lower explosive limit and rich limit or upper limit. The explosion only will occur if fuel and air are mixed within the upper and lower explosive limit.

In many practical applications for power generation, such as gas turbines, there has been strong interest in achieving lean premixed combustion because nowadays, people started to aware about the safety and environment besides concern about the efficiency of the operation (Ramanan and Hong, 1994).

In internal combustion engine there is a situation when we used Liquefied Petroleum Gas (LPG) vehicles, the ‘cold start phenomenon’ is occur at the initial stage of combustion, either in conventional or catalytic combustion. The problem is where by the failure in internal combustion engine increase the volumetric emission produced. This problem can be solved if the combustion can be run at leaner condition.

LPG fuel consists mainly of propane and butane in various proportions according to its state or origin. The composition of LPG fuel varies very widely from one country to another. As one of clean fuel, LPG fuel has attracted increased interest in the recent years (Wang Bin *et al.*, 2008). LPG is extensively used nowadays, both as alternative fuel in automotive engine and as domestic fuel. In comparison with conventional engine fuel (gasoline and diesel), LPG is considered an attractive alternative fuel since its combustion in air is characterized by the reduced emissions of nitrogen oxide (NOx), carbon monoxide (CO) and unburned hydrocarbon.

Hydrogen holds significant promise as a supplemental fuel to improve the performance and emissions of ignited spark and compression ignited engines. Hydrogen has the ability to burn at extremely lean equivalence rations. Hydrogen will burn at mixtures seven times leaner than gasoline and five times leaner than methane (Bauer C and Forest, 2001). This lower limit is governed by the Le Chatelier Principle (Bortnikov, 2007). The flame velocity of hydrogen is much faster than other fuels allowing oxidation with less heat transfer to the surroundings. This improves thermal efficiencies because hydrogen has a very small gap quenching distance allowing fuel to burn more completely (Wang, 2007).

1.2 Problem Statement

Global warming and the need for a stable energy market world wide have resulted in an increased focus on hydrogen as an energy source. A transition solution to the use of pure hydrogen may be the use of mixtures of hydrogen and hydrocarbons, based on both the availability and low cost of petroleum supply within the next decades. Another reason for the increasing interest in the use of internal combustion engines operating on alternative gaseous fuels is the demand for the reduced exhaust emissions combined with improvements in efficiency. Reduced emissions and improvements in efficiency include reduced carbon dioxide (CO_2) emissions, implying less negative impact on the greenhouse effect.

Liquefied Petroleum Gas spark ignition (SI) engines either run stoichiometrically, with exactly enough air for a complete combustion, or with an excess of air named lean burn engine. Running the LPG engine lean has many advantages, such as higher efficiency and lower heat losses. But as the engine runs close to the so called lean limit, problems may occur such as cold start phenomena. The lean limit is the maximum air-fuel ratio where the engine may run without experiencing misfire. This problem can be solved by adding hydrogen to liquefied petroleum gas result in the engine being able to operate with higher air/fuel ratios than without the hydrogen, as a result of the ignition and combustion characteristics of hydrogen.

Therefore, ultra lean limit explosion is needed in order to overcome these problems. This is because the lean premixed explosion conditions make explosion possible at the lower flame or ignition temperature that needed to minimize the nitrogen emission and help to improve fuel efficiency due to improvements in combustion efficiency to start the engine without using petrol.

1.3 Objective of Study

1. To determine the explosive limit of mixed LPG/air mixture in a combustion bomb at atmospheric pressure and ambient temperature.
2. To determine the effect of hydrogen enrichment on explosive limit of mixed LPG/air mixture in a combustion bomb at atmospheric pressure and ambient temperature.

1.4 Scope of Study

This study is conducted to determine the explosive limit of fuel air mixture in a constant volume spherical vessel with a volume of 20 L by using a conventional spark ignition system which is located at the centre of vessel. In this study, butane and propane with 70 % and 30 % purity is used to investigate the explosive limit. The lower explosive limit and upper explosive limit of LPG/air mixture are determined at concentration from 1 to 8 vol %. The effect of hydrogen in LPG/air mixture was investigated at hydrogen enrichment up 8 vol % hydrogen of air by total volume at LPG concentration from 1 to 8 vol %.

1.5 Significant of Study.

The automotive engineering has undergone continuous improvements, but at the same time, various global environmental issues related to vehicle uses are becoming more serious. With the increasing needs to both conserve fossil fuel and minimize toxic emissions, much effort is being focused on the advancement of current combustion technology.

The pollution levels recorded in large urban areas are raising concerns for public health and substantial reductions in pollutant emissions have become an important issue (Heywood and John, 1988). From an environmental point of view there is an increasing interest among the suppliers to investigate LPG as a transportation fuel. It was found that the LPG, roughly a mixture of propane and butane, which gives a benefit in terms of toxic hydrocarbons emissions and ozone formation due to its composition and CO_2 emission levels (Heffel, 2003). Karim *et al.* (1996) described that hydrogen is the primary fuel options under consideration for fuel cell vehicles. The ideal fuel would eliminate local air pollution, reduce greenhouse gas emissions and oil imports (Kim *et al.*, 1999).

Hydrogen, as an energy medium has some distinct benefits for its high efficiency and convenience in storage, transportation and conversion (Ma *et al.*, 2003). Hydrogen has much wider limits of flammability in air than methane, propane or gasoline and the minimum ignition energy is about an order of magnitude lower than for other combustibles (Cracknell *et al.*, 1992) and with hydrogen cold start phenomenon can be solved where it can be used for starting up the engine instead of petrol.

CHAPTER 2

LITERATURE REVIEW

2.1 Flammability

Flammability is a self-sustaining propagation of a localized combustion zone at subsonic velocities. The localized means flame occupies only a small portion of the combustible mixture at any one time. Flammability limits of mixtures of several combustible gases can be calculated using Le Chatelier's mixing rule for combustible volume fractions x_i as shown in equation 1:

$$LFL_{mix} = \frac{1}{\sum \frac{x_i}{LFL_i}}$$

Equation 1

LFL_{mix} : lower flammability of mixtures by volume,
x_i : concentration of component, i in the gas mixture on an air-free basis by volume,
LFL_i : lower flammability for component i by volume.
and similar for UFL.

Temperature and pressure also influences flammability limits. Higher temperature results in lower LFL and higher UFL, while greater pressure increases both values. The effect of pressure is very small at pressures below 10 millibar and difficult to predict, since it has hardly been studied.

2.2 Explosion and Explosive Limit

Explosion may be defined by combustion of combustible mixture (gas cloud), causing rapid increase in pressure. The pressure generated by the combustion wave will depend on how fast the flame propagates and how the pressure can expand away from the gas cloud (governed by confinement).

Explosive limit include the LEL and UEL. The explosion range is from LEL and UEL of a specific substance. Vapour/air mixtures will ignite and burn only over a well-specified range of compositions (Craknell *et al.*, 2002). The LEL/UEL of gas or vapour is the lowest/highest concentration at which gas or vapour explosion is not detected in three consecutive tests. Generally, for a material that lowers the LEL or wider explosion range, the greater its flammability hazard degree would be.

Lower Explosive Limit (LEL) is the limiting concentration (in air) that needed for the gas to ignite and explode. The lowest concentration (percentage) of a gas or a vapour in air will capable of producing a flash of fire in presence of an ignition source (arch, flame, heat). At concentration in air below the LEL there is not fuel to continue an explosion. Concentrations lower than LEL are "too lean" to burn. For example methane gas has a LEL of 4.4 vol %. If the atmosphere has less than 4.4 vol % methane, an explosion will not occur even if a source of ignition is present. When methane (CH_4) concentration reaches 5 vol % an explosion can occur if there is an ignition source. Each combustible gas has its own LEL concentration.

Upper Explosive Limit (UEL) is a highest concentration (percentage) of a gas or a vapour in air capable of producing a flash of fire in presence of an ignition source (arch, flame, heat). Concentration higher than UEL are "too rich" to burn.

2.3 Experimental Method

The standardized measurements of explosive limit are usually in the closed vessels. There are several criteria to determine explosive 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. Measurement of pressure 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 would induce a rapid pressure increase and temperatures 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 measurement is 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 (Jiang *et al.*, 2005).

2.4 Explosion Pressure

Knowledge of pressure-time variation during explosions of fuel-air mixtures in enclosures is a very important component of safety recommendations for wide range human activities, connected to production, transportation or use fuels.

The characteristic parameters of a closed vessel explosion are the explosion pressure, 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:

1. The explosion pressure is the highest pressure reached during the explosion in a closed volume at a given fuel concentration.
2. The maximum explosion pressure is the highest pressure reached during a series of explosions of mixtures with varying fuel concentration.
3. The explosion time is the time interval between ignition time and the moment when the explosion pressure attained.

Explosion pressures and explosion times are important for calculating laminar burning velocities from closed vessel experiments, vent area design, and characterizing transmission of explosion between interconnected vessels (Razus *et al*., 2006).

2.5 Liquefied Petroleum Gas

Liquefied petroleum gas (also called LPG, GPL, LP Gas, or auto gas) is a mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles, and increasingly replacing chlorofluorocarbons as an aerosol propellant and a refrigerant to reduce damage to the ozone layer.

LPG is synthesized by refining petroleum or 'wet' natural gas, and is usually derived from fossil fuel sources, being manufactured during the refining of crude oil, or extracted from oil or gas streams as they emerge from the ground. It currently provides about 3 % of the energy consumed, and burns cleanly with no soot and very few sulfur emissions, posing no ground or water pollution hazards. LPG has a typical specific calorific value of 46.1 MJ/kg compared to 42.5 MJ/kg for diesel and 43.5 MJ/kg for premium grade petrol (gasoline). However, its energy density per volume unit of 26 MJ/l is lower than either that of petrol or diesel.

LPG is a low carbon emitting hydrocarbon fuel available in rural areas, emitting 19 % less CO_2 per kWh than oil, 30 % less than coal and more than 50 % less than coal-generated electricity distributed via the grid. Being a mix of propane and butane, LPG emits more carbon per joule than propane and LPG emits less carbon per joule than butane.

When LPG is used as fuel for internal combustion engines, it is often referred to as auto gas or auto propane. In some countries, it has been used since the 1940 s as an alternative fuel for spark ignition engines. More recently, it has also been used in diesel engines. Its advantage is that it is non-toxic, non-corrosive and free of tetra-ethyl lead or any additives, and has a high octane rating. It burns more cleanly than petrol or diesel and is especially free of the particulates from the latter.

2.6 Spark-Ignition Engine Technology

The two most common types of engines are gasoline-fuelled engines and diesel-fuelled engines. These engines have very different combustion mechanisms. Gasoline-fuelled engines initiate combustion using spark plugs, while diesel fuelled engines initiate combustion by compressing the fuel and air to high pressures. Thus these two types of engines are often more generally referred to as "spark-ignition" and "compression-ignition" (or SI and CI) engines, and include similar engines that used other fuels. SI engines include engines fuelled with liquefied petroleum gas (LPG) and compressed natural gas (CNG).

2.6.1 Theory of Cold Start Phenomena

Natural gas and propane are generally considered to reduce engine maintenance and wear in spark-ignited engines. The most commonly cited benefits are extended oil change intervals, increased spark plug life, and extend engine life. Natural gas and propane both exhibit reduced soot information over gasoline. Reduced soot concentration in the engine oil is believed to reduce abrasiveness and chemical degradation of the oil. Gasoline fuelled engines (particularly carburetted engines) require very rich operation during cold starting and warm up. Some of the excess fuel collects on the cylinder walls, “washing” lubricating oil off walls and contributing to accelerated wear during engine warm up. Gaseous fuels do not interfere with cylinder lubrication.

Gaseous fuelled engines are generally considered easier to start than gasoline engines in cold weather. This is because they are vaporized before injection to engine. However, under extremely cold temperatures, there is cold-start difficulty for both propane and natural gas. This is probably due to ignition failure because very difficult ionization conditions, sluggishness of mechanical components. Hot starting can present difficulties for gaseous fuelled vehicles, especially in warm weathers. After an engine is shut down, the engine coolant continues to absorb heat from the engine, raising its temperature. If the vehicle is restarted within a critical period after shutdown, (long enough for the coolant temperature to rise, but before the entire system cools), the elevated coolant temperature will heat the gas more than normal, lowering its volumetric heating value and density. This would result in mixture enleanment.

2.7 Hydrogen

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. Hydrogen coexists in two phases, para and ortho hydrogen, whose partition depends on the temperature. At low temperatures, < 80 K, the para phase presents the more stable form. Hydrogen exhibits in part a positive “Thomson-Joule effect” meaning a positive temperature change upon pressure decrease. The effect is found for hydrogen at temperatures > 200 K, for example, an increase of 6 °C when released from 20 MPa to ambient conditions.

Table 2.7 shows the comparison of hydrogen, propane, methane and gasoline. Mixtures of hydrogen with oxygen are flammable over a wide range of concentrations, 4-75 vol %. A stoichiometric hydrogen- air mixture contains 29.5 vol % H_2. Despite its relatively high auto ignition temperature, the minimum energy required for an ignition (0.02 MJ) is very low, further reduced by increasing temperatures or pressure or oxygen content. Catalytically active surfaces can ignite hydrogen-air mixtures even at much lower temperatures. The hydrogen flame is non luminous, comparatively hot, but hardly radiates any heat.

Hydrogen holds significant promise as a supplemental fuel to improve the performance and emissions of spark ignited and compression ignited engines. Hydrogen has the ability to burn at extremely lean equivalence rations. Hydrogen will burn at mixtures seven times leaner than gasoline and five times leaner than methane (Bauer C and Forest, 2001). This lower limit is governed by the Le Chatelier Principle (Bortnikov, 2007).

Table 2.7: Comparison of Propane, Hydrogen, Methane and Gasoline. Source by Wang (2007).

Properties	Hydrogen	Methane	Propane	Gasoline
Molecular Weight	2.02	16.04	44.10	114.00
Minimum Ignition Energy (mJ)	0.02	0.29	0.26	0.24
[a]Flame Speed (cm/s)	237	42	46	42
[b]Diffusion Coefficient (cm^2/s)	0.61	0.16	0.12	0.05
Quenching Gap (cm)	0.06	0.20	0.20	0.20
Higher Heating Value (MJ/Kg)	142	55	50	47
Lower Heating Value (MJ/Kg)	120	50	46	44

[a] at 20 C [b] at stochiometric condition

The flame velocity of hydrogen is much faster than other fuels allowing oxidation with less heat transfer to the surroundings. This improves thermal efficiencies. Efficiencies are also improved because hydrogen has a very small gap quenching distance allowing fuel to burn more completely.

2.8 Spark Ignition

Spark ignited engines can be either fuelled by liquid fuels or gaseous fuels. Propane and methane are the gaseous fuels and gasoline and ethanol are the liquid fuels commonly used. It can be seen in table 2.7 that gaseous fuels and liquid fuels have different properties and react differently to hydrogen addition, but both still benefit from hydrogen addition.

Various methods have been used to introduce hydrogen into the engine. In one study, hydrogen was mixed with air and compressed in a cylinder before introduction into the engine (Andrea, 2004). In studies using gaseous fuels hydrogen flow rate is matched with the primary fuel in order to achieve the desired percentage of hydrogen enrichment (Ma, 2007). The ultimate design for hydrogen introduction into an engine would be using a computer control system that would vary hydrogen percentage, equivalence ratio and throttle with the vehicles gas pedal for optimal running conditions (Bauer C and Forest, 2001).

2.8.1 Compression Ignition

Compression Ignition engines can be fuelled with standard diesel, biodiesel or straight vegetable oil. These engines have two options for introducing hydrogen into the combustion process. Hydrogen can be inducted with air into the intake manifold or it can be directly injected into the cylinder similar to the diesel fuel (Masood, 2007).

2.9 Hydrogen Enriched Combustion

Thermal efficiency generally is increased with the introduction of hydrogen into an engine but it must be properly tuned in-order to gain these benefits. Results also seem to vary depending on the fuel used. A properly tuned compression engine will increase in thermal efficiency at high loads for hydrogen mass about 8 % (Kumar, 2003). For an engine to have optimal thermal efficiency the timing must be retarded to account for hydrogen fast burn velocity (Saravannan, 2007).

Thermal efficiency is related to fuel consumption with the addition of hydrogen in all of the studies fuel consumption decreased (Kumar, 2003). Hydrogen addition gives the engine the ability to be operated in the very lean mixture region.

Lean mixtures allow for complete combustion decreasing carbon monoxide emissions (Fanhua and Yu, 2008). Unburned hydrocarbon emissions are reduced because hydrogen allows lean mixtures. They are also reduced because high flame velocity and small quenching distance of hydrogen promote complete combustion (Choi, 2005).

The addition of hydrogen increases combustion temperatures therefore creating conditions where it is easier for NOx to form if proper tuning is not utilized. Several studies have shown that if mixtures are made lean and spark timing is retarded NOx can be reduced to a point below normal hydrocarbon combustion (Saravannan, 2007).

2.10 20-L-Apparatus

The experimental 20-L-Apparatus (or 20 Liter Spherical Explosion Vessel) was obtained from Adolf Kühner AG and is shown in figure 3.1. The test chamber is a stainless steel hollow sphere with a personal computer interface. The top of the cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap which is controlled by the KSEP 310 unit of the 20-L-Apparatus. The KSEP 332 unit uses piezoelectric pressure sensors to measure the pressure as function of time (ASTM, 1991; Operating Instructions for the 20-L-Apparatus, 2006). A comprehensive software package KSEP 5.0 is available, which allows safe operation of the test equipment and an optimum evaluation of the explosion test results.

In the past, the international standards have described the 1 m^3 vessel as the standard test apparatus. In recent years, increased use has been made of the more convenient and less expensive 20-L-Apparatus as the standard equipment. The explosion behaviour of combustible materials (combustible dusts, flammable gases, or solvent vapours) must be investigated in accordance with internationally recognized test procedures. For the determination of combustible gases or vapours,