Effect of H₂ enrichment on the explosive limits of Liquefied Petroleum Gas (LPG) in conventional combustion

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Abstract

The use of hydrogenated fuels shows a considerable promise for the applications in gas turbines and internal combustion engines. Hydrogen holds a 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 ratios. In addition, it is important to analyze the explosive limits for safety reasons and to increase the efficiency in operation of many industrial and domestic applications that use the explosion concept. The aims of this study are to determine the explosive limits of liquefied petroleum gas/air mixture and to investigate the effect on the explosive limits of liquefied petroleum gas/air mixture enriched up to 8% vol of hydrogen at atmospheric pressure and ambient temperature. The experiments were performed in a constant volume of 20 liter closed spherical vessel. The mixtures were ignited by using a spark permanent wire that was placed at the centre of the vessel. The pressure-time variations during the 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 the explosion pressure is greater than 0.1 bar. In this study, the result shows the explosive limits range from 2 to 8% vol of liquefied petroleum gas/air mixture and has revealed that the addition of hydrogen in liquefied petroleum gas/air mixture decreases the lower explosive limit from 2 to 1% vol and for the upper explosive limit, the limit is also decrease from 8 to 7% vol.

Keywords: explosive limits, hydrogen enrichment, liquefied petroleum gas, closed explosion vessel.



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1 Introduction

Explosion is a combustion of mixed combustible mixtures (gas cloud) that cause a rapid increase of pressure. When the combustion of fuel is not controlled within the confines of the burner system, the limit of flammability is called explosive limit. Analysis of the explosive limit is important for safety reasons and increases the operation efficiency in many industrial and domestic applications that use the concept of explosion. 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 be aware about the safety and environment besides the classical concerns about the efficiency of the operation [1]. Liquefied Petroleum Gas (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 a known fuel with less emission, LPG has attracted increased interest in recent years [2]. LPG is extensively used both as an alternative fuel in automotive engine and as a domestic fuel. In comparison with conventional engine fuel (gasoline and diesel), LPG is considered as 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. In addition, hydrogen holds significant potential as an added fuel to improve the performance and emissions of ignited spark and compression ignited engines. It also has the ability to burn at extremely lean equivalence ratios. Hydrogen will burn at mixtures seven times leaner than gasoline and five times leaner than methane [3]. This lower limit is governed by the Le Chatelier Principle [4]. 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 [5].

Explosion may be defined by a combustion of combustible mixtures (gas cloud), causing a rapid increase of 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). An explosion range is started from the Lower Explosive Limit (LEL) to the Upper Explosive Limit (UEL) of a specific substance. Vapour-air mixture will ignite and burn only over a well-specified range of compositions [6]. 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. LEL is the limiting concentration (in air) that needed for the gas to ignite and explode. At any concentrations in air that is below the LEL, there is no fuel to continue an explosion. Concentrations lower than LEL are "too lean" to burn. UEL is the highest concentration (percentage) of a gas or a vapour in air capable of producing a flash of fire in the presence of an ignition source (arch, flame, heat). Concentration higher than UEL are "too rich" to burn.



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 a very rich operation during cold starting and warming up. Some of the excess fuel collects on the cylinder walls, and "washing" lubricating oil off walls is 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 a cold-start difficulty for both propane and natural gas. This is probably due to ignition failure because very difficult ionization conditions and sluggishness of mechanical components. The effect of hydrogen enrichment of hydrocarbon combustion on emissions and performance were investigated by Wall [7] which have shown that added hydrogen in percentage as low as 5-10% of hydrocarbon fuel can reduce that hydrocarbon fuel consumption. The theory behind this concept is that the addition of hydrogen can expand the lean operation limit, improve the lean burn ability and decrease burn duration.

Based on the pressure time traces, three regimes of explosion development or combustion conversion can be identified. The regimes depend on the initial mixture composition, at given conditions, as illustrated in figure 1. In the first one, marked as 1, the pressure increases fast and smoothly to the maximum value, after ignition. This type of pressure development is seen for near stoichiometric mixtures. In the second regime, the pressure trace is distinctly S shaped (a shoulder). Such type of pressure development is present in a narrow fuel lean concentration range and in a wider concentration range with fuel rich mixtures. In the third regime the shoulder disappeared, and the increases are low and slow [8].



Figure 1: Three different combustion regimes.

WIT Transactions on Ecology and the Environment, Vol 143, © 2011 WIT Press www.witpress.com, ISSN 1743-3541 (on-line) This study was conducted to determine the explosive limits of LPG/air mixture in a constant volume of 20 liter spherical vessel by using a conventional spark ignition system which was located at the centre of the vessel. In this study, the LPG composed of butane and propane in a 70/30 ratio was used to investigate the explosive limits. The LEL and UEL of LPG/air mixture were determined at concentration from 1 to 8% vol. The effect of hydrogen in LPG/air mixture was investigated at hydrogen enrichment up to 8% vol hydrogen of air by the total volume of LPG concentration from 1 to 8% vol.

2 Methodology

2.1 Materials and equipment

A cross-sectional diagram of the experimental 20 liter spherical vessel is shown in figure 2. The test chamber is a 20 liter hollow sphere made of stainless steel. The ignition source is located at the centre of the sphere. On the measuring flange, two "Kistler" piezoelectric pressure sensors are installed. The top of the cover contains holes for the lead wires to the ignition system. The opening provided for ignition which is controlled by the KSEP 320 units of 20 liter spherical vessel. A comprehensive software package KSEP 6.0 is used to allow a safe operation of the test equipment and an optimum evaluation of the explosion test results. The KSEP 332 unit uses piezoelectric pressure sensor to measure the pressure as a function of time and controls the valves as well as the ignition system of the 20 liter spherical vessel. The measured values to be processed by a personal computer are digitized at high resolution. The use of two completely independent measuring channels gives good security against erroneous measurements and allow for self checking. For the determination of combustible gases or vapors, the test is accomplished in a quiescent state for which the ignition delay time is tv = 0 s.



Figure 2: Cross-sectional diagram of the 20 liter spherical vessel.

2.2 Experimental conditions

The explosive limits of LPG/air mixture and LPG/air mixture with hydrogen enrichment up 8% vol hydrogen of air were investigated at LPG concentration from 1 to 8% vol. In this study, a LPG with a 30/70 ratio of propane and butane was used. The initial pressure in the 20 liter spherical vessel was regulated to 1 bar abs. A water jacket was used to dissipate the heat of explosions or to maintain the testing temperatures. It is necessary to keep the operating temperature at approximately 20 °C which was achieved by water cooling whereby the operating temperature would correspond to room temperature. Water is circulated and the outlet temperature of the cooling medium never exceeds 25 °C. Ignition is achieved by a permanent spark which is placed at the centre of the vessel. Since the experiment was conducted under auiescent conditions, the ignition energy and ignition delay were set to 10 J and 0 s respectively. The igniter releases 10 J independently of pressure or temperature. The pressure evaluation after ignition was measured by a Kistler 701A piezoelectric pressure transducer connected to a Charge amplifier (Kistler 5041B). Figure 3 shows the schematic diagram of experimental setup where the equipment was closely placed to the LPG, hydrogen gas tank and computer system.



Figure 3: Schematic diagram of experimental setup.

2.3 Experimental procedures

Figure 4 shows the work flows of the experiment. The LPG and hydrogen fuel from the cylinder storage and air from surrounding were fed in to the vessel via the outlet valve and nozzle. The required composition LPG/hydrogen/air mixture was produced readily with the partial pressure procedures. After ignition, the



pressure evolution was measured by a pressure transducer and shown in a graph of pressure versus time by the software KSEP 6.0. After each test, the ball valve was opened to release out the exhaust gas and the remaining pressure in the vessel. The steps were repeated for each fuel gas compositions.



Figure 4: Experimental work flows.

3 Results and discussion

Chang and Shu [9] studies showed that a spherical explosion vessel was treated as an ideal device to detect various explosion properties of flammable material. This device does not allow visual observation of the flame, so it uses an indirect measurement of the flame propagation which is the pressure explosion. This is because a successful ignition would induce a rapid pressure increase and temperature rise within a short time as well as produce a propagating flame front that could be readily observed [10]. Thus, pressure explosion criterion is used to define the explosive limits of LPG. In this experimental study, flame propagation is said to have occurred if ignition is followed by a pressure explosion of 0.1 bar or greater.

3.1 Experimental results of LPG/air mixture

The explosive limits of LPG/air mixture were determined at various concentration of LPG by volume as shown in table 1. The test was conducted at various LPG volumes, from 1 to 8% vol. Based on the results, a pressure explosion greater than 0.1 bar was observed at a concentration of LPG from 2 to



8% vol which is equivalent to the explosive limits of LPG/air mixtures of this study. The data for LPG concentration of 1 and 2% vol shows a pressure explosion of 0 bar. There was some burning near the spark but only limited to the upward propagation beyond the ignition sources which could not be considered as a propagation in this study. At LPG concentration of 3% vol, the pressure explosion obtained was 5.8 bar. There was significant flame propagate through more than half of the chamber. The highest pressure explosion from the measurements is 6.4 bar which was obtained at LPG concentration of 4% vol. Closer to the stoichiometric mixture, the flame speed was fast and it took the lowest time (100 s) for the flame to propagate from its point of ignition to the chamber wall compare to other LPG/air mixture. When the concentration of LPG was 7% vol, with 93% vol of air, the explosion pressure was decrease to 0.5 bar which means that there might be some burning near to the spark but only limited to the upward propagation beyond the ignition source.

	LPG		Air		Down	Time
No	Concentration	Pressure	Concentration	Pressure	(bar)	
	(% vol)	(bar)	(% vol)	(bar)	(Ual)	(5)
1	1.0	0.01	99.0	0.99	0	0
2	2.0	0.02	98.0	0.98	0	0
3	3.0	0.03	97.0	0.97	5.8	112
4	4.0	0.04	96.0	0.96	6.4	100
5	5.0	0.05	95.0	0.95	4.7	332
6	6.0	0.06	94.0	0.94	3.1	1050
7	7.0	0.07	93.0	0.93	0.5	466
8	8.0	0.08	92.0	0.92	0	0

Table 1:Experimental result of LPG/air mixture.

Generally, the small pressure explosion is assumed to be associated with a limited upward propagation of the flame and is typically observed for mixtures on the edge of explosion. The high pressure explosion indicates that the mixture is almost completely consumed and the propagation was both upwards and downwards [11]. The upward propagation is easier than other propagation directions because combustion products are hotter and less dense than the reactants from which they are generated [12].

3.2 Comparison data with the previous studies

It is demonstrated that LEL in this study is slightly higher compared to Mishra and Kenneth's [13] experimental data. In this study, the LEL is observed at 2% vol of LPG (by volume). In contrast, the UEL is comparatively lower at 8% vol. In order to validate our present results, a comparison is made with the available explosion data in literature for propane/air and butane/air mixture as given in table 2. It can be noticed from this table that the present result falls between the



Reference	Gas mixture	LEL	UEL
D.P. Mishra	D.P. Mishra LPG - air		8.86
D.P. Mishra	Butane - air	1.80	8.40
L.Kenneth	Propane - air	2.00	9.60
This study	LPG - air	2.0	8.0

Table 2: Comparison of explosive limits [13].

result of explosive limits for both butane/air and propane/air mixtures. Therefore, the present results of explosive limit for LPG/air mixture are considered still within the expected values.

However, if the readings of the pressure gauge were accurate up to 0.5% vol, the explosive limits could be obtained in smaller decimal points with higher accuracy.

3.3 Experimental results of LPG /air mixture with hydrogen addition

The objective of this study is to determine the effect of the explosive limits of LPG/air mixture when the various amount of hydrogen were added into the LPG/air mixture. As shown in table 5, the mixture was tested with 1, 2 and 8% vol of hydrogen over the total volume of mixture. The value of explosion pressure for LPG/air mixture showed a non-significant difference when 1% vol of hydrogen was added into the mixture. There were changes in the explosion pressure (Pexp) when 2% vol of hydrogen was added in LPG/air mixture where the explosion pressure was equal to 4.9 bar of 2.0% vol LPG. When hydrogen 8% vol was added into the mixture, the explosion became significant at 2.5 bar of 1.0% vol of LPG. Beside the changes in explosion pressure, there were also differences in time of explosion for these different values of hydrogen addition. The hydrogen addition of 8% vol in LPG/air mixture showed the fastest time of combustion (58 and 59 s) at both explosion pressures of 6.2 bar. The maximum explosion pressure for 1, 2 and 8% vol of hydrogen addition was 6.2, 6.5 and 6.2 bar respectively. At these conditions, the flame speed is the fastest, and it takes lowest time (55 to 90 s) for the flame to propagate from its point of ignition to the chamber wall compared to other LPG/air/hydrogen mixture. At this level, the entire mixture inside the spherical vessel is considered almost completely consumed

As exhibited in figure 5, the increase of hydrogen percentage in fuel has expanded the explosive limits of LPG/air mixture. Graph a) shows that the LEL of LPG/air mixture was initially 2% vol and the graph b) shows that after the addition of 1% vol hydrogen, the LEL was unchanged but the curve of explosive limits was rather widely expanded if compared to the first graph a). Similarly, the UEL in graph b) had no change within limits which was still 8% vol after 1% vol hydrogen addition. Graph c) shows the result of explosion of LPG/air mixture when 2% vol of hydrogen was added into the mixture and the LEL had expanded to 1% vol. There was no change for the UEL when 2% vol of





Figure 5: Explosion pressures with the various H_2 addition.

hydrogen was added, but when the addition of hydrogen was increased to 8% vol, the UEL changed to 7% vol as shown in graph d).

Changes in fuel composition, particularly with the addition of hydrogen affect both the chemical and physical processes occurring in flames. These changes affect the flame stability, emissions, combustor efficiency and other important quantities [14]. Hydrogen has been proved to be a green alternative fuel that can be applied on vehicle. Due to high auto ignition temperature of hydrogen (858 K), it is more suitable to adopt hydrogen on spark ignition engine rather than compression ignition engines. Besides, hydrogen has unique combustion properties that benefit the engine efficiency and emission performance. Hydrogen diffusion coefficient is larger than n-propane and n-butane as shown in table 3 which improves mixing process of fuel/air, also helps in improving the homogeneity of combustion mixture. Adiabatic flame speed of hydrogen (237 cm/s) is larger than both n-propane and n-butane which contributes to improve the engine operating stability. Flammability range of hydrogen in air is 4 to 75% vol which is much wider than n-propane and n-butane. Therefore, a hydrogen/fuelled engine is able to work under much leaner condition [15].

Since the ignition energy of hydrogen is lower than LPG, the hydrogen/LPG mixture can be more easily ignited and hydrogen enriched LPG engine can gain a smooth start and in good operating stability under a lean condition. It has been

Properties	Hydrogen	n-propane	n-butane
Molecular mass (g/mol)	2.02	44.10	58.10
Stoichiometric concentration (% fuel)	29.6	4.0	3.8
Flammability range (% fuel)	4-75	2.1-9.5	1.8-8.4
Maximum explosion pressure (bar)	8.01	9.28	10.00
Ignition energy (mJ)	0.017	0.26	0.25
Adiabatic flame speed (cm/s)	237	46	45
Diffusion coefficient (cm^2/s)	0.61	0.12	0.11

 Table 3:
 Properties of hydrogen, n-propane and n-butane.

commonly agreed that the proper lean combustion is an effective way to improve engine thermal efficiency and emission performance.

Figure 5 shows that an increase of hydrogen percentage affects both of the explosive limits of fuel/air mixture. Schefer [14] has shown that for fuel/hydrogen/air mixtures at atmospheric pressure and ambient temperature using the premixed tube gives in high of hydroxyl (OH) concentration and expanded the lean stability limits of the mixture. In this study, Schefer [14] used methane as a fuel and the addition of up to 20% vol of hydrogen into methane mixed together with air inside the premixed tube.

In recent studies [16] have also shown that the lower explosive limit of fuel/air mixture with hydrogen enrichment could be expanded by increasing the volume of hydrogen addition in a spark ignition engine. This study had used methane as the fuel and the most obvious and important advantage methane engines could benefit from the hydrogen addition is the improvement in lean burn capability which is manifested as the expansion of lean operation limit.

4 Conclusion

In this paper, the experimental study has shown the effect of explosive limits of LPG when hydrogen is added into LPG/air mixture. The result for hydrogen enrichment in the LPG/air mixture were analyzed at 1, 2 and 8 vol% of hydrogen and the pressure explosion criterion was used to define the explosive limits. Based on the result of the experiment, there is a small difference of explosion pressure when the LPG/air mixture is added at 1% vol hydrogen. Remarkable changes are observed when the volume of hydrogen is increased to 8% vol. It is proven that hydrogen properties such as high auto ignition temperature, diffusion coefficient and adiabatic flame speed help to expand the explosive limits of LPG/air mixture. Besides, hydrogen enrichment also contributes to the changed of LEL and UEL of LPG. Thus the present of hydrogen in LPG/air mixture will have a high potential to assist in solving the cold start phenomenon that always occurs in spark and compress ignition engines.



References

- [1] Ramanan, S., & Hong, G. I., Effect of Hydrogen Addition on the Flammability Limit of Stretched Methane/Air Premixed Flames, *Department of Mechanical Engineering*, University of Michigan Ann Arbor, MI 48109, 1994.
- [2] Wang, .B B., Qiu, R. & Jiang, Y., Effects of Hydrogen Enhancement in LPG/Air Premixed Flame, *State Key Laboratory of Fire Science*, University of Science and Technology of China, Hefei , 24(7), pp. 1137–1142, 2008.
- [3] Bauer, C. & Forest, T., Effect of Hydrogen Addition on the Performance of Methane-Fueled Vehicles. Part II: Driving Cycle Simulation, Int J Hydrogen Energy, 26, pp. 71–90, 2001.
- [4] Bortnikov, L., Combustion of a Gasoline-Hydrogen-Air Mixture in a Reciprocating Internal Combusti Engine Cylinder and Determining the Optimum Gasoline-Hydrogen Ratio, *Combustion, Explosion, and Shock Waves*, 43, pp. 378–383, 2007.
- [5] Wang, J., Combustion Behaviors of a Direct-Injection Engine Operating on Various Fractions of Natural Gas-Hydrogen Blends, *International Journal* of Hydrogen Energy, 32, pp. 3555–3564, 2007
- [6] Cracknell, R. F., Alcock, J. L., Rowson, J.J., Shirvill, I. C. & Ungut, A. Safety Considerations in Retailing Hydrogen, *SAE paper*, 01, pp. 1928, 2002.
- [7] Wall, J., Effect of Hydrogen Enriched Hydrocarbon Combustion on Emissions and Performance, *Department of Biological and Agricultural Engineering*, University of Idaho, 1994.
- [8] Pekalski, A.A., Schildberg, H.P., Smallegange, P.S.D., Lemkowitz, S.M., Braithwaite, M., Zevenbergn J.P., & Pasman, H.P., Determination of the explosion behaviour of methane and propane in air or oxygen at standard and elevated conditions, *Process Safety and Environmental Protection*, 83 (B5), pp. 421–429, 2005.
- [9] Chang & Shu, M., Inert effects on the flammability characteristics of methanol by nitrogen or carbon dioxide, *Akademiai Kiado*, Hungary. DOI 10.1007/s10973-009-0028-1, 2009.
- [10] Liao, S.Y., Jiang, D.M., Huang, Z.H., Cheng, Q. & Gao, J., Approximation of flammability region for natural gas-air-diluent mixture, *Journal of Hazardous Materials*, A125, pp 23–28, 2005.
- [11] Vandebroek, L., Van den Schoor, F., Verplaetsen, F., Berghmans, J., Winter, H., & Van't Oost, E., Flammability limits and explosion characteristics of toluene-nitrous oxide mixtures, *Journal of Hazardous Materials*, A120, pp 57–65, 2005.
- [12] Cashdollar, K., Zlochower, I., Green, G., Thomas, R. & Hertzberg, M., Flammability of methane, propane and hydrogen gases, *Journal of Loss Prevention in the Process Industries*, 13, pp. 327–340, 2000.
- [13] Mishra, D.P., & Kenneth, L., An Experimental Study of Flammability Limits of LPG/air mixtures, *Indian Institute of Technology*, Kanpur India, 82, pp 863–866, 2003.

- [14] Schefer R.W., Hydrogen enrichment for improved lean flame stability, *International Journal of Hydrogen Energy*, 28, pp. 1131–1141, 2003.
- [15] Changwei, J. & Shuofeng, W., Effect of hydrogen addition on the idle performance of a spark ignited gasoline engine at stoichiometric condition, *International Journal of Hydrogen Energy*, 34, pp. 3546–3556, 2009.
- [16] Fanhua, M. & Yu, W., Study on the extension of lean operation limit through hydrogen enrichment in a natural gas spark-ignition engine, *International Journal of Hydrogen Energy*, 33, pp. 1416–1424, 2008.

