AN EXPERIMENTAL STUDY ON LPG/ H₂O₂ MIXTURE FOR COMBUSTION

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ABSTRACT

Liquefied petroleum gas (LPG) has a mark as traditional hydrocarbon structure as conventional fuels. Thus the objective of this research is to study the characteristics of LPG/ H_2O_2 blends in various compositions in the presence of homogeneous catalyst and controlling the exhaust emission by reducing green house gases. Hydrogen peroxide (H₂O₂) is recently reported as fuel combustion enhancer and to be a low-emission highquality fuel blend replacement of hydrogen. Consequently, this research discussed the influence of hydrogen peroxide (H_2O_2) combination with LPG in various percentages for combustion. Materials used in this experiment include LPG, hydrogen peroxide (H_2O_2) with a concentration of 50% technical grade, homogeneous catalyst and augar. The addition of H₂O₂ at various percentages to LPG in LPG/H₂O₂ blends will be used for the experiments and measurements can be made to study the characteristics, combustion, and exhaust emissions. A comparative study was carried out to analyze the exhaust emissions from the combustion, the characterization of fuel blend and the corrosion (copper strip) test according to the ASTM standard. From the experiment, the result shows that H₂O₂ as additive to LPG could contribute to reduction of emissions by decreasing generation of carbon monoxide (CO) in the form of carbon dioxide (CO₂) because of excessive oxygen in H_2O_2 Hence, this research contributes to lesser exhaust emissions and hopefully it can be produced and use as alternative fuels for transportation.

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ABSTRAK

Gas petroleum cecair (LPG) telah lama dikenal sebagai suatu struktur hidrokarbon untuk bahan api sejak dahulu lagi. Jadi, tujuan kajian ini dijalankan adalah untuk mengkaji ciri-ciri campuran bahan api LPG/ H2O2 dalam pelbagai komposisi dengan kehadiran pemangkin dan mengawal penghasilan pencemaran dengan mengurangkan kadar pengeluaran gas-gas rumah hijau. Hidrogen peroksida (H₂O₂) pula dilaporkan berpotensi menjadi penggalak kepada pembakaran bahan api dan sebagai bahan gantian kepada hydrogen yang berkualiti tinggi serta rendah kandungan pencemarannya. Oleh yang demikian, kajian ini turut dijalankan bagi mengkaji tentang keberkesanan kombinasi antara H₂O₂ dan LPG dengan komposisi yang berbeza dalam pembakaran. Bahan kimia yang digunakan dalam eksperimen ini ialah LPG, hydrogen peroksida (H₂O₂) dengan kepekatan 50% mengikut gred teknikal, bahan pemangkin dan augar. Penambahan pelbagai komposisi H₂O₂ dalam LPG bagi campuran LPG/H₂O₂ ini akan digunakan dalam eksperimen untuk mengkaji kadar pembakaran, ciri-ciri bahan api dan kadar pencemaran yang dihasilkan. Kajian pembandingan juga dilakukan bagi menganalisis kadar pembakaran, ciri-ciri bahan api dan kadar kakisan dengan mengikut piawaian yang ditetapkan oleh ASTM. Dari eksperimen ini, keputusan menunjukkan H₂O₂ sebagai bahan tambahan kepada LPG ini boleh menyumbang kepada penurunan kadar pencemaran dengan mengurangkan pembentukan karbon monoksida (CO) kepada pembentukan karbon dioksida (CO2) disebabkan lebihan oksigen dalam H2O2 Maka, kajian ini dapat membantu dalam mengurangkan kadar pencemaran oleh pembakaran bahan api dan diharapkan ia mampu dihasilkan di samping menjadi bahan api alternatif untuk tujuan pengangkutan.

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LIST OF ABBREVIATIONS AND SYMBOLS

%		Percentage
°F	-	Fahrenheit
ASTM	-	American Society for Testing and Materials
C ₃ H ₈		Propane
C ₄ H ₁₀		Butane
CO		Carbon Monoxide
CO ₂	-	Carbon dioxide
H_2O_2	_	Hydrogen Peroxide
HC	_	Hydrocarbons
kg	-	Kilogram
kJ	.	Kilo joule
LPG		Liquefied Petroleum Gas
m	-	Meter
m³	-	Meter cubic
MJ		Mega joule
NO		Nitric oxide
NOx		Nitrogen oxides
PM	-	Particulate matter
RON	-	Research Octane Number
S	-	Second
v	_	Volume
wt		Weight

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Concerning the energy conservation and environmental protection, improving spark ignition engine economics and emissions performance has attracted more and more attention. Liquefied petroleum gas (LPG) is extensively used as an alternative "clean" fuel in automotive engines, replacing gasoline and diesel, and as a fuel for domestic use (Razus et. al., 2009).

According to Jothi et. al. (2006), LPG has a high octane rating and it is therefore well suited for spark-ignition engine. When LPG is burnt in the conventional diesel engine there was a difficulty in self-ignition because of its lower cetane number. If LPG is to be used as an alternative to diesel the cetane rating needs to be improved with additives or other positive means of initiating combustion. Adding a cetane number improver to LPG is one method to improve its cetane number and its ignition quality.

In this project, the additive for LPG fuel combustion, which is hydrogen peroxide (H_2O_2) act as ignition enhancer in spark-ignition engine and allow important reduction of CO and NOx emissions as well. Hydrogen peroxide (H_2O_2) is a highly reactive and storable energetic liquid oxidizer that has been applied to many combustion

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applications. The most combustion studies involving H_2O_2 have focused on the performance characteristics of hybrid rocket engines, using solid or liquid fuels. It can also be used to run automobiles as an alternative or replacement for hydrogen gas. H_2O_2 is an energy-dense fuel that burns as cleanly as H_2 . (Sabourin et. al., 2008).

The use of Liquefied petroleum gas (LPG) with the additive of hydrogen peroxide (H_2O_2), a clean environment friendly oxidizer can contribute to the reduction in emissions. With increasing environmental consciousness and responsibility, the benefits as becoming an important consideration in future and a step forward towards sustainable development for the world. As a new type of alternative fuel of the future, it is also reasonable in terms of costing and financial matter. (Razus et. al., 2009).

1.2 Problem Statement

Most of the energy requirement in the world is supplied by fossil fuels such as petroleum, natural gas and coal. Fossil fuel reserves are being most of the world's energy demand, at present time.(Kahraman et. al., 2006). One of the problems with petroleum is the emission of pollutants, such as CO_2 , NO_x , CO and hydrocarbons (HC), particularly in terms of the greenhouse gas emissions per unit of useful energy released. (Akansu et. al., 2007).

The toxic emissions from automobiles have become the main factors which deteriorate the earth's environment, thus more strict emission regulation is mandated in many areas of the world, especially in some large cities which possess a great number of automobiles. (Jingding et. al., 1998).

In recent years, the increasing cost of liquid fuels derived from crude oil and future depletion of worldwide petroleum reserves encourage studies to search for alternate fuels. Liquefied petroleum gas (LPG) is considered to be the one of the most promising alternative fuel not only as a substitute for petroleum but also due to its economical costs, high octane number, high calorific values and lower polluting exhaust emissions. (Jothi et. al., 2006). LPG has been widely used in commercial vehicles, and promising results have been obtained from the fuel economy.

It is very well known that the solution to these problems is to replace the existing fossil fuel systems with the clean renewable energy ones, even though this could impose some design modifications. Therefore, alternative fuel research becomes the main purpose nowadays. (Kahraman et. al., 2006).

1.3 Research Objectives

The objectives of this research are:

- 1. To study the characteristics of LPG/ H_2O_2 mixture in various compositions in the presence of homogeneous catalyst.
- 2. To examine the exhaust emissions of LPG/ H_2O_2 combustion.

1.4 Scope of Research

In order to achieve the objectives, the following scopes of research work have been made:

- 1. To determine the effect of hydrogen peroxide (H_2O_2) on combustion.
- 2. To control exhaust emissions by reducing green house gases especially carbon monoxide (CO).
- 3. To study the copper strip corrosion test for various composition of LPG/ H_2O_2 .

1.5 Significance of Research

The significances of this research are:

- 1. More suitable for the spark plug ignition engine.
- 2. Applicable when the research is scaled up to industry level.
- 3. Reasonable in term of environmental and safety aspects for future use.
- 4. Develop as a new type of environmentally fuel

CHAPTER 2

LITERATURE REVIEW

2.1 Liquefied Petroleum Gas (LPG)

2.1.1 Introduction to Liquefied Petroleum Gas (LPG)

Liquefied petroleum gas, commonly called LPG, is also known by the names of its principal generic components, propane and butane. The normal constituents of LPG are propane (C_3H_8) , propylene (C_3H_6) , butane (C_4H_{10}) and butylenes (C_4H_8) . These are commercial products and may contain other impurities such as smaller quantities of C5+ hydrocarbons. LPG as a liquid is colorless, and in vapor form it cannot be seen. Pure LPG has no smell, but for safety reasons an odoring agent, usually a mercaptan, is added during manufacture to aid detection at very low concentrations. LPG exists in a gaseous form under normal atmospheric pressure and temperature. It is easily liquefied by moderate pressure at ambient temperature, which means it can be easily and conveniently stored as a liquid, a big advantage over natural gas, which can be liquefied only at a very low temperature and high pressure. LPG as a liquid is 250 times denser than LPG as a vapor, so a large quantity can be stored in a relatively small volume. (Parkash, 2010). In the study by Mobley (2001), it was stated that Liquefied petroleum gases (often referred to as LPG of LPGas) are a constituent of crude oil or the condensate of natural gas fields (NGL). They are the C_3 and C_4 hydrocarbons, propane and butane, respectively, which have the property of being gases at normal ambient temperature but can be liquefied and kept in the liquid state by quite moderate pressure. Today, LPG sold into the product to fuel gas market meets the requirements for automotive LPG. The Standard sets the limits of the constituents for commercial propane and commercial butane since they are always mixtures of C_3 and C_4 with one or the other predominating.

Gilles (2004) also elaborated further that liquefied petroleum gas (LPG) is similar to gasoline chemically and is a product of gasoline refining. It can also be obtained from natural gas. LPG is mostly propane but contains a small percentage of butane (up to 8%). Because of this, many people simply refer to LPG as propane. LPG is a vapor above -40°F, rather than a liquid. It is called "liquefied" because it is stored as a liquid in a bottle under pressure. The pressure increased its boiling point and turns it into a liquid. LPG requires a different fuel system to meter the gas vapor into the engine. Because the fuel is already under the pressure, no fuel pump is required.

LPG is increasingly being used as automobile fuel because of its cost advantages over gasoline and diesel. LPG is a clean-burning fuel. The absence of sulfur and very low levels of nitrogen oxides (NOx) and particulate emissions during its combustion make LPG a most environmentally friendly source of energy. The use of LPG can result in lower vehicle maintenance costs, lower emissions, and fuel cost savings compared with conventional gasoline or diesel fuels. LPG is considered a particularly suitable fuel for heavy vehicles, buses, and delivery vehicles because of its significantly lower particulate emissions compared with diesel-powered buses. The use of LPG as automotive fuel varies from country to country depending on the relative cost of alternative fuels such as gasoline and diesel. (Parkash, 2010). The Figure 2.1 composition chart below outlines the typical components of LPG as supplied via Gas Malaysia's distribution system. In Malaysia mostly the composition in LPG is approximately consists of 30% propane and 70% butane. As in the chart below, propane is 28.70% while butane is 69.97% and 1.22% is other hydrocarbon content. This is the exact composition of mole percentage in LPG usage. (Gas Malaysia, 2009).



Figure 2.1 Gas Malaysia LPG composition chart

2.1.3 Properties of Liquefied Petroleum Gas (LPG)

Table 2.1 shows the properties of LPG which it is comprises mainly of propane (C_3H_8) and butane (C_4H_{10}) . Table 2.2 indicates the mole fractions of main component in LPG consists of propane, isobutene, butane, dimethyl-propylene and butadiene. (Gong et al. 2003).

Properties	LP	G
	Propane	Butane
Formula	C ₃ H ₈	C ₄ H ₁₀
Relative Molecular Mass	44	58
Density (kg/m ³)	508	584
Boiling Point (°C)	-42.0	-0.5
Research Octane Number (RON)	111	103
Auto-Ignition Temperature (°C)	480	440
Stoichiometry air-fuel ratio	15.65	15.43
Flammability Limit (% v)	2.2-9.5	1.9-8.5
Calorific value (MJ/kg)	46.1	45.5
Flame Speed (m/s)	0.38	0.37

Table 2.1: Properties of LPG

Table 2.2: Mole Fractions of Main Components in LPG

Propane (%)	Isobutane (%)	Butane (%)	Dimethyl-propylene (%)	Butadiene (%)
49	21	15	8	5

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2.1.4 The Advantages and Disadvantages of LPG

The following are advantages and disadvantages of LPG when compared to gasoline have been identified by Gilles (2004).

Advantages:

- LPG burns cleanly, produces fewer emissions, and lacks the objectionable exhaust odor of incompletely burned gasoline.
- Because it vaporizes easily, LPG does not tend to settle out as liquid in the intake manifold. The engine can start easily in very cold weather and cold driveability is better.
- Less frequent oil change intervals are required because LPG is a dry gas so it does not create carbon in the combustion chamber. Also, there is no fuel wash to dilute the engine oil.
- LPG has a higher octane; therefore, it can be used in engines with higher compression ratios. Pure butane has a 93 octane rating, pure propane is 100 octanes. The octane of the LPG will depend on the ratios of the mixture of these two fuels.

Disadvantages:

- The heat energy per volume of LPG is less than gasoline.
- LPG must be stored under high pressure so its storage tank must be strong.
- It is also more difficult to locate refueling stations for LPG.
- Refilling an LPG tank is time consuming.

2.2 Hydrogen Peroxide (H₂O₂)

2.2.1 Introduction to Hydrogen Peroxide (H₂O₂)

According to The Columbia Encyclopedia (2008), hydrogen peroxide chemical compound (H₂O₂), is a colorless, syrupy liquid that is a strong oxidizing agent and, in water solution, a weak acid. It is miscible with cold water and is soluble in alcohol and ether. Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about 80°C. It also decomposes in the presence of numerous catalysts such as most metals, acids, or oxidizable organic materials. A small amount of stabilizer, usually acetanilide, is often added to it. Hydrogen peroxide has many uses and available for commercial use in several concentrations. Highly concentrated solutions were first used in World War II by the military as fuels for rockets and torpedoes. It is also used as a bleaching agent for textiles, in paper manufacture and in chemical manufacture. Hydrogen peroxide is prepared commercially by oxidation of alkylhydroanthraquinones and by electrolysis of ammonium bisulfate. It can also be prepared by reaction of barium peroxide with sulfuric acid and is prepared (with acetone) by oxidation of isopropanol.

2.2.2 Properties of Hydrogen Peroxide (H₂O₂)

Table 2.3 shows the properties of hydrogen peroxide (H_2O_2) identified by Ashok and Saravanan (2008).

Table 2.3: Properties of Hy-	drogen Peroxide (H ₂ O ₂)
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Properties	Hydrogen Peroxide	
Chemical Formula	H ₂ O ₂	
Boiling Point (°C)	155.5	
Cetane Number	>125	
Self-ignition temperature (°C)	160	
Stoichiometric air/fuel ratio (wt/wt)	11.1	
Viscosity (centipoises) (at 20°C)	1.245	
Density (kg/m ³) (at 25°C)	1442	

2.2.3 Concentration of Hydrogen Peroxide (H₂O₂)

According to the US Peroxide (2010), depending on its concentration, H_2O_2 may be considered an Oxidizer (fire hazard), a Corrosive (health hazard), and/or Unstable/Reactive (explosion hazard). And with H_2O_2 , concentration can mean the difference between toothpaste and rocket fuel. In general, small quantities of high strength H_2O_2 may present a greater hazard than large quantities of low strength H_2O_2 . The Table 2.4 below summarizes the hazard ratings of various strengths of H_2O_2

Concentration		Description
<8%	Examples:	Baking soda-peroxide toothpaste (0.5%) Contact lens sterilizer (2%) Hair bleach (7.5%)
	Rating:	Non-hazardous
	Example:	Pool shock (27%)
8% - 28%	Rating:	Oxidizer - Class I. An oxidizer whose primary hazard is that it slightly increases the burning rate but does not cause spontaneous ignition when it comes into contact with combustible materials.
	Examples:	Most industrial strength grades
28.1% - 52%	Rating:	 Oxidizer - Class 2. An oxidizer that will cause a moderate increase in the burning rate or that may cause spontaneous ignition of combustible materials with which it comes into contact. Corrosive. A substance that "burns" skin and tissue when it comes into contact with them. Unstable (reactive) - Class 1. (35 - 52% H2O2). Materials which in themselves are normally stable but which can become unstable at elevated temperatures and pressures.

Table 2.4: Concentration and hazard ratings of	H_2O_2
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Concentration	<u></u>	Description
52.1%-91%	Examples:	Specialty chemical processes, shipping to very large users (70% shipped and diluted/stored onsite at $< 52\%$).
	Rating:	Oxidizer - Class 3. An oxidizer that will cause a severe increase in the burning rate of combustible materials with which it comes in contact or that will undergo vigorous self-sustained decomposition due to contamination or exposure to heat.
		<i>Corrosive</i> . A substance that "bums" skin and tissue when it comes into contact with them.
		Unstable (reactive) - Class 3. Materials which in themselves are capable of detonation or of explosive decomposition or explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation. This degree includes materials which are sensitive to thermal or mechanical shock at elevated temperatures.
	Examples:	Rocket propellant
>91%	Rating:	Oxidizer - Class 4. An oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock. In addition, the oxidizer will enhance the burning rate and may cause spontaneous ignition of combustibles.
		Corrosive. A substance that "bums" skin and tissue when it comes into contact with them.
		Unstable (reactive) - Class 3. Materials which in themselves are capable of detonation or of explosive decomposition or explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation. This degree includes materials which are sensitive to thermal or mechanical shock at elevated temperatures

2.3 Working of Spark Ignition Engine

Several researchers have widely studied the working of spark ignition engine (Federal Aviation Administration, 2009; Kojima, 2001).

The two primary reciprocating engine designs are spark ignition and the compression engine. The spark ignition reciprocating engine has served as the powerplant of choice for many years. In an effort to reduce operating costs, simplify design, and improve reliability, several engine manufacturers are turning to compression ignition as a viable alternative. The main mechanical component of the spark ignition and the compression ignition engine are essentially the same. Both use cylindrical combustion chambers and pistons that travel the length of the cylinders to convert linear motion into the rotary of the crankshaft. The main difference between spark ignition and compression engine is the process of igniting the fuel. Spark ignition engines use a spark plug to ignite a pre-mixed fuel/air mixture. (Fuel/air mixture is the ratio of the "weight" of fuel to the "weight" of air in the mixture to be burned.). While a compression ignition engine first compresses the air in the cylinder, raising its temperature to a degree necessary for automatic ignition when fuel is injected into the cylinder (Federal Aviation Administration, 2009).

There are two types of automotive engines, compression ignition and spark ignition engine. All diesel engine vehicles have compression ignition, while gasoline and dedicated NGVs have spark ignition. Compression ignition engines rely on self.ignition upon injection into hot, high pressure compressed air, and enjoy a number of advantages over spark ignition engines, which ignite a homogeneous and compressed pre-mixed mixture of fuel and air with a spark. These advantages include lower fuel consumption, longer life and safer operation. Compression ignition engines run "lean", or at a high air-to-fuel ratio, so that combustion occurs in the presence of excess air. In contrast, spark ignition engines typically run "stoichiometric", meaning that the air-to fuel ratio is adjusted so that the amount of oxygen in the air is exactly that needed to combust all hydrocarbons in gasoline (Kojima, 2001).

2.4 Combustion and Pollutant Formation in Spark-Ignition Engines

Faiz et. al (1996) were investigated the exhaust emissions are caused by combustion process. Spark ignition engines emit carbon monoxide (CO), nitrogen oxides (NOx), hydrocarbons (HC), particulate matter, (PM), and lead (where leaded gasoline is used), as well as other toxics.

2.4.1 Nitrogen Oxides (NOx)

The two main nitrogen oxides emitted from combustion engines are nitric oxide (NO) and nitrogen dioxide (NO₂). Most nitrogen oxides from combustion engines 90% are nitric oxide. This gas is formed from nitrogen and free oxygen at high temperature. Most nitrogen oxide emissions form early in the combustion process, when the piston is near to top of its stroke and temperature are highest. Nitrogen oxide emissions are controlled by reducing the flame temperature (by retarding combustion, diluting the reacting mixture, or both) and by minimizing the time that burned gases stay at high temperatures. (Faiz et. al., 1996).

2.4.2 Carbon Monoxide (CO)

Carbon monoxide emissions are caused by the combustion of rich mixtures, where the air-fuel ratio, is less than 1.0. In such mixtures, there is insufficient oxygen to convert all carbon to carbon dioxide. A small amount of carbon monoxide is also emitted under lean conditions because of chemical kinetics effects. Carbon monoxide emissions are controlled in the engine by adjusting the air-fuel ratio of the charge entering the cylinder. (Faiz et. al., 1996).