

**EXPEREMENTAL STUDY OF HYDROGEN PEROXIDE/METHANE
COMBUSTION**

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ABSTRACT

In this comparative study, a relationship of methane a traditional hydrocarbon fuel and hydrogen peroxide (H_2O_2) a combustion enhancer and oxidizer has been studied. Different concentrations of H_2O_2 were mixed for combustion and hazardous gases (CO_x) emissions. H_2O_2 was directly inserted into the burner by induction through the inlet manifold for dual fueling. 3L/m of methane diffused into 500ml of solutions which contained H_2O_2 at various volume percentages to form a mixture of methane/ H_2O_2 used for the experiments to study the performance, combustion, and emissions characteristics. The flame became lean with full blue flame produced as the amount of oxygen produced increased through the functional groups obtain inside the blend which mainly formed by C-O stretching. Concentration graphs showed the amount of CO and unburnt methane decreased while CO_2 concentration increased Thus, this experimental study filled the objective of this study where is the addition of hydrogen peroxide can extend the lean operation limit, improve the lean burn ability and controlling the exhaust emission by reducing green house gases.

ABSTRAK

Dalam kajian perbandingan ini, hubungan antara metana bahan bakar hidrokarbon tradisional dan hidrogen peroksida (H_2O_2) penambah pembakaran serta oxidizer telah dikajii. Kepekatan H_2O_2 yang berbeza digunakan untuk pembakaran dan penghasilan gas berbahaya (CO_x). Kajian secara perbandingan telah dijalankan bagi menganalisis kesan penambahan langsung H_2O_2 yang disalurkan bagi tujuan menggandakan bahan bakar melalui inlet manifold pada alat pembakar. Sebanyak 3L / minit metana tersebar ke dalam 500 ml larutan yang mengandungi peratusan H_2O_2 yang dipelbagaikan bagi tujuan membentuk campuran metana/ H_2O_2 untuk dikaji, agar prestasi, pembakaran, dan ciri-ciri bahan bebas bakar dapat dikaji. Nyalaan api didapati lebih lancar dengan api biru penuh terhasil apabila jumlah oksigen yang terbebas hasil campuran yang mengandungi kumpulan fungsi terdiri kebanyakannya daripada regangan molekul C dan O. Berdasarkan pola grafik, jumlah kepekatan CO dan metana tidak terbakar menurun sedangkan jumlah kepekatan CO_2 meningkat. Justeru, kajian eksperimentasi ini telah memenuhi tujuan kajian yang mana penambahan hidrogen peroksida boleh melancarkan, meningkatkan prestasi pembakaran serta mengawal bahan bebas bakar melalui pengurangan gas rumah hijau.

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LIST OF SYMBOLS

CH_4	-	Methane
H_2O		Steam
H_2O_2	-	Hydrogen Peroxide
O_2	-	Oxygen
NO_x	-	Nitric Oxides
CO	-	Carbon Monoxide.
CO_2	-	Carbon Dioxide
C_xH_x	-	Hydrocarbons
AFR	-	Air/fuel ratio
λ	-	Lambda
ϕ	-	Equivalent ratio
ΔH		Heat of reaction
kJ		kilojoules
atm	-	Pressure
K	-	Temperature
L	-	Volume
min	-	Minute
K	-	Coefficient
m	-	Meter

CHAPTER 1

INTRODUCTION

1.1 Background to the study

Fossil fuels are the main conventional energy source for industrial and household consumers. While producing the effective energy for industrial requirement, it is important to know that fossil fuels are limited sources and can not be regenerated. The fact is, fossil fuels that are mined from the earth are quickly getting extinguished. According to estimates, in another 10 to 15 years, most of the fuel reserves will be gone and the day is not far away when we will not have any energy left to use unless we look at alternative fuels [1].

The term of alternative fuels are also known as non-conventional or advanced fuels of any materials or substances that can be used as fuels, other than conventional fuels. One of them is methane. In addition, methane is recognized as a promising alternative fuel. Besides offering significant economic [2], methane also an

environmental [3] gas, as it can be more easily harnessed than other fuel methods and produces very few greenhouse gases.

While promising both advantages above, methane comparatively has the worse ignition properties and also has low burning velocity [4]. This conditions causing the instability and low power output for the combustion process. Thus, these weaknesses become disadvantages for industrial who always requiring the maximum utilization of energy source. In other way, a normal combustion of methane should be improved to maximize the output power so that the industrial demand can be filled [1].

Actually, oil and gas industries today already acknowledge hydrogen peroxide as an oxidizer in some early liquid-propellant rocket engines, including those of the German Messerschmitt 163 aircraft and the British Black Knight missile [5]. In fact, hydrogen peroxide has not been used since for this purpose on a large scale because it is dangerous to handle and easily decomposes, making it difficult to store. However, it has been used as a monopropellant in some small thrusters that provide attitude control on satellite [6].

From the scientific view, hydrogen peroxide is a strong oxidizer that release oxygen during reaction and will initiate or sustain a combustion process quite readily. Adding hydrogen peroxide into fuel-air combustion theoretically will reduce the ignition delay of the fuel [7], improving the combustion itself [4].

Thus, the study of hydrogen peroxide effects on methane-air combustion is a need to overcome the shortcoming of methane-air combustion, so that the methane-air combustion method can be improved to sustain the utilization of fuel source for the future energy requirement.

1.2 Problem Statement

Sufficient of conventional fuel consumption is leading to increase of fuel price. When a conventional fuel attains its global peak production level, it cannot longer support growth in energy demand, which impacts the economic growth. In detail, when the demand exceeds the production and availability, the existing economy cannot continue to function or to even feed the population. This fact leads the industries to seek for alternative fuels which required for development and widespread implementation to be a level with the conventional fuel. In addition, the existing economy does not run on hypothetical. We need more than decade to make an alternative energy source fully functional for the conventional utilities in the industries. While methane is a promising alternative fuel for the industries economically and environmentally, it has a comparatively worse ignition properties and also a lower burning velocity, causing combustion instabilities and lower power output, especially when it is utilized in modified conventional energy conversion systems.

In the same time, the environmental issue of greenhouse gases emission by fossil fuel, starts being the concern of government today. Reflected by the researches and predictions that carried out through various media, this issue tends to be the higher concern of the world today rather than the profits offered by the oil and gas industries. This urge both of government and industries to make better efforts to overcome the emissions effects from the fossil fuel. Thus, it makes a sense if this issue gives the industries a new challenge to make profits while producing less greenhouse gas emissions.

1.3 Research Objectives

1. To improve the lean ability and extend lean operation limit of methane combustion
2. To determine the effects of hydrogen peroxide on the exhaust gas composition of methane-air combustion

1.4 Scope of research

In order to achieve the objectives of the study, the scopes of research were listed down as below:

1. The study of hydrogen peroxide effects on methane-air combustion will be determined on turbulent and premixed fuel.
2. The condition of methane-air combustion will be at atmospheric pressure and temperature.
3. The study of hydrogen peroxide effects on methane-air combustion will be studied by using Bunsen burner.

1.5 Significant of study

Methane is offering oil and gas industries a long term energy source and green energy to be utilized. While the price market of conventional fuel is increasing rapidly, the demand of users is offering more economical alternatives. For the industries, which use the large scale of fuel source, profits always is the priority and every source will be utilized to the fullest. This study will be an enhancer for the industrial application as it is

providing the improvement method to overcome the shortcomings of normal methane-air combustion.

CHAPTER 2

LITERATURE REVIEW

2.01 Background of combustion

In order to improve the methane-air combustion, it is very important to know how the combustion works. In general, combustion only occurs with combination of fuel, oxygen, and ignition source. Combustion takes place when fuel, most commonly a fossil fuel, reacts with the oxygen in air to produce heat. The heat created by the burning of a fossil fuel is used in the operation of equipment such as boilers, furnaces, kilns, and engines [8]. Along with heat, carbon dioxide and water are created as by-products of the exothermic reaction. A kind of engine, which applied the combustion, is the internal combustion engine. An internal combustion engine is a heat engine or a device in which thermal energy is converted into mechanical energy in which the heat source is a combustible mixture [9]. There are two types of internal combustion engine, which are spark plug ignition and compression ignition [10]. In fact, methane-air combustion process commonly uses the spark plug ignition.

2.02 Spark plug ignition

Spark ignition (SI) engine cycles consist of four consecutive processes: intake, compression, combustion (including expansion) and exhaust [11]. In a conventional spark ignition engine, the fuel and air are mixed together in the intake system, inducted through the intake valve into the cylinder, where mixing with residual gas takes place, and then compressed. Under normal operating conditions, combustion is initiated towards the end of the compression stroke at the spark plug by an electric discharge. Following inflammation, a turbulent flame develops, propagates through this essentially premixed fuel, air, burned gas mixture until it reaches the combustion chamber walls, and then extinguishes to begin the expansion stroke until the exhaust valve opening [12].

Compared to conventional spark ignition engine which used liquid fuel, methane is the fuel in gaseous form. However, among the gaseous fuels, methane is gaining acceptance in practice because of low emission level, high octane rating, economical [2], and environmentally [3]. Mehmet E.A [13] stated that direct introducing of methane into the conventional spark ignition engine will be a manifold as the output power will drop 30%. Thus, he stated that a mixer was needed to mix methane with air during intake process until the compression process, before the combustion process take place. This method reduced the space in the fuel that occupied by methane and increase the amount of air entering the engine. Thus, the volumetric efficiency increased and the power loss can be reduced.

2.03 Bunsen burner

The Bunsen type burner with dual flow is a very simple experimental configuration that avoids many complications of modern gas turbine combustors such as

complex fluid mechanics and high levels of turbulence. The laminar Bunsen flame is however a non ideal burning environment that also shows similarities to the gas turbine combustor environment. The flame is stabilized by a delicate balance between heat loss and fluid mechanical strain. The flame is surrounded by a shroud of dilution air that affects the burning.

The Bunsen type burner model shows that global chemical luminescence measurements can be modeled and understood using simple physical principles without detail information about the exact burning process. Through the understanding of chemical luminescence several other aspects of the burning process can be elucidated, at the very least at a qualitative level. Thus, it can be simplified that Bunsen burner can be alternative for the gas burner which represent the spark ignition principle, as the hydrogen peroxide is well known very corrosive and not properly suitable directly introduce into the gas burner unless the modification need to carried out.

2.04 Hydrogen peroxide potential

The idea of reducing the molecular space in methane gas using the air actually also can be applied by substituting the air with suitable strong oxidizer, such as hydrogen peroxide. Hydrogen peroxide is a safe, effective, powerful and versatile oxidant widely used in the minerals, food processing, paper pulp, cosmetic, pharmaceutical, and textile industries. Commonly, hydrogen peroxide is provided in a solution with water ranging from 2-70% concentration, depending on application.

A few recent studies have indicated some potential promise in utilizing hydrogen peroxide for improving combustion processes for a wide range of energy conversion systems. Golovitchev et al. [7] examined the possibility of promoting methane auto-ignition in air using hydrogen peroxide. They found that the ignition delay was reduced

significantly via the addition of a small amount of hydrogen peroxide (10% by volume of the fuel). The ignition delay was shortened by an order of magnitude for CH₄/O₂/Ar mixtures in 2.55–13.01 atm and combustion temperature from 1525 to 2025 K, and also for CH₄/air mixtures in 0.4–10 atm and 1100–2000 K.

A subsequent study by Golovitchev and Chomiak [14] found that methane auto-ignition promotion was much stronger for hydrogen peroxide than for hydrogen. The reduction was due to the dominant role of the O and OH radicals generated by the rapid decomposition of hydrogen peroxide. Kim et al. [15] discovered that hydrogen peroxide assisted the conversion of harmful nitric oxide to nitrogen dioxide in diesel exhaust gas. In addition, Born and Peters [16] found that proper injection of hydrogen peroxide into a diesel engine reduced soot and NO_x drastically. Also, Martinez et al. [17] determined that the concentrations of unburnt hydrocarbons, CO and NO_x from their industrial pilot plant scale combustion chamber fuelled with natural gas were lowered significantly by the injection of a few hundred ppm of hydrogen peroxide.

David and Graham [4] found that the flame temperature, CO concentration, and NO_x production in the methane-air flame increased with the addition of hydrogen peroxide in their simulation study. The percentage increases were most significant for the leanest mixture.

Thus, in the experimentation and performance analysis of methane combustion behaviour in the ambient condition, several parameters are needed to quantify the results. Some of these parameters include air/fuel ratio, equivalence ratio, flame behaviour, fuel consumption, and emissions

2.05 Air/fuel ratio

The fuel-air ratio is the proportion of fuel to air during combustion. The optimal ratio or the stoichiometric ratio occurs when all of the fuel and all of the oxygen in the reaction chamber balance each other out perfectly. Rich burning is when there is more fuel than air in the combustion chamber while lean burning occurs when there is more air than fuel in the combustion chamber [8]. In this experiment, (λ) is used to represent the air/fuel ratio value and the equation for the value of λ is:

$$AFR = \frac{m_{air}}{m_{fuel}} \quad (1)$$

$$\lambda = \frac{AFR}{AFR_{stoich}} \quad (2)$$

2.06 Equivalent ratio

The equivalence ratio is defined as the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio. Stoichiometric combustion occurs when all the oxygen is consumed in the reaction, and there is no molecular oxygen in the products. If the equivalence ratio is equal to one, the combustion is stoichiometric. If it is < 1 , the combustion is lean with excess air, and if it is > 1 , the combustion is rich with incomplete combustion [18]. The equation of equivalent ratio:

$$\phi = \frac{m_{fuel}/m_{oxygen}}{(m_{fuel}/m_{oxygen})_{st}} \quad (3)$$

Where, m represents the mass, n represents number of moles, suffix st stands for stoichiometric conditions

2.07 Turbulent flame

Combustion requires that fuel and oxidizer to be mixed at the molecular level. This depends on the turbulent mixing process. The general view is that once a range of different size two caps has developed, strain and shear at the interface between, enhance the mixing. During the eddy break-up process and the formation of smaller eddies, strain and shear will increase and thereby steepen the concentration gradients at the interface between reactants, which in turn enhances their molecular inter-diffusion [19]. Molecular mixing of fuel and oxidizer, as a prerequisite of combustion, therefore takes place at the interface between small eddies. Technical processes in turbulent combustion can be divided in terms of mixing into: premixed, non-premixed, or partially premixed turbulent combustion

2.09 NO_x

There are generally three primary sources of NO_x: thermal NO_x, fuel NO_x, and prompt NO_x [8]. Thermal NO_x is formed at very high temperatures, usually above 2200° F, and is a result of the oxidation of the diatomic nitrogen found in combustion air. Thermal NO_x is the most produced form of NO_x created during combustion. It is a function of the temperature and the residence time of the nitrogen at that temperature; the higher the temperature of the flame the higher the formation of thermal NO_x. Fuel NO_x is formed when the nitrogen in fuels combines with the excess oxygen in the air. Prompt

NO_x is formed in the earliest stage of combustion. Prompt NO_x is made by the reaction of atmospheric nitrogen with radicals in the air. The levels of prompt NO_x are generally very low, so it is usually only of interest for the most exacting emission targets.

2.10 CO_x

Carbon Dioxide, CO₂, is always a by-product of combustion [16]. The level of carbon dioxide released is dependent upon the type of fuel used and the combustion process. Meanwhile, carbon monoxide, CO, is a highly toxic gas that can form during incomplete combustion. CO is colourless, odourless, and extremely harmful to the respiratory system [17]. Overexposure to carbon monoxide can cause headache, dizziness, and sometimes death. It is of the greatest importance to measure CO emissions to maintain safety. During combustion most of the carbon burned reacts to form carbon dioxide, however some of the carbon stays in the intermediary stage as carbon monoxide [8]. Excess levels of CO can be created due to incomplete combustion, poor burner design, bad firing conditions, or a leaky furnace.

CHAPTER 3

METHODOLOGY

3.1 Materials

The main materials used for this experiment were hydrogen peroxide and methane gas. Hydrogen peroxide at least 50 percent (concentration) from MERCK Germany. The raw material for methane gas was in nature gas cylinder tank that consists about 90% of methane composition.

3.1.1 Experiment set up and Theoretical Analysis

The main equipments for this study were Bunsen burner, mixing vessel and gas analyzer. Bunsen burner performed the combustion of premix fuel with the air so that the required data for this study can be obtained. In order to get more precise data, the combustion was done in no presence of air so that the difference in each blend can be

figure out directly. The gas analyzer will be used to analyze the emissions of the stack gas for the burner. The gas analyzer was set to detect the light gases with the dry basis reading which means there was no reading of water content in the stack gases.

The mixing vessel was an equipment that most focused on this experimental study as the mixing process of the hydrogen peroxide and methane gas was carried out through this vessel. The main material used in fabricated this vessel was two (2) inch diameter, 1.5 meter length of transparent polyethylene (PE) pipe so that the diffusion of methane through hydrogen peroxide solution could be visually observed. The material selection for the vessels was from polyethylene material so that any blast or unexpected conditions caused from the flammable methane did not out of control although the PE pipe itself could withstand 10 bar of operating pressure which in fact, far save compared to the ambient pressure applied for this experimental study. Flow diagram for this study is shown in Figure 1:

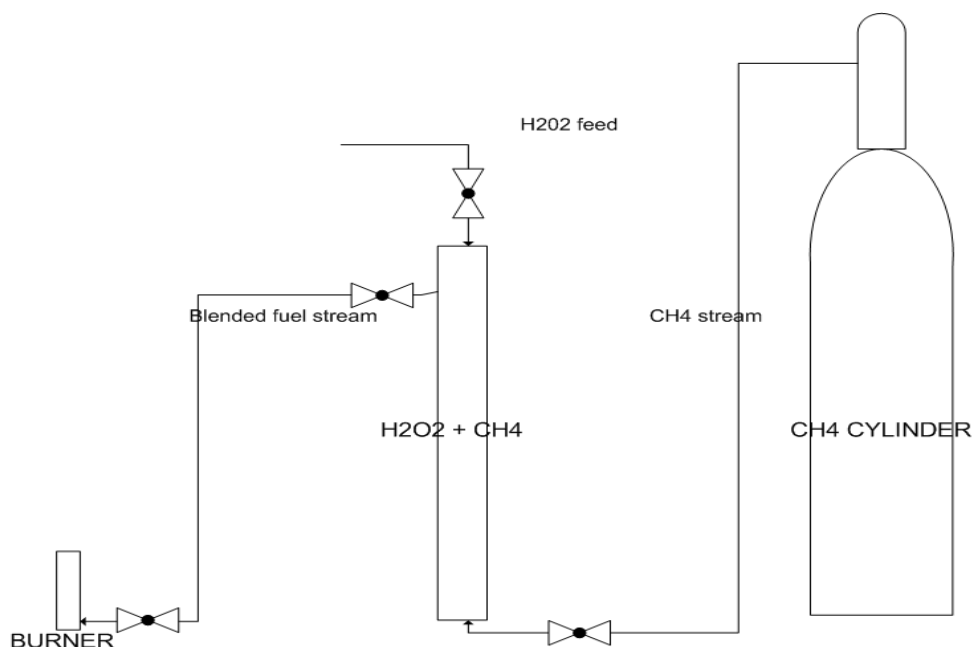
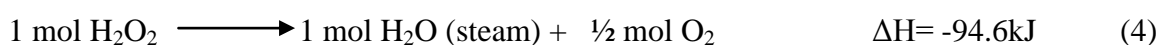


Figure1: flow diagram of methane-H2O2-air combustion

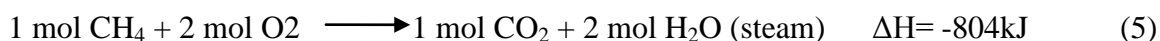
Figure 1 showed the flow process for this experimental study. The methane gas which came from the methane cylinder flowed through 10mm of hose tube and flowed about 3 L/min through the bottom of the mixing vessel. The methane gas then bubbled up through 500mL of hydrogen peroxide and diffused with the solution so that the mixed vapour flowed through the outlet stream of the vessel which connected to the Bunsen burner. The Bunsen burner air inlet was set off so that the mixed fuel did not mix with the ambient air before the combustion process occurred.

3.2 Experimental process

There will be two parts of process highlighted in this study. First part of process generally describes about the preparation of premixed methane and the second part is about the combustion process. In the first part, Hydrogen peroxide decomposed in presence of silver catalyst to form water in the form of steam and gave free half mole of oxygen with enormous amount of heat that could enhance the efficiency of methane combustion. The reaction for decomposition is:



In the combustion process of methane, the reaction is:



In this reaction, air fuel ratio is 2:1 which means 2 mol of oxygen is needed for every mole of methane burnt. Calculating the amount of oxygen from the air and hydrogen peroxide, we will obtain enough excess air to perform a lean combustion that theoretically will reduce the unburned fuel and emissions of CO. However, in this experimental study, the oxygen source from air was eliminated by closing the air inlet at

the Bunsen burner so that the effect of hydrogen peroxide on the methane fuel can be optimized which in fact giving the air/fuel ratio equals to zero.

3.2.1 Preparation of hydrogen peroxide-methane mixture.

Methane feed valve at the bottom and vapour outlet valve at the top were fully closed before the vessel filled with the hydrogen peroxide solution. 500mL of hydrogen peroxide was introduced into the vessel by opening the hydrogen feed valve at the bottom and then closed properly so that the risk of oxygen contained inside the hydrogen peroxide would escape from the vessel can be eliminated.



Figure 3.2.1a: Mixing vessel with hydrogen peroxide