

**THE EFFECT OF VACUUM PRESSURE ON THE FLAMMABILITY
LIMITS OF H₂ ENRICHMENT IN NATURAL GAS (NG)**

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H₂ ENRICHMENT IN NATURAL GAS (NG)**

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ABSTRACT

Hydrogen- enriched natural gas has been widely used in all over the world for application in gas turbine and internal combustion engine. The theory behind this concept is the addition of hydrogen in natural gas can extend the lean operation limit, improve the lean burn ability, and decrease the emission of NO_x, CO and unburned hydrocarbon. The aims of this study are to determine the effect of vacuum pressures on the flammability limits of hydrogen enrichment in natural gas. In this experiment, methane is use to replace the natural gas. The experiments were performed in a 20 L closed explosion vessel. The mixtures were ignited by using spark permanent wire that placed at the centre of the vessel. The explosion pressure data is used to determine the flammability limits, when the low pressure is used in the explosion, the explosion limit will become wide. In this study, the result shows the flammability limits of methane is from 5 % volume to 15 % volume of methane and have revealed that the addition of hydrogen in methane /air mixture will reduce the lower flammability limit initially at 5 % volume to 1 % volume of methane at 0.98 bar. As the conclusion, we can come out that explosion of methane at lower pressure with addition of hydrogen has proven benefit of widen the flammability limit of methane, improving the combustion stability, reduce the emission of NO_x, CO and unburned hydrocarbon and decreasing the spark timing. Hence, the cold start phenomenon that usually occurs at the initial stage of combustion could be overcome by adding hydrogen at low pressure.

ABSTRAK

Penggunaan campuran hidrogen dan gas asli telah banyak digunakan di seluruh dunia untuk aplikasi pada turbin gas dan enjin pembakaran dalaman. Teori di balik konsep ini adalah penambahan hidrogen dalam gas asli dapat memanjangkan had bawah pembakaran, meningkatkan kemampuan bawah pembakaran, dan mengurangkan pembebasan NO_x, CO dan hidrokarbon tidak terbakar. Tujuan kajian ini adalah untuk mengetahui pengaruh tekanan vakum pada batas mudah terbakar pengayaan hidrogen dalam gas asli. Dalam kajian ini, metana digunakan untuk menggantikan gas asli. Percubaan dilakukan dalam bekas letupan yang tertutup. Campuran ini dicucuh dengan wayar percikan tetap yang terletak di tengah bekas letupan. Data tekanan letupan digunakan untuk menentukan had pembakaran dimana pergerakan nyalaan dianggap berlaku apabila menggunakan tekanan rendah dalam letupan, had letupan akan menjadi lebar. Dalam kajian ini, hasilnya menunjukkan had pembakaran metana dari 5 % kepada 15 % isipadu gas asli menunjukkan penambahan hidrogen dalam pembakaran gas asli dan udara melanjutkan had bawah pembakaran daripada 5 % kepada 1 % isipadu metana pada 0.98 bar. Sebagai kesimpulan, kita boleh membuktikan bahawa letupan metana pada tekanan rendah dengan penambahan hidrogen telah membuktikan manfaat memperluaskan had pembakaran metana, meningkatkan kestabilan pembakaran, mengurangkan pembebasan NO_x, CO dan hidrokarbon tidak terbakar dan mengurangkan masa letupan . Oleh kerana itu, fenomena sejuk mula yang biasanya terjadi pada peringkat awal pembakaran boleh diatasi dengan menambah hidrogen pada tekanan rendah.

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LIST OF ABBREVIATIONS

NG	Natural gas
H ₂	Hydrogen
CH ₄	Methane
UFL	Upper flammability limit
LFL	Lower flammability limit
P _{exp}	Explosion pressure
Vol %	Volume percent
t ₁	Ignition time
P _{max}	Maximum explosion pressure
P _m	Corrected explosion overpressure
LPG	Liquefied petroleum gas

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Flammability limits, also called flammable limits, or explosive limits give the proportion of combustible gases in a mixture, between which limits this mixture is flammable. Flammability limits indicates the region of fuel–air mixture ratios within which flame propagation can be possible while outside that flame cannot propagate. There are two distinct separate flammability limits for a mixture. The lean fuel limit up to which the flame can propagate is termed as the lower flammability limit (LFL); whereas, the rich limit is called as the upper flammability limit (UFL). The flammability region is namely restricted within the two flammability limits (Liao, 2005).

A fuel-air mixture is considered to be flammable if it produces a flame that can propagate throughout the available mixture when it is ignited. A flammable mixture might fail to ignite if the ignition source is too weak. However, successful ignition does not guarantee successful flame propagation. In some cases, the ignition source is strong enough to initiate a small flame, but the flame is extinguished as it moves away from the ignition source. In such cases, only a portion of the available mixture is burned, and the mixture is not, therefore, considered flammable (Gardiner, 2008).

Limited fossil fuel and increasing requirement to reduce emissions lead the study about the alternative fuels around the world. Among many potential candidate fuels that

can be used in passenger car engines, natural gas (mainly methane) is one of the most promising alternative fuels and has already been used in many metropolises in the world. But due to its rather low value of burning velocity and high ignition energy, the natural gas-fueled engines usually suffer from low efficiency and high unburned hydrocarbon at low load and idling operations and have poor lean burn capacity (Chenglong Tang, 2009).

In internal combustion engine there is a situation when using of Natural Gas Vehicles such as taxis, where petrol is needed for starting up in firstly running then replaced with natural gas when the temperature is sufficient for starting the ignition. This is called 'Cold Start Phenomenon' which is occurring in fuel-air mixtures within the flammable range or outside the flammable range, at fuel-rich compositions, at temperatures below the auto-ignition temperature (Pekalski, 2002). It is caused by chemical reactions occurring spontaneously at relatively low temperatures and is favoured by elevated pressure. This problem can be solved if the combustion be able to run at leaner condition.

One method to overcome this problem is by hydrogen enrichment in natural gas. Hydrogen is a potential alternative to gasoline in the future. Hydrogen will burn at mixtures seven times leaner than gasoline and five times leaner than methane. It is considered a near perfect energy storage medium, as it can be created from fossil or non-fossil sources. Hydrogen is regarded the best gaseous candidate for natural gas due to its very high burning velocity, and this combination is expected to improve the performance and emissions of spark ignited and compression ignited engines. When compared to natural gas, hydrogen has a low flammability limit. For the safe use of hydrogen-enriched hydrocarbon fuels, explosion data are needed. When the temperature is kept constant and the pressure is increased progressively, then the duration of the induction period falls continuously and the intensity of the cool flame increase, hence the flammability limit will increase widely (Choi, 2005).

The used of hydrogen enrichment in natural gas can extend its lean burn capacity, improve engine performance at low load operation and decrease burn duration. Also, the addition of hydrogen enrichment shows the decreasing the formation of NO_x, CO and

unburned hydrocarbons and increase the fuel efficiency. Its use in conventional combustion engines has generally shown decreased pollutant emissions primarily due to the lean-burn characteristics of hydrogen and a reduction of carbon in the fuel. Mixtures of hydrogen and natural gas are considered viable alternative fuels to gasoline due to lower overall pollutant emissions but suffer from problems associated with on-board storage resulting in limited vehicle range. To date, vehicle engines have run on methane where using a fixed hydrogen-natural gas fraction of 20 % and fixed air-to-fuel ratio but it may be possible to leverage greater advantage from hydrogen addition due to its unique lean-burn properties (C.G. Bauer, 2001).

1.2 Problem Statement

The main problem on the environment by fossil fuel combustion is emissions of nitrogen oxide (NO_x), carbon dioxide (CO) and unburned hydrocarbons. The negative effect of burning fossil fuel on the geopolitical climate is the lack in supply of these fuels and the effect of pollution. With the limited energy sources crisis, the use of natural gas as alternative fuel has widely use in all over the world recently. Natural gas is chosen because it is the world cleanest burning fossil fuel and the usage can overcome the pollution problem to the environment.

But, the problem encountered when using the natural gas as a fuel are the cold start phenomenon where in this case, natural gas will not explode in the presence of a flame until it reaches a very specific concentration in the air - below a certain level it is deemed too lean to burn and above a certain level it may be too rich to burn. One of the major mechanisms for increasing the explosion of natural gas in engine is with adding the hydrogen gas. Hydrogen is an excellent additive to methane or gasoline due to its unique characteristics. Based on an examination of hydrogen properties, it is seen that hydrogen is able to burn ultra-lean at an equivalence ratio 1 of 0.1. Hence, hydrogen addition gives the engine the ability to be operated in the very lean mixture region. Lean mixtures allow for complete combustion, hence decreasing carbon monoxide emissions.

Next, the other problem is to determine the suitable pressure for operating in the spark ignition engine. NGV that been run with hydrogen addition permits complete combustion process under very lean operation conditions. But for better performance, the combustion should be operate at high pressure because it enabling stable combustion at leaner condition. Also, it will decrease the combustion duration and keep a reasonable performance of the internal combustion engines.

1.3 Objective of Study

The objective of this study is to determine the flammability limits of natural gas-air mixture with hydrogen enrichment in a closed vessel at various ranges of vacuum pressure and ambient temperature.

1.4 Scope of study

To achieve the objective of this research, there are two scopes that have been identified:

- i. To determine the effect of flammability limit of natural gas at various pressure below 1 bar.
- ii. To investigate the effect of hydrogen enrichment in natural gas-air mixture.

1.5 Rationale and Significance of Study

In this study, the effect of various pressures below 1 bar in combustion of natural gas with hydrogen enrichment is investigated. Significant of addition of hydrogen is said can reduce the lean flammability limit of natural gas-air mixture. When the initial pressures increase at ambient temperature, the lean flammability limit of natural gas will also decrease. Consequently, hydrogen addition gives the engine the ability to be operated in the very lean mixture region.

The second significant of this study are to overcome the pollution of the environment. Natural gas vehicles (NGVs) are a potential alternative to gasoline vehicles in the short term. They are less polluting, and the fuel is widely available. Lean mixtures allow for complete combustion hence decreasing carbon monoxide emissions. Studies have shown that added hydrogen in percentages as low as 5 -10 % of the hydrocarbon fuel can reduce that hydrocarbon fuel consumption. By using this alternative fuel, the crisis of lacking of fossil fuel can be solved. In this study methane is used to replace the natural gas. Methane can be used to indicate the properties of natural gas since the major component in natural gas is methane.

CHAPTER 2

LITERATURE REVIEW

2.1 Flammability Limits

Flammability limits, also called flammable limits, or explosive limits give the proportion of combustible gases in a mixture, between which limits this mixture is flammable. Gas mixtures consisting of combustible, oxidizing, and inert gases are only flammable under certain conditions.

Knowledge of flammability limits are essential for a quantitative risk assessment of the explosion hazard associated with the use of the flammable gases, especially when handling with flammable mixture to ensure the safe and also economic operation of many industry and domestic application.

The lower flammable limit, LFL describes the leanest mixture that is still flammable, while the upper flammable limit, UFL gives the richest flammable mixture. Increasing the fraction of inert gases in a mixture raises the LFL and decreases UFL. A premixed fuel-air mixture will only burn as long as the fuel concentration is between the upper and lower flammability limits (Carl and William, 2001).

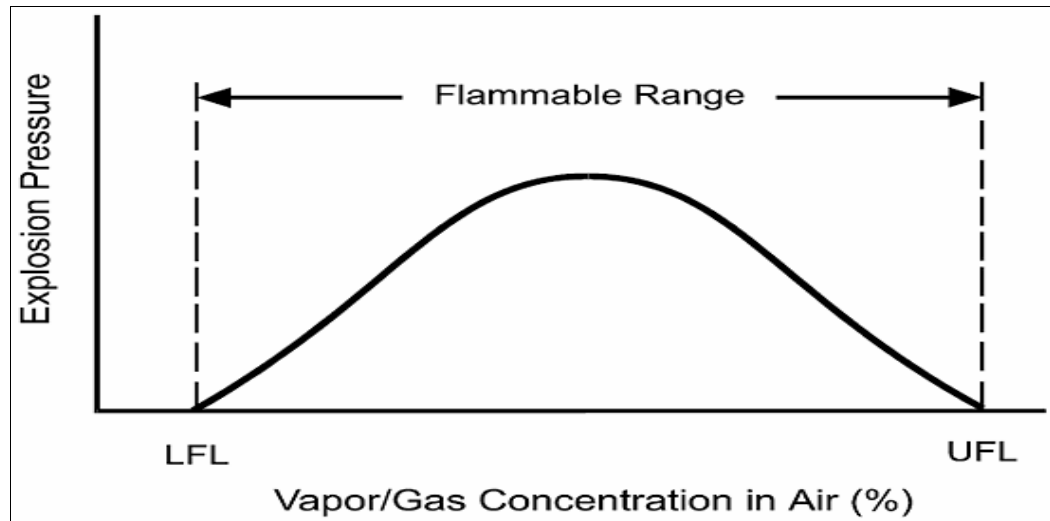


Figure 2.1: Schematic represents flammability limit

Source: Dag Bjerketvedt (1992)

Figure 2.1 shows the schematic represents flammability limit of vapor/gas concentration in air. When the combustion of the fuel is not controlled within the confines of the burner system, the limits of flammability can be called the Explosive Limits. The explosive limits of NG are approximately

- LEL = 5 %
- UEL = 15 %

where,

LEL is the lower explosive limit

UEL is the upper explosive limit

The flammability limits are experimentally determined data. The flammability limits in air depend on initial temperature and pressure. Standard test conditions are 25 °C and 1 atm. Figure 2.1 shows the flammable range for some fuel-air mixtures.

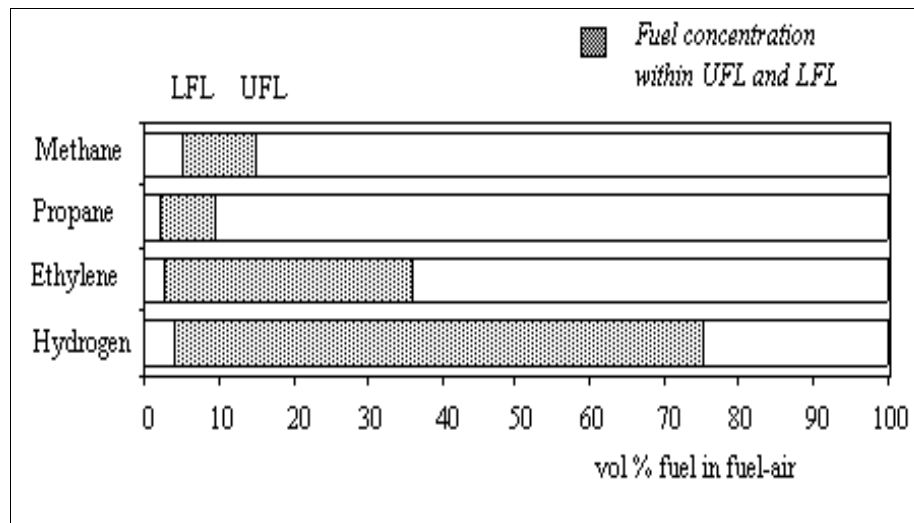


Figure 2.2: Flammability range for fuel-air mixtures at 1 atm and 25 °C

Source: Dag Bjerketvedt (1992)

Figure 2.2 shows the flammability range for fuel-air mixtures at 1 atm and 25 °C. The wide flammable range of hydrogen which is from 4 to 75 volume % explains that it is easy to get a flammable cloud of hydrogen in air. For propane and methane, the flammability range is much narrower. Meanwhile, the flammability range for ethylene is wider compared to methane and propane which is from 3 to 36 volume %.

2.1.1 Flammability Limits Change Factor

The flammability limits are generally changed with 3 factors that are inert, temperatures and pressure. In chemistry, the term inert is used to describe something that is not chemically active. The noble gases were described as being inert because they did not react with the other elements or themselves. It is now understood that the reason that inert gases are completely inert to basic chemical reactions (such as combustion, for example) is that their outer valence shell is completely filled with electrons. With a filled outer valence shell, an inert atom is not easily able to acquire or lose an electron, and is therefore not able to participate in any chemical reactions.

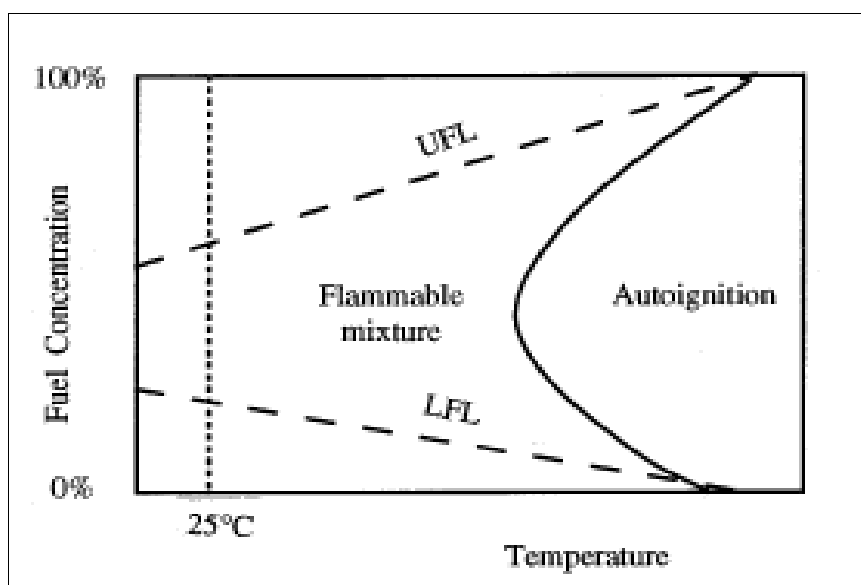


Figure 2.3: The effect of temperature on LFL and UFL

Source: Dag Bjerketvedt (1992)

As shown in Figure 2.3, the flammable range will widen when the initial temperature is increasing. Changes in initial pressure will for hydrocarbons in air not change the LFL significantly, but the UFL will increase.

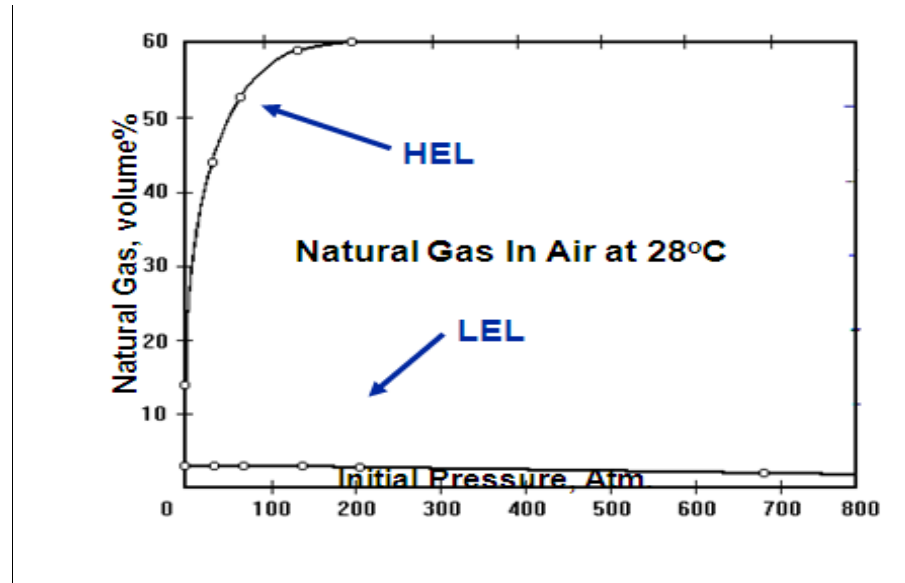


Figure 2.4: The effect of pressure on the LEL and HEL

Source: Toups (2003)

where

HEL = UEL = higher explosive limit

LEL = lower explosive limit

As shown in Figure 2.4, the HEL will increase with increasing pressure. But, at certain pressure, the HEL will remain constant even though the pressure is keep increase. Meanwhile, the LEL have not much change when the pressure increases.

2.1.2 Flammability Limit Dependence on Pressure

The initial pressure has little effect on the LEL except at very low pressure (<50 mmHg absolute), where flames do not propagate. The UEL increase significantly as the initial pressure is increased, broadening the flammability range. An empirical expression for the UEL for vapors as a function of pressure is available.

$$UEL_P = UEL + 20.6(\log P + 1) \quad (2.1)$$

Where P is the pressure (mega Pascal absolute) and UEL is the upper flammability limit (volume % of fuel at 760 mmHg). However, the empirical expression for the UEL for vapors as a function of pressure is not available for all gases / vapors; nevertheless, an empirical expression can be found for the UEL by the regression of experimental data. Correlated their data to an equation for the pressure dependence of the UEL (Eq. (2.2))

$$UEL(P_1) = UEL(P_0) \left[1 + a \left(\frac{P_1}{P_0} - 1 \right) + b \left(\frac{P_1}{P_0} - 1 \right)^2 \right] \quad (2.2)$$

Source: Shu-Ching Chen (1999)

To estimate the UEL at the different initial pressures, Eq (2.1) is used. If the error in UEL using Eq. (2.1) is significant, then coefficients a and b can be fed to Eq. (2.2). The prediction of UEL by the empirical expression of Eq. (2.2) is practically close to the real UEL of OX (Shu-Ching Chen, 1999).

2.1.3 Le Chatelier's Law

Eqn (2.3) below shows the flammability limits for fuel mixtures that can be calculated by Le Chatelier's law:

$$LFL_{\text{Mtx}} = \frac{100}{\frac{C_1}{LFL_1} + \frac{C_2}{LFL_2} + \dots + \frac{C_i}{LFL_i}} \quad (2.3)$$

where $C_1, C_2 \dots C_i$ [vol.%] is the proportion of each gas in the fuel mixture without air

Source: Dag Brerketyedt (1992)

Von Niepenberg et al. (1978) used Le Chatelier's rule for predicting flammability limits for fuel mixtures containing inert gas. (Hustad and Sønju, 1988) found a good agreement between experiments and Le Chatelier's law for LFL at elevated temperature and pressure for fuel mixtures. It should be noted, however, that the formula does not work properly for H_2 and for unsaturated hydrocarbons. It is also only valid if the components are chemically similar.

2.2 The Cold Start Phenomenon

Cold start phenomenon is the situation usually happen in internal combustion engine. When Natural Gas is use as a fuel for vehicles, the problem commonly happen is failure for starting up in firstly running of the internal combustion engine. To overcome this problem, supplemental fuel is needed to starting up the firstly running then replaced the supplemental fuel with natural gas when the temperature is sufficient for starting the ignition. The most excellent candidate of the supplemental fuel are hydrogen because the ability to run at leaner condition. Cold start phenomenon have been reported in dynamic systems such as combustion engines, flow tubes and static systems (Pekalski, 2002).

2.2.1 Effect of Pressure and Temperature

In hydrocarbon–fuel mixtures, for each temperature in the cool-flame zone, there is a certain critical initial pressure above which cool flames arise following an induction period. Below the critical pressure, cool flames are not formed. Below the critical pressure, cool flames are not formed.

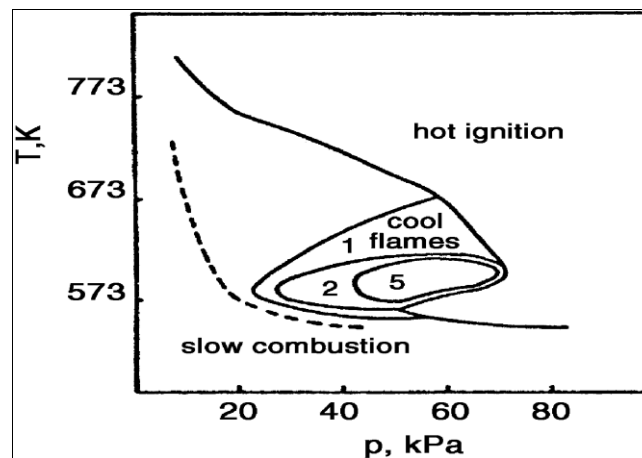


Figure 2.5: The ignition diagram of a propane/oxygen (1:1) mixture. The numbers 1, 2, and 5 refer, to the number of cool flames occurring in the respective region.

Source: Pekalski (2002)

Figure 2.5 shows the ignition diagram of propane/oxygen mixture. The induction period of a cool flame is defined as the time from the introduction of the mixture into the reaction vessel until the cool-flame luminescence starts. Inside the cool-flame zone, an increase in temperature for a certain constant initial pressure is accompanied by a decrease in the induction period and increase in intensity (brightness of luminescence, magnitude of pressure increase) of the cool flame. Further increase in temperature results in an even greater decrease in the induction period, but with a decrease, instead of an increase, in intensity of the cool flame. This effect is due to the disappearance of the peroxy radical, whose presence is necessary for the further low temperature oxidation path. If, on the other hand, the temperature is kept constant and the pressure is increased progressively, then the duration of the induction period falls continuously and the intensity of the cool flame increases. This effect is due to the fact that the low temperature oxidation path thus cool flames are favoured by increasing pressure. Since reactions leading to the cool flame are not isothermal, obviously the greater the volume, the shorter the induction period, since relative heat loss decreases as vessel size increases (Pekalski, 2002).

2.3 Concept of Explosion

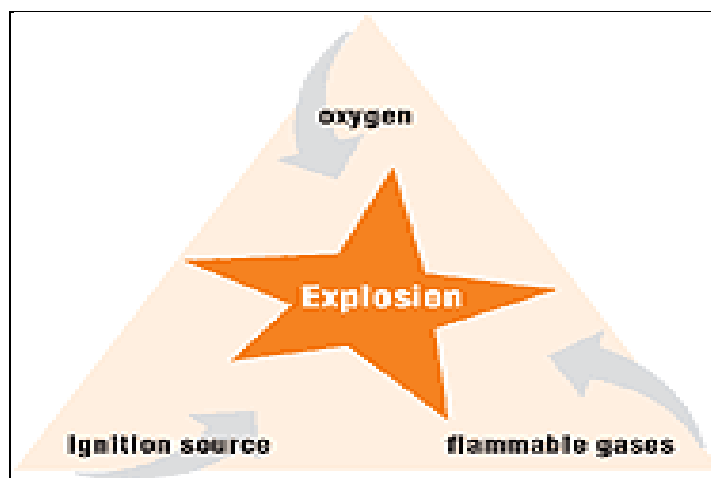


Figure 2.6: Explosion triangle

Source: Dag Bjerketvedt (1992)