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Flammability limits of hydrogen-diluent mixtures in air

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Flammability Limits of Hydrogen-Diluent Mixtures in Air

By

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ABSTRACT

The flammability limits of hydrogen-diluent fuel mixtures in air for upward and downward flame propagation at ambient pressure were determined experimentally. A wide range of diluent concentrations were examined, up to 95% by volume in the fuel mixture. The diluents employed were helium, argon, carbon dioxide and nitrogen. The effects of changes of the initial mixture temperature on the flammability limits were determined for fuel mixtures containing 50% diluent by volume. It was observed that helium was more effective than argon at narrowing the flammable range of hydrogen mixtures. The value of the lean flammability limit was increased to a greater extent by the addition of helium than carbon dioxide despite the low heat capacity of helium. Values of the flammability limits predicted using the constant adiabatic flame temperature concept are in generally good agreement with the experimentally obtained values. The agreement between the two sets of values was better for the rich flammability limits than the corresponding lean flammability limits and was particularly poor for lean mixtures involving high concentrations of helium.

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LIST OF SYMBOLS AND ACRONYMS

α_l	Characteristic constant of the lean limit of a fuel-diluent mixture
α_r	Characteristic constant of the rich limit of a fuel-diluent mixture
ASTM	American Society for Testing and Materials
C_p	Heat capacity, kJ/ kmol K
D	Diffusion coefficient, m^2/s
DIN	German Institute for Standardization
EN	European Standards
H	Enthalpy, J/ mol
ΔH_f	Enthalpy of formation, J/ mol
k	Thermal conductivity, W/m K
$L_{f,l}$	Lean flammability limit of combustible gas, % by vol.
$L_{f,r}$	Rich flammability limit of combustible gas, % by vol.
$L_{m,l}$	Lean flammability limit of fuel-diluent mixture, % by vol.
$L_{m,r}$	Rich flammability limit of fuel-diluent mixture, % by vol.
M	Molecular mass, kg/ kmol
ρ	Density, kg/ m^3
T_A	Adiabatic flame temperature, K
T_{IN}	Initial mixture temperature, K
T_0	Reference temperature, K
V	Volume, %

CHAPTER 1

INTRODUCTION

1.1 Background

Fire and explosion hazards are important safety considerations associated with the usage of fuels, particularly of hydrogen. The determination of flammability limits is a primary concern in addressing these hazards. Values of the lean and rich flammability limits indicate the respective minimum and maximum volumetric concentrations of fuel in the fuel-air mixture where a flame just fails to propagate after ignition from an external source. These limits exist when the energy required to heat the immediately adjoining un-burnt fuel-air mixture and the energy dissipated to the surroundings are greater than the energy released from the chemical reaction at the flame front. At present, the limits are determined mainly through experimentation. The apparatus size and design affect the values of the flammability limits determined, which are discussed and cited in the literature review.

The present investigation aims to establish experimentally a comprehensive set of values for the lean and rich flammability limits of hydrogen in the presence of the diluents helium, argon, carbon dioxide, and nitrogen. Helium as a diluent is a focus in this investigation as it is a highly buoyant, diffusive, and conductive gas compared to other commonly used diluents. It appears that there is only limited data on the flammability limits of hydrogen-helium mixtures in an air atmosphere available in the open literature.

A particular application of the information obtained about the flammability limits of hydrogen-helium mixtures is determining to what extent hydrogen, as a relatively cheap but flammable gas, can be used to replace more expensive helium in dirigible applications without compromising the safety considerations of using helium only. This issue has been examined earlier (Satterly, J. And Burton, E.F., 1919), as referenced by Coward and Jones (1952), in which balloons filled with hydrogen-helium mixtures with less than 28% hydrogen by volume would not burn. However, this is not consistent with later investigations of the flammability limits of some hydrogen-helium mixtures (Coward H.F., and Jones, G.W., 1952; Boon, S.L., 1982; Kumar, R.K., 1985; Shebeko, Y.N., et al., 1995).

The flammability limits of hydrogen are of particular interest in the nuclear industry as the failure of the reactor cooling system may result in the production of hydrogen gas. A release of hydrogen could result in an explosion where radioactive material is dispersed into the atmosphere. Helium was also used in investigating hazards involved with the release of hydrogen into the atmosphere, as the rates of the diffusive propagation are somewhat similar for both gases (Fardisi,S., 2009). It is therefore important to determine how the addition of helium affects the limiting permissible concentrations of hydrogen in air.

Diluents can also be potentially used as a means to suppress fires. The release of helium above of a fire or a flame would be less effective than the release of a heavy gas such as carbon dioxide. As a highly buoyant gas, helium would mix slowly and much of it would remain above the flammable mixture.

However, helium is potentially more effective as a fire suppressant when released at the base of a flame or below fires adjacent to ceilings within enclosed spaces.

The experimentally determined limits can also be used to validate some available predictive approaches. In particular, this investigation compares the accuracy of predictive methods that are based on the assumption of constant adiabatic flame temperature for limiting mixtures (Bade Shrestha, S., 1992; Wierzba, I., et al., 1994, 1995 & 1996; Bade Shrestha, S. et al., 2009).

1.2 Objectives

The objectives of this investigation are to:

- To determine consistently the experimental flammability limits of binary mixtures of hydrogen with the diluents helium, argon, carbon dioxide and nitrogen at atmospheric temperature and pressure
- To compare the values of flammability limits established for upward flame propagation of some hydrogen-diluent mixtures to those established for downward flame propagation under the same operating conditions
- To determine the effects of changes in the initial temperature on values of the flammability limits
- To evaluate the effectiveness of predictive methods based on the assumption of constant adiabatic flame temperature for mixtures at the flammability limit

CHAPTER 2

LITERATURE REVIEW

Safety is a primary concern when dealing with flammable gases and the study of flammability limits is an important consideration in addressing this issue. Over the last half century, there have been several extensive reviews on the subject of flammability limits. (Coward, H. and Jones, G.W., 1952; Zabetakis, M.G., 1965; Lovachev, L.A., et al., 1973; Lovachev, L.A., 1979; Jarosinski, J., 1986). Early investigations into flammability limits were concerned with improving safety in mining operations. As the use of flammable gases expands, so does the need to increase our understating of the flammability limits. To date, experimental work has outpaced theoretical work in the field and as previous studies have shown, there is a wide range of parameters that can affect the determination of the flammability limits.

2.1 Experimental Studies

There are many factors that influence the determination of flammability limits. This extends to the very definition of what constitutes a flammability limit. Coward and Jones (1952), and Zabetakis (1965) defined two separate flammability limits, the minimum and maximum concentration of fuel in the oxidizer that is non-flammable as well as the minimum and maximum fuel concentration when the mixture just becomes flammable. The definition of

flammability limits as when the fuel mixture just fails to sustain flame propagation has been used in many previous studies and it is used in the present investigation. (Boon S.L., 1982; Cheng, T.K.H., 1985; Kumar, R.K., 1985; Harris, K.P., 1990, Ale, B.B., 1998; Kilchyk, V., 2000; Wang, Q., 2004).

Several different combustion chamber configurations have been employed and standardized for the determination of flammability limits. The US Bureau of Mines standardized the use of a vertical transparent cylinder with a diameter of 51 mm (2 in) and a length of 1.8 m (6 ft). It was found that cylinders with diameters smaller than 51 mm produce narrower flammability limits, as there are increased heat losses to the cylinder wall. Cylinders with diameters greater than 51 mm did not produce significantly different results due to the shrinking ratio of surface area to volume (Coward, H. and Jones, G.W., 1952). Chamber lengths over one metre are recommended to eliminate the effect of the ignition source on flame propagation. Many studies have employed a similar apparatus, where the flame tube was a vertical steel cylinder, insulated to minimize the effects of heat loss from the chamber. (Boon S.L., 1982; Cheng, T.K.H., 1985; Kumar, R.K., 1985; Harris, K.P., 1990, Ale, B.B., 1998; Kilchyk, V., 2000; Wang, Q., 2004).

Flammability limits have been determined in shorter cylinders of 30 cm in height with widths of 6 cm and 8 cm according to European standards DIN 51649 and EN 1839. It is noted that the flammability limits determined in such vessels are considerably wider than flammability limits determined in chambers over one metre in length (Takahashi, A., et al., 2003; Van den Schoor, F. and Verplaesten,

F., 2007). Additionally, it was found by Takahashi (2003) that for shorter vessels of 40 cm in length, the flammability limits of methane and propane mixtures narrowed as the vessel diameter increased (Takahashi, A., et al., 2003). It was suggested that this occurred due to the walls of the smaller diameter tubes reflecting radiation back towards the centreline of the vessel, which aided flame propagation.

There have been many studies where spherical reaction vessels have been used to determine the flammability limits of mixtures. The American Standards have adopted two vessels of 5 dm^3 and 4 dm^3 capacities (ASTM E 681, E 2079). Some studies have also been conducted in larger chambers. Shebeko (1995) used a 20 dm^3 chamber, Cashdollar et al. (2000) used a 20 dm^3 and 120 dm^3 chamber, and Burgess (1982) used a larger 25.5 m^3 chamber. Smedt (1999) compared the difference in flammability limit values between 20 dm^3 sphere and those obtained in a cylindrical vessel of 30 cm in height and 6cm in diameter (DIN 51649). It was found that the cylinder produced wider limits due to the less restrictive criteria employed.

There have been several methods employed to detect the presence of flame propagation. Visual detection of flame propagation can be used when flammability tests are conducted in a transparent container. This method of detection has been used in many studies for both standards developed by the US Bureau of Mines, and European standards (Coward, H.F. and Jones, G.W., 1952; Levy, A., 1965; Andrews, G. E. and Bradley, D., 1973; Panlilio J.V., 1981;

Takahashi, A., et al., 2003; Van den Schoor, F. and Verplaetsen, F., 2007). For closed insulated vessels or those not constructed from transparent materials, a pressure rise, often of 7%, is used for the determination of flammability limits (Bunev, V.A., 1972; Smedt, G.De., et al., 1999; Van den Schoor, F. and Verplaesten, F., 2006). Smedt (1999) found that better agreement could be achieved with European Standards if the pressure rise criteria in a 20 dm^3 vessel was changed to 2%. Additionally, it was observed by Cashdollar et al. (2000) that when determining the lean flammability limit of hydrogen in increasingly large spherical vessels, a greater concentration of hydrogen was required to cause a 7% pressure rise. For cylindrical test chambers open to the atmosphere, the detection of a temperature rise beyond a certain threshold is the most convenient way to detect flame propagation (Boon, S.L., 1982; Kumar R.K., 1985; Hustad, J.E. and Sonju, O.K., 1988; Ale, B.B., 1998). However, hot gases from an extinguished flame may continue to rise up the cylinder for small distances of up to 15 cm (Levy, A., 1965).

The direction of flame propagation has been shown to influence the flammability limits of the mixture. Upward flame propagation, where the mixture is ignited at the bottom of the cylinder and the flame propagates to the top of the cylinder, produces wider flammability limits than downward flame propagation where the mixture is ignited at the top of the cylinder and the flame propagates downward. The flammability limits for horizontal flame propagation were found to be between that of the upward and downward limits (Andrew, G.E., and Bradley,

D., 1973; Hertzberg, M., 1976; Macek, A., 1979; Kumar, R.K., 1985; Jarosinski, J., et al., 1982). It was found that very lean upward propagating flames were driven by the buoyant effects on a rising bubble of the heated products of combustion. Heat transfer from the flame front to the un-burnt mixture was aided by natural convection. The extinction of lean upward propagating flames was attributed to flame stretch. Very lean downward propagating flames need to overcome the effects of buoyancy and heat transfer from the front to the un-burnt mixture occurs through thermal conductivity. The extinction mechanism for downward propagating flames was found to be due to heat loss to the cold walls of the chamber followed by the effects of buoyancy driving cooled products ahead of the flame (Jarosinski, J., et al., 1982). Flammability limits in zero gravity, where the effects of buoyancy would be eliminated, have been examined in several studies (Ronney, P.D., et al., 1985; Ronney, P.D., and Wachman, H.Y., 1985; Strethlow, R.A., et al., 1988). It was found that flammability limits in a zero gravity environment are between the limits for upwards and downwards propagation under normal gravity conditions.

Studies have shown that the ignition source can greatly influence the flammability limits of a mixture. Ignition methods used in previous investigations include spark ignition, pilot flame, hot rods or wires, chemical igniters, fused wires, and plasma jets (Coward, H.F. and Jones, G.W., 1952; Zabetakis, M.G. and Richmond, J.K. 1953; Boston, P.M., et al., 1984; Vince I.M., et al., 1984). Spark ignition systems, allow the ignition energy to be accurately controlled

through the power and duration of the spark. Optimized electrode spacing, ignition voltage and spark duration have been previously reported (Blanc, M.V., et al., 1949; Zabetakis, M.G. and Richmond, J.K., 1953). If the electrode gap is too narrow, the flame will quench due to heat loss along the electrodes. However, larger electrode gaps require higher voltage to ionize the mixture (Lewis, B. and von Elbe, G., 1987).

Many investigations have examined the affect of initial temperature on the flammability limit (White A.G., 1925, Coward, H.F. and Jones, G.W., 1952; Zabetakis, M.G., 1965; Boon, S.L., 1982; Hustad, J.E. and Sonju, O.K., 1988; Harris, K.P., 1990; Ale, B.B., 1998; Kilchyk, V., 2000; Wang, Q., 2004, Kondo, S., et al., 2011). These studies have employed different test chambers with increasing and decreasing initial temperatures and agree that there is a linear relationship between the initial temperature and the value of the flammability limit. Zabetakis (1965) suggested the modified Burgess-Wheeler Law as a method to correlate the initial temperature and flammability limits. This correlation can be explained by a threshold temperature that must be reached in order for the flame to propagate. As the initial temperature increases, less energy is required to heat the mixture to the threshold temperature. The energy released from the reaction is directly related to the amount of fuel in the lean limit and the amount of oxygen in the rich limit.

The initial pressure of the mixture can influence the flammability limits. Limits tend to remain unchanged as pressures drop below atmospheric until an

absolute pressure is reached below which the flame will not propagate (Lewis, B. and von Elbe, G., 1987). Pressures above atmospheric tend to widen the flammability limits (Bone, W.A., et al., 1928; Coward, H.F. and Jones, J.W., 1952; Zabetakis, M.G., 1965; Lovachev, L.A. 1979; Vanderstraeten, B. et al., 1997; Van den Schoor, F. and Verplaesten, F., 2006). The relationship between pressure and flammability limits is not well understood. Vanderstraeten (1997) found a second order relationship between initial pressure and the rich flammability limit of methane mixtures. Van den Schoor (2006) found that for hydrogen and methane mixtures the rich flammability limits varied linearly with increasing pressure from 1 bar to 10 bar. Additionally, it was found that the flammability limits of carbon monoxide narrow with increasing pressure (Bone, W.A., et al., 1928; Coward, H.F. and Jones, J.W., 1952).

Several studies have shown that chamber material, residence time and initial temperature can influence the flammability limits of certain fuels. Reactions occurring in steel vessels at elevated temperatures and increasing residence time produced narrower flammability limits (Ale, B.B., 1998; Wang, Q., 2004). This phenomenon was evident in hydrogen, carbon monoxide and ethylene fuels. Gas analysis determined that pre-ignition reactions occurred in the chamber, thus altering the mixture prior to ignition. This behavior was attributed to the catalytic reaction between the fuel and the steel wall of the chamber. These reactions became significant at initial temperatures higher than 200°C and at residence times longer than 5 minutes. It was found that using a quartz cylinder

eliminated the pre ignition reactions that occurred with carbon monoxide and reduced the pre ignition reactions that occurred with hydrogen and ethylene (Wang, Q., 2004). The flammability limits of methane did not vary greatly between the stainless steel and quartz vessels.

The addition of diluents to fuel mixtures alters the thermodynamic and physical properties of the mixture, such as specific heat, diffusivity, thermal conductivity, and density. As a result, the flammability limit changes (Coward, H.F. and Jones, G.W., 1952; Barret H.C. and Hibbard, R.R., 1957; Zabetakis, M.G., et al., 1965; Boon, S.L., 1982; Cheng, T.K., 1985; Kumar, R.K., 1985; Harris K.P., 1990; Shebeko, Y.N., et al., 1995; Kilchyk, V., 2000). The addition of diluents with high specific heat capacities such as carbon dioxide and water vapor narrows the flammability limits. Conversely, diluents with low specific heat capacities such as argon widen the flammability limits. However, the flammability limits of lean mixtures of hydrogen have been found to narrow with the addition of helium, which has been attributed to the high thermal conductivity of helium (Kumar, R.K., 1985), and the high diffusivity of helium (Shebeko, Y.N., et al., 1995). The effects of adding low specific heat capacity diluents to fuels such as hydrogen could prove beneficial to increasing the efficiency of spark ignition engines as a result of higher temperatures and faster burning velocity (Karim, G.A., 2002).

The determination of flammability limits is generally done with quiescent, homogenous mixtures. There have been investigations into the effect of

turbulence on the limits. It has been shown that moderate turbulence in the mixture does not significantly influence the flammability limits whereas high levels of turbulence narrows the flammable range (Coward, H.F. and Jones, G.W., 1952; Cashdollar, K.L., 2000). It has also been shown that turbulence can disperse the energy from spark ignition, impeding the formation of the flame kernel (Lovachev, L.A., et al., 1973; Kumar, R.K., et al., 1983).

2.2 Theoretical Studies

The theory of flammability limits has lagged behind the experimentally determined limits. Early theories on flammability limits and flame propagation attributed the phenomenon to heat loss (Spalding, D.B., 1957; Mayer, E., 1957; Lovachev, L.A., 1971; Hertzberg, M., 1976). Other theories proposed that the preferential diffusion of active radicals or reactants was a primary mechanism in flame propagation (Lewis, B. and von Elbe, G., 1987). More recently, chemical kinetic models have been introduced to explain the existence of flammability limits (Peters, N. & Smooke, M.D., 1984; Law, C.K. & Egolfopoulos, F.N., 1990). The limiting factor of many of these theories is the reliance on one factor for determining the flammability limits whereas the actual mechanisms of flame propagation and quenching are likely more complex.

Thermal theories of the flammability limits of fuels attribute the existence of these limits to heat loss from the flame front (Zeldovich, Y.B., 1944; Spalding, D.B., 1957; Mayer, E., 1957; Lovachev, L.A., 1971). The flame front is the area

where the chemical reactions are occurring. The heat generated by the reactions in the flame front must exceed the heat losses to the surroundings. If the heat losses are too high, the temperature of the flame front decreases and reactions slow down, resulting in flame quenching. Spalding (1957) attributed the heat loss mechanism to radiative heat loss to the walls of the combustion chamber. His results, however, did not agree well with experimental data. Lovachev (1971) was able to explain the difference in limits between upward and downward flame propagation by considering convection as a heat transfer mechanism from the flame front. Later, Hertzberg (1976) included conductive, convective, and radiative heat loss in his theory of flammability limits. This more inclusive model provided closer estimations to experimental results for horizontally propagating flames.

Diffusion theories have also been developed to explain the existence of certain flammability limit phenomena. Very lean mixtures of hydrogen, with concentrations lower than 8% hydrogen by volume in the mixture, propagate as a cellular flame enabled by the preferential diffusion of hydrogen to the flame front (Goldmann, F., 1929), as referenced by Coward and Jones (1952). Additionally, Lewis & von Elbe (1987) attempted to explain the lower than expected flame temperatures in the flame front. They proposed that the diffusion of radicals from the flame front to the un-burnt mixture was the primary mechanism of flame propagation. However, this theory does not explain the existence of flammability limits (Lewis, B. and von Elbe, G., 1987; Jarosinski, J., 1982).

Chemical kinetic theories have been proposed to explain the existence of flammability limits (Peters, N. & Smooke, M.D., 1984; Law, C.K. & Egolfopoulos, F.N., 1990). These theories propose that flame propagation is driven by the balance between chain-branching reactions that produce active radicals and chain terminating reactions that consume active radicals. If the chain terminating reactions outpace the chain branching reactions, the overall reaction rate slows, causing the flame to extinguish. The models presented in recent studies accounting for the effect chemical kinetics as well as transport processes and the effects radiative heat loss in an effort to achieve more accurate predictions of the flammability limits (Law, C.K. & Egolfopoulos, F.N., 1992; Van den Schoor, F., et al., 2008). The software packages used in these studies include CHEMKIN (Law, C.K. & Egolfopoulos, F.N., 1992), and CHEM1D (Van den Schoor, F., et al., 2008).

It has been noted in many studies that the adiabatic flame temperature remains nearly constant as the initial temperature of the mixture is changed or diluent is added for mixtures at the flammability limit, known as limiting mixtures (White, A.G., 1925; Zabetakis, M.G., 1965; Cheng, T.K.H., 1985; Shrestha, S.O., 1992). It has been suggested that a threshold flame temperature must be reached in the flame front in order for the flame to propagate and this minimum flame temperature is proportional to the adiabatic flame temperature. This adiabatic flame temperature can be assumed to remain constant for limiting

mixtures of a fuel as the initial temperature is changed or a diluent is added (Cheng, T.K.H., 1985; Bade Shrestha, S.O., 1992).

The constant adiabatic temperature concept was reported to yield reasonable estimates for a variety of mixtures and temperatures (Bade Shrestha, S.O., 1992, Ale, B.B., 1998; Wang, Q., 2004; Zlochower, I.A., 2012). However, it was found that the upper flammability limits for ethylene and dimethyl ether determined in a 120 dm^3 chamber diverged significantly from the limits predicted using the constant adiabatic temperature concept (Zlochower, I.A., 2012). This method can also be used to predict the limiting concentrations of fuel-diluent mixtures by accounting for the change in heat capacity of the mixture as diluent is added. Again, there was found to be good agreement between the predicted and experimental values for limiting mixture concentrations (Wang, Q., 2004; Vidal, M. et al., 2006; Bade Shrestha, S.O., et al., 2009).

Another useful estimating tool is Le Chatelier's Rule which predicts the flammability limits of mixtures containing more than one fuel. This category includes a wide array of gases including natural gas and bio gases. This method states that any mixture of limiting fuel-air mixtures is itself a limiting mixture, represented by the following equation,

$$L_m = \frac{100}{\sum \frac{Y_i}{L_i}} \tag{2.1}$$

where,

L_m is the flammability limit of the fuel mixture in air, % by vol.

L_i is the flammability limit for the '*i*'th fuel species, % by vol.

Y_i is the corresponding concentration of the fuel species, % by vol.

This method provided a reasonable level of accuracy for predicting the lean limits of a wide variety of fuel mixtures, but was less accurate for the rich limits of certain mixtures (Boon S.L., 1982; Cheng, T.K.H., 1985; Harris, K.P., 1990; Ale, B.B., 1998; Kilchyk, V., 2000; Wang, Q., 2004; Kondo, S., et al., 2008). Cheng reported that mixtures involving hydrogen significantly deviated from the limits predicted by Le Chatelier's rule.

2.3 Summary

This study used a similar apparatus to that used by the US Bureau of Mines, with a 51mm diameter and a one-metre length. These dimensions allowed the widest flammability limits to be observed that would propagate on their own in air while minimizing the influence of the ignition source. The ignition source likewise had been optimized in regards to the spark gap and duration to minimize local quenching to produce the widest flammability limits. The flammability limits were determined at constant pressure to ensure that the mechanisms of flame propagation remained constant as the flame traveled the length of the tube. A wide range of diluent concentrations were tested to explore the effects of diluent addition to hydrogen. Moderate initial temperatures were also considered and used to evaluate the effectiveness of assuming a constant adiabatic flame temperature for limiting mixtures.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental Apparatus

The apparatus employed was similar to that used by the U.S. Bureau of Mines for the determination of the flammability limits at atmospheric pressure. It was used in previous investigations conducted at the Department of Mechanical and Manufacturing Engineering at the University of Calgary (Boon, S.L., 1982; Harris, K.P., 1990; Ale. B.B., 1998; Kilchyk, V., 2000; Wang, Q., 2004). The apparatus consists of:

- Stainless steel vertical cylindrical flame tube
- Electric heating system
- Electric spark ignition system
- Mixing chamber with stirring fan
- Compressed air supply
- Vacuum exhaust system
- Gas cylinders

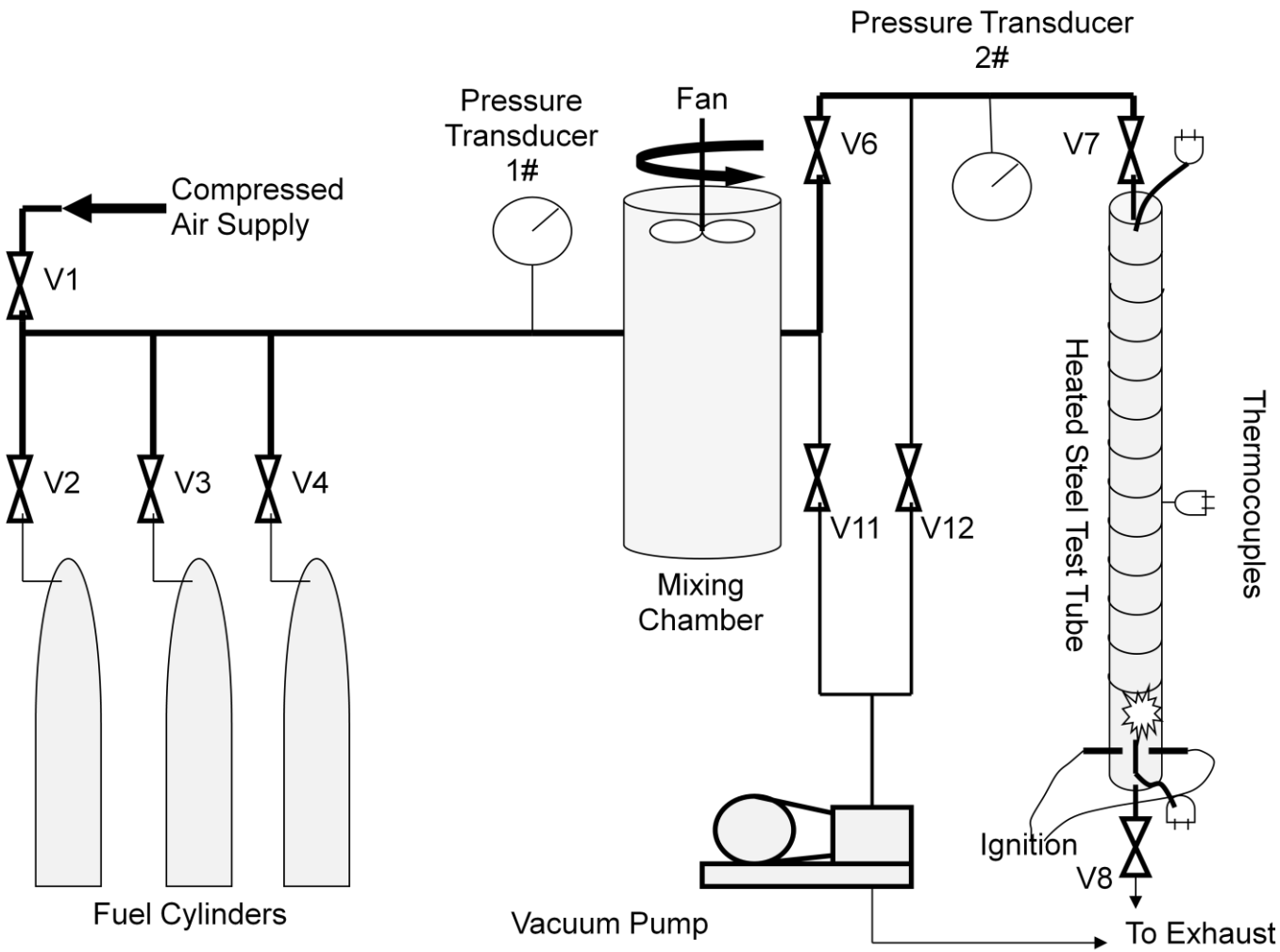

Figure 3.1. Schematic of the apparatus

Figure 3.2. Photograph of the apparatus

The smooth cylindrical flame tube had a 50.8 mm diameter and was one metre in length. It was made of stainless steel type 316. The flame tube was heated externally by electric heaters. The main heater was controlled with an automatic temperature controller. Two additional heaters at the ends of the flame tube were manually controlled to maintain a uniform temperature profile along the flame tube. The flame tube and heaters were covered in ceramic heat-insulation to decrease heat loss. A set of Chromel-Alumel (k-type, diameter 0.125mm) thermocouples were centered in the flame tube at the top and bottom to detect sudden transient changes in the mixture temperature due to flame propagation.

The flame tube was fitted with a spark ignition system. For establishing the flammability limits for upward flame propagation, the conical tungsten electrodes were located at the base of the flame tube. The electrodes had a 6.5 mm gap and were centred in the cylinder, 38 mm from the base. The electric power used for ignition was supplied by a 10 kV, 23 mA centre-taped transformer hooked to an 110 V, 60 Hz electrical supply. The ignition system was optimized in terms of the electrode gap and spark duration to yield the widest flammability limits.

The test mixtures were prepared on the basis of partial pressure of the component gases in a 100 mm diameter, 4.3 L, stainless steel mixing chamber. The pressure of the mixture was measured using a strain gage pressure transducer (Omega, model PX425-030V). The accuracy of the pressure transducers used was reported to be ±0.19% with a repeatability of ±0.05% of the span of the transducer from 0 kPa to 200 kPa. A fan installed in the mixing

chamber was driven by an electric motor at 500 rpm and was used to ensure the homogeneity of the mixture.

Air was supplied by a compressor. The compressed air passed through an oil/water separator before entering the mixing chamber. The air was at the relative humidity supplied by the compressor and was estimated to be 35%. The gases were supplied from compressed gas cylinders. A vacuum pump was hooked up to the system to evacuate the chambers and piping after each test. A system of valves was used to evacuate specific portions of the apparatus independently.

3.2 Experimental Procedure

For the flammability limit values determined at higher than ambient initial mixture temperatures, the flame tube was heated to the desired temperature using the electric heaters. The temperature of the automatic heater was set using a digital temperature controller. The temperature of gas mixture at the ends of the flame tube were monitored using thermocouples. The time required to achieve a uniform temperature profile along the flame tube was about one hour.

At the beginning of each test, the entire apparatus was evacuated with the vacuum pump and then re-filled with air. It was then re-evacuated, re-filled with air and evacuated once more to ensure that any residual gas within the system was only air. The test mixtures were prepared in the mixing chamber on the basis of partial pressure. Air was introduced into the chamber first to eliminate any

residual air from contaminating the mixture. The diluent and fuel gases were then added to the mixing chamber respectively. Between each gas, the supply lines to the chamber were evacuated, filled with the next gas and evacuated again. The total pressure in the mixing chamber ranged from 185 kPa to 195 kPa. Once the desired mixture composition had been reached, the mixing chamber was isolated and the mixing fan ran for about 5 minutes to ensure a homogeneous mixture. The flame tube was then isolated from the vacuum pump and the test mixture was allowed to flow from the mixing chamber into the flame tube. The flame tube was filled to just above atmospheric pressure (Calgary, 89 kPa). After a residence time of 5 minutes, the valve on the bottom of the flame tube was opened and spark ignition was activated. The flame propagation occurred under atmospheric pressure.

An increase in the reading of the thermocouple located at the top of the flame tube indicated successful flame propagation. A mixture was considered to be non-flammable if the flame failed to propagate the full length of the flame tube. If there was successful flame propagation in a test mixture, a new mixture was prepared with a lesser concentration of hydrogen for lean mixtures or a greater amount of hydrogen for rich mixtures. The mixture was considered non-flammable if the flame failed to propagate on three repeated tests and a 0.1% change in hydrogen concentration in the fuel-air mixture resulted in successful flame propagation. The procedure was repeated for a wide range of hydrogen-diluent mixture compositions. Using this procedure, the flammability limits of

various hydrogen-diluent mixtures were determined at initial temperatures up to 150°C.

To establish the flammability limits for downward flame propagation, the flame tube was flipped vertically. In this arrangement, the mixture entered at the bottom of the chamber and the valve exposing the mixture to the atmosphere was located at the top of the chamber. Spark ignition then occurred at the top of the flame tube and the flame propagated away from the open end of the tube. Successful flame propagation was detected by the thermocouple at the base of the flame tube. Flammability limits were determined for methane in air and compared to limits previously established on the same apparatus to ensure consistency. The lean and rich flammability limits for methane in air were observed to be 5.0% and 14.1% in this study, respectively, compared to 4.9% and 14.0% as reported by Wang (2004). Some of the flammability limits observed early in this study where re-determined at a later date with a repeatability within 0.1%.

All fittings were regularly checked for possible leaks. When the apparatus was not in use, the air and gas supplies were closed and lines bled to atmospheric pressure. The purity of gases used in the investigation are given in Table 3.1.

Table 3.1. Declared purity of gases used in this investigation

Gases	Purity %
Hydrogen	99.9
Helium	99.95
Argon	99.995
Carbon dioxide	99.8
Nitrogen	99.7
Methane (pipeline natural gas)*	97.9

* Contained ethane (1.7%), propane (0.1%) and carbon dioxide (0.3%)

CHAPTER 4

FLAMMABILITY LIMITS OF HYDROGEN AND HYDROGEN-DILUENT MIXTURES IN AIR

The flammability limits of hydrogen-diluent mixtures reported in this chapter were determined experimentally for both upward and downward flame propagation at atmospheric pressure (Calgary, 89 kPa) in the apparatus described in Chapter 3. The flammability limits are presented as the concentration of the fuel in the total fuel-air mixture according to the following equation,

$$L_m = \frac{V_F + V_D}{V_F + V_D + V_{air}} \tag{4.1}$$

where,

L_m is the flammability limit of the mixture, % by volume

V_F is the volume fraction of fuel in the total mixture

V_D is the volume fraction of diluent in the total mixture

V_{air} is the volume fraction of air in the total mixture.

The fuel mixture refers to the volume of hydrogen plus the volume of the diluent considered. The diluents employed were helium, argon, carbon dioxide and nitrogen. Some mixtures were tested at elevated temperatures up to 150ºC.

4.1 Flammability limits of Hydrogen

The flammability limits for hydrogen, on its own in air, were established for both upward and downward flame propagation and are shown in Table 4.1. For comparison the flammability limit values reported previously by Coward and Jones (1952), and Wang (2004) are also given. It appears that the results of this investigation are similar to those reported earlier.

Table 4.1. Comparison of lean and rich flammability limits of hydrogen

Report	Flammability limit, % by vol.			
	Upward		Downward	
	Lean	Rich	Lean	Rich
Current	3.9	74.1	8.8	74.1
Wang (2004)	3.9	74.7		
Coward and Jones (1952)	4.1	74	9.0	74

Hydrogen differs from other flammable gases as it has an extremely large flammable mixture zone extending from 3.9% to 74.1% in air. It has been reported earlier that hydrogen flames with less than 8% hydrogen by volume do not propagate as a planar flame front but instead propagate in a cellular manner as observed by Goldmann (1929), referenced by Coward and Jones (1952). The cellular flame propagation has been attributed to the preferential diffusion of the hydrogen in the mixture towards the flame front. As a result of the preferential diffusion, the actual hydrogen concentration in the flame front is higher than the overall concentration, resulting in a higher flame temperature (Goldmann, F., 1929).

4.2 Flammability Limits of Hydrogen-Diluent Mixtures for Upward Flame Propagation

4.2.1 Hydrogen-Helium Fuel Mixtures

The values of the flammability limits of hydrogen-helium mixtures in air established at initial temperatures of 20°C and 50°C are listed in Table 4.2 and shown in Figure 4.1. At an initial temperature of 20°C, fuel mixtures with 92% helium just failed to propagate flame. For mixtures with slightly less helium, at 91% helium in the fuel mixture, distinct flammability limits were observed. The increase in the concentration of helium in fuel mixtures at the rich flammability limit raises the observed value of the rich flammability limit only slightly. Similarly, for mixtures with less 60% helium at the lean flammability limit, there is only a slight increase in the value of the limit. However, helium concentrations above 60% yield a large increase in the value of the lean limit. It appears the effect of the change in initial mixture temperature between 20°C and 50°C is rather small. This is probably due to the relatively small difference between the two temperatures considered.

Table 4.2. Flammability limits of hydrogen-helium mixtures in air, for upward flame propagation

He in the fuel mixture, % by vol.	Flammability limit of the H_2-He mixtures, % by vol.			
	T_{IN} = 20°C		T_{IN} = 50°C	
	Lean Limit	Rich Limit	Lean Limit	Rich Limit
0	3.9	74.1	3.9	74.3
20	4.8	75.3	4.8	75.6
40	6.6	76.3	6.5	76.8
50	8.0	77.6	7.9	77.3
60	10.0	77.5	9.9	77.8
80	21.9	78.5	21.5	78.8
90	53.0	79.0		
91	61.1	79.0		

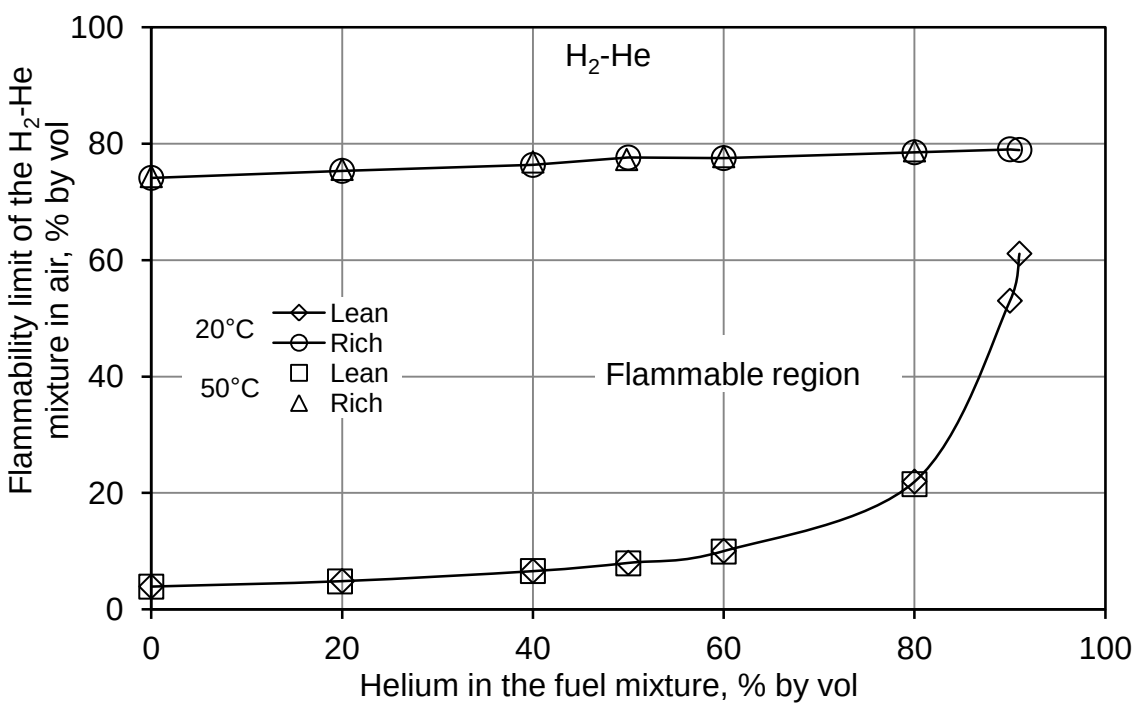

Figure 4.1. Flammability limits of hydrogen-helium mixtures in air as a function of helium concentration in the fuel mixture, for upward flame propagation

4.2.2 Hydrogen-Argon Fuel Mixtures

The flammability limits of hydrogen-argon fuel mixtures were also determined for two different initial temperatures of 20°C and 50°C and are listed in Table 4.3 and shown in Figure 4.2. Similarly, to the addition of helium, the addition of argon to hydrogen increases the lean and rich flammability limits of the fuel mixture. It can also be seen that the flammability limits of hydrogen-argon mixtures are wider than those of hydrogen-helium mixtures. Fuel mixtures remain flammable in air even when the concentration of argon in the fuel mixture is at 95%. As in the case of hydrogen-helium fuel mixture, the values at the flammability limits of the two temperatures considered are close.

Table 4.3. Flammability limits of hydrogen-argon mixtures in air for, upward flame propagation

Ar in the fuel mixture, % by vol.	Flammability limit of the H_2-Ar mixtures, % by vol.			
	T_{IN} = 20°C		T_{IN} = 50°C	
	Lean Limit	Rich Limit	Lean Limit	Rich Limit
0	3.9	74.1	3.9	74.3
20	4.8	76.2	4.8	76.9
50	7.6	79.0	7.6	80.0
80	18.5	81.0	18.5	82.5
90	34.5	82.0	34.5	85.0
95	60.0	84.0		

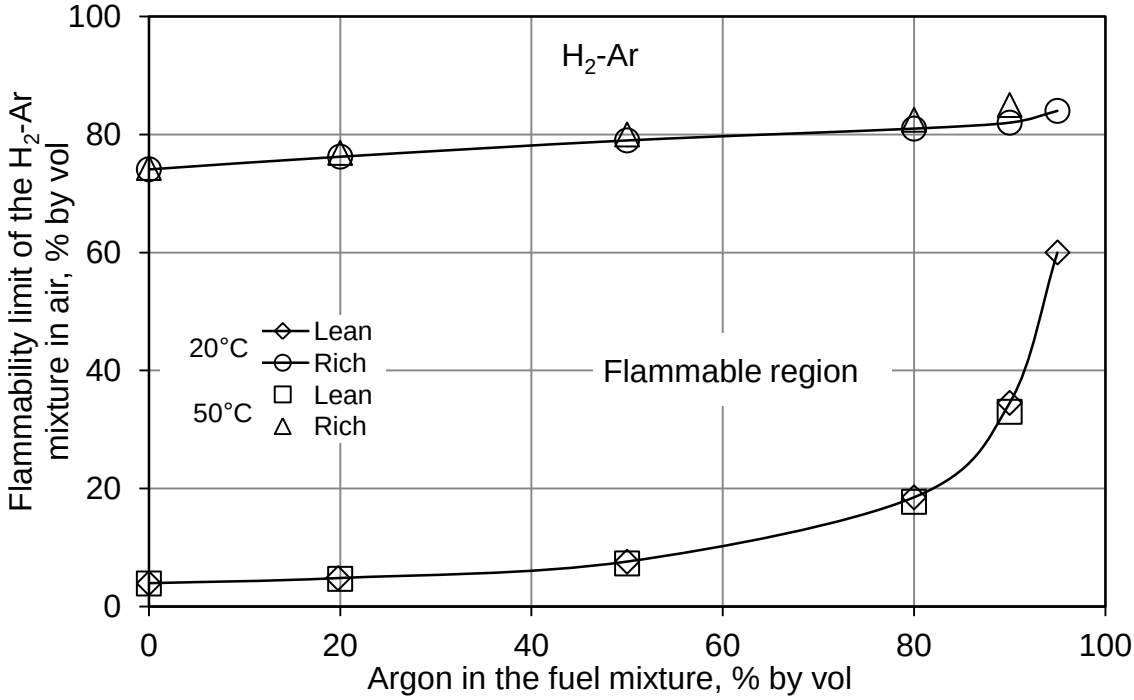

Figure 4.2. Flammability limits of hydrogen-argon mixtures in air as a function of argon concentration in the fuel mixture, for upward flame propagation

4.2.3 Hydrogen-Carbon Dioxide and Hydrogen-Nitrogen Fuel Mixtures

The flammability limits for hydrogen-carbon dioxide and hydrogen-nitrogen mixtures determined at an initial temperature of 20°C are listed in Table 4.4 and shown in Figures 4.3 and 4.4. As expected, carbon dioxide addition to the fuel mixture appears to decrease considerably the flammable region. The addition of nitrogen to the fuel mixture appears to raise the lean and rich limits; however, the effect is relatively small.

Table 4.4. Flammability limits of hydrogen-carbon dioxide and hydrogen-nitrogen mixtures in air, for upward flame propagation

Diluent in the fuel mixture, % by vol.	Flammability limit of the H_2-diluent mixtures, % by vol.			
	Carbon Dioxide		Nitrogen	
	Lean Limit	Rich Limit	Lean Limit	Rich Limit
0	3.9	74.1	3.9	74.1
20	4.9	72.4	4.9	75.1
40	6.7	70.8		
50	8.0	69.4	7.8	75.8
60	10.1	67.8		
80	20.5	66.5	19.5	76.0
90	46.0	66.0		

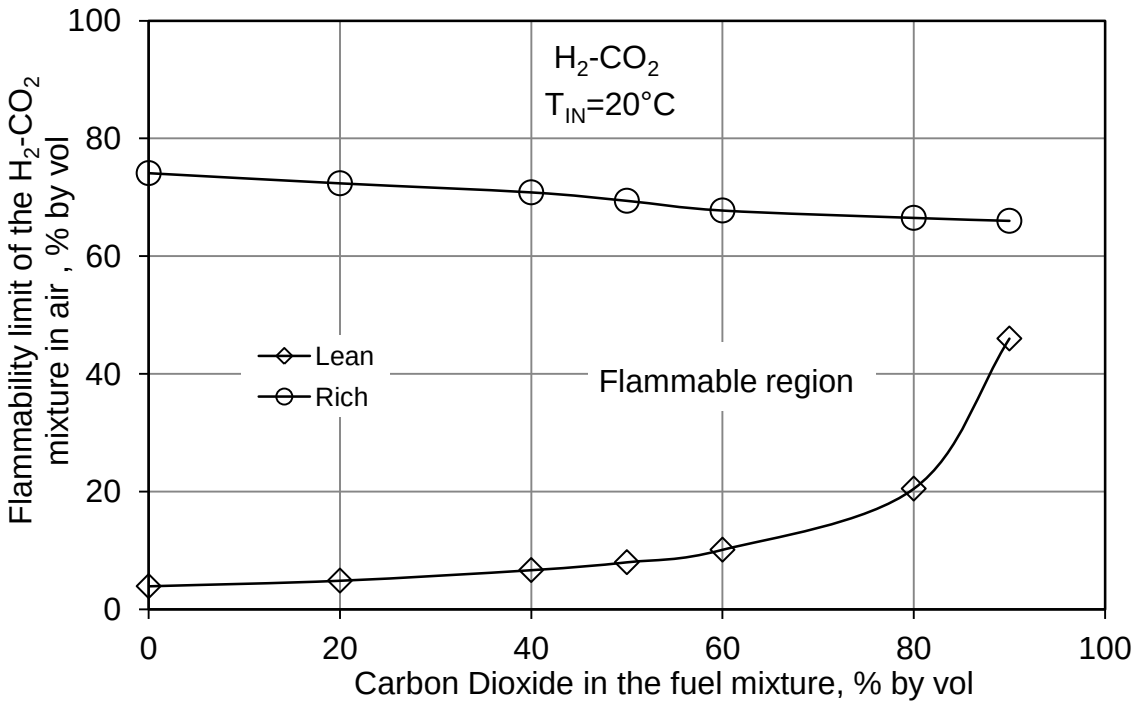

Figure 4.3. Flammability limits of hydrogen-CO_2 mixtures in air as a function of CO_2 concentration in the fuel mixture, for upward flame propagation

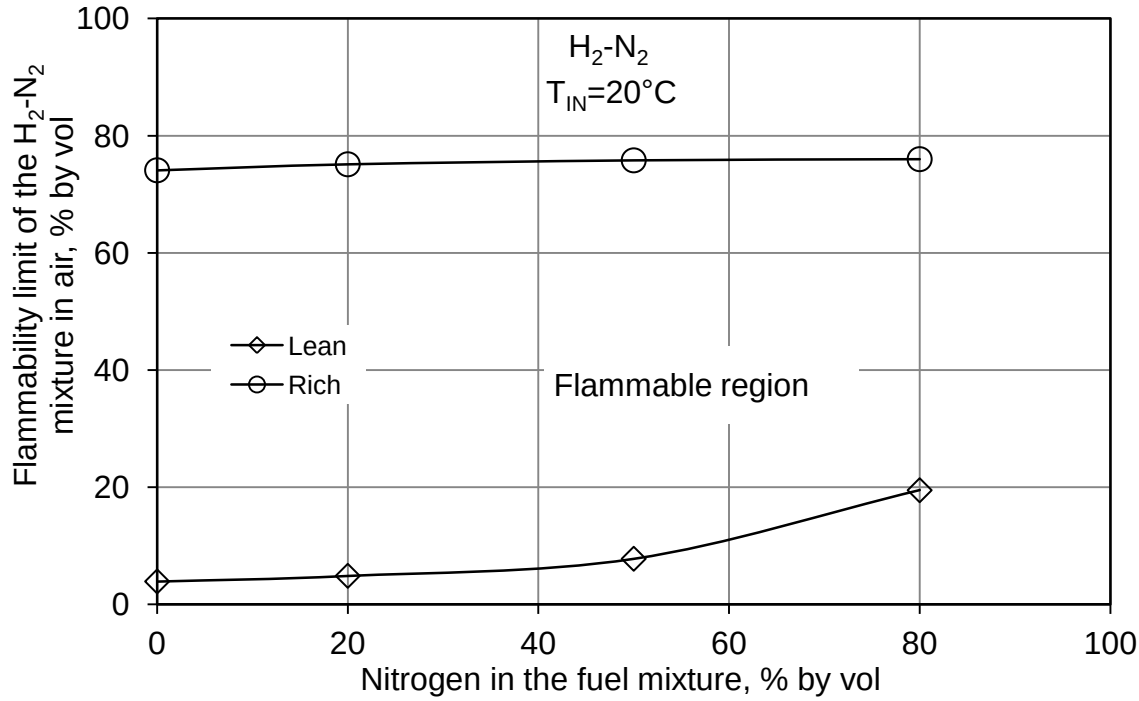

Figure 4.4. Flammability limits of hydrogen-nitrogen mixtures in air as a function of nitrogen concentration in the fuel mixture, for upward flame propagation

4.2.4 Comparison of the Effect of Diluents on the Flammability Limits for Upward Flame Propagation

A comparison of the effect of different diluents on the flammability limits for upward propagating flames of hydrogen-diluent mixtures is shown in Table 4.5 and Figure 4.5. It can be seen that the lean limit of hydrogen-diluent mixtures is approximately the same for all diluents when their concentrations in the fuel mixture do not exceed 80%. When the diluent concentration in the hydrogen-diluent mixture exceeded 80%, the value of the lean flammability limit increased to the greatest extent when helium was the diluent, followed by carbon dioxide, nitrogen, and lastly argon. For the rich flammability limit, the effects of argon and

helium are very similar, with argon being slightly more effective at raising the value of the rich limit. As expected, the addition of carbon dioxide to the hydrogen-diluent mixture considerably lowered the value of the rich limit. The addition of nitrogen to the hydrogen-diluent mixture raised the value of the rich limit by a relatively small amount.

Table 4.5. A comparison of the flammability limits of hydrogen-diluent fuel mixtures, T_{IN}=20°C, for upward flame propagation

Diluent in the fuel mixture, % by vol.	Flammability limit of the H_2-diluent mixtures, % by vol.							
	Helium		Argon		Carbon dioxide		Nitrogen	
	LL	RL	LL	RL	LL	RL	LL	RL
20	4.8	75.3	4.8	76.2	4.9	72.4	4.9	75.1
40	6.6	76.3			6.7	70.8		
50	8.0	77.6	7.6	79.0	8.0	69.4	7.8	75.8
60	10.0	77.5			10.1	67.8		
80	21.9	78.5	18.5	81.0	20.5	66.5	19.5	76.0
90	53.0	79.0	34.5	82.0	46.0	66.0		
95			60.0	84.0				

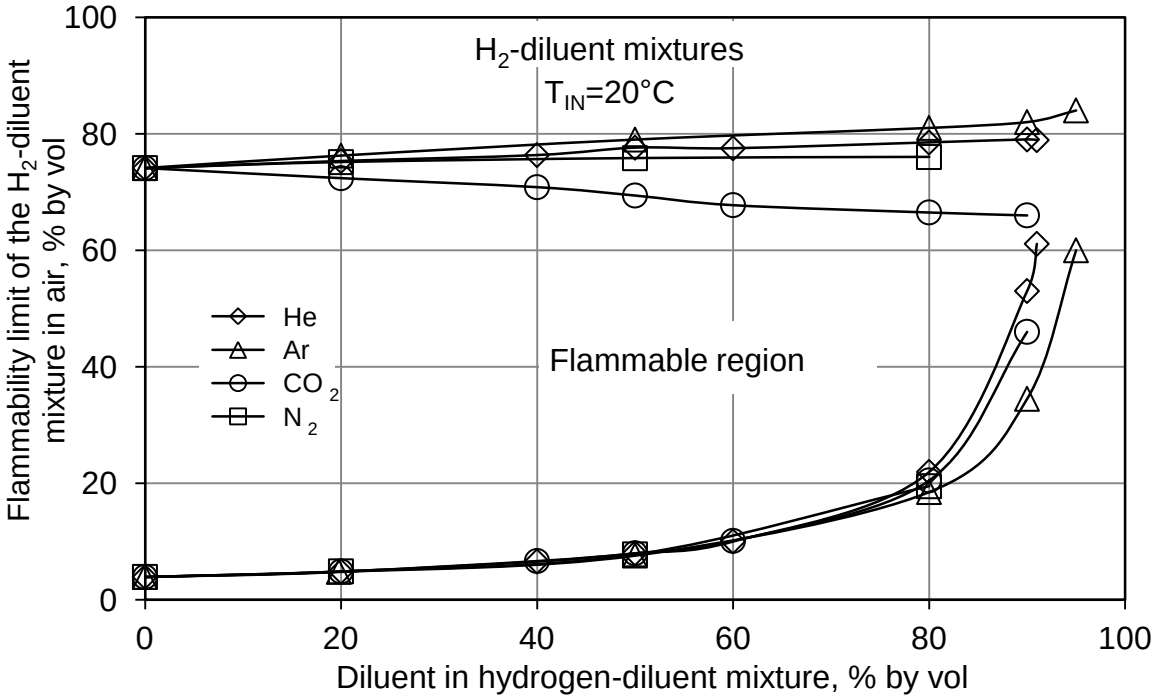

Figure 4.5. Flammability limits of hydrogen-diluent mixtures in air as a function of diluent concentration in the fuel mixture.

In the case of any non-stoichiometric combustion reaction, there is a limiting reactant that will be completely consumed while the non-limiting reactant or reactants will remain in excess in the products of combustion. In lean limiting mixtures, there is an excess of oxygen and the limiting reactant is hydrogen. In rich mixtures, there is an excess of hydrogen and the limiting reactant is oxygen. Figures 4.6 and 4.7 show the effect of the addition of diluents to the fuel mixture on the concentration of the limiting reactant in the mixture at the flammability limit.

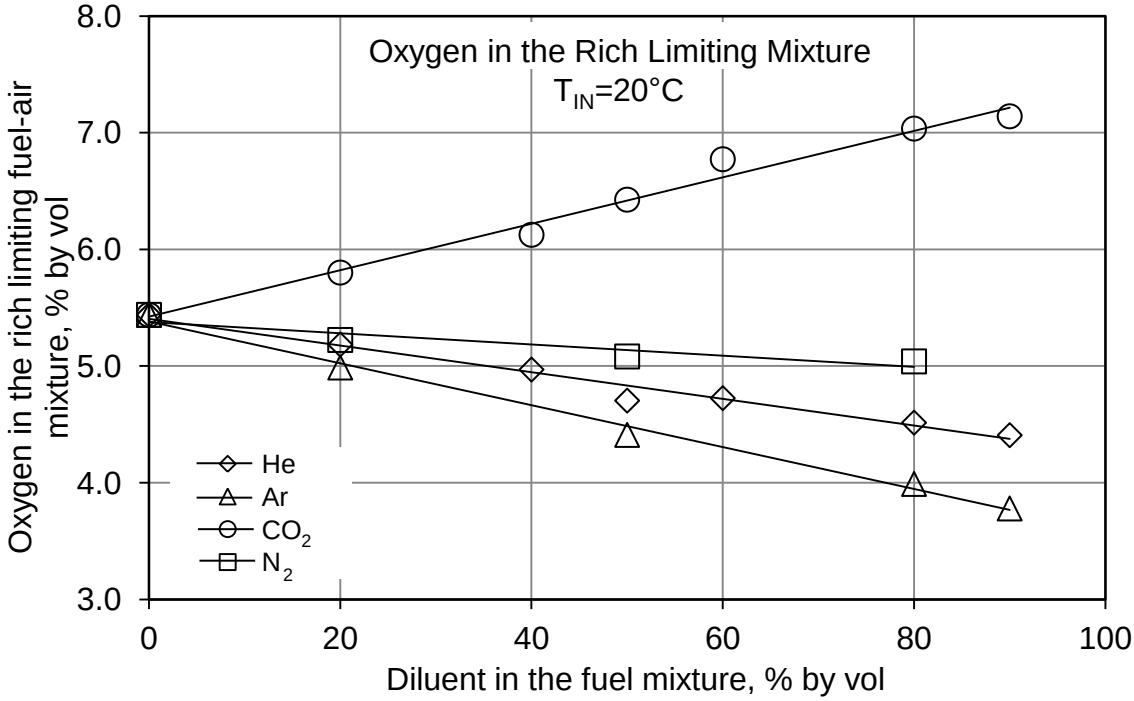

Figure 4.6. Oxygen concentration in the rich limiting mixtures as a function of diluent in the fuel mixture

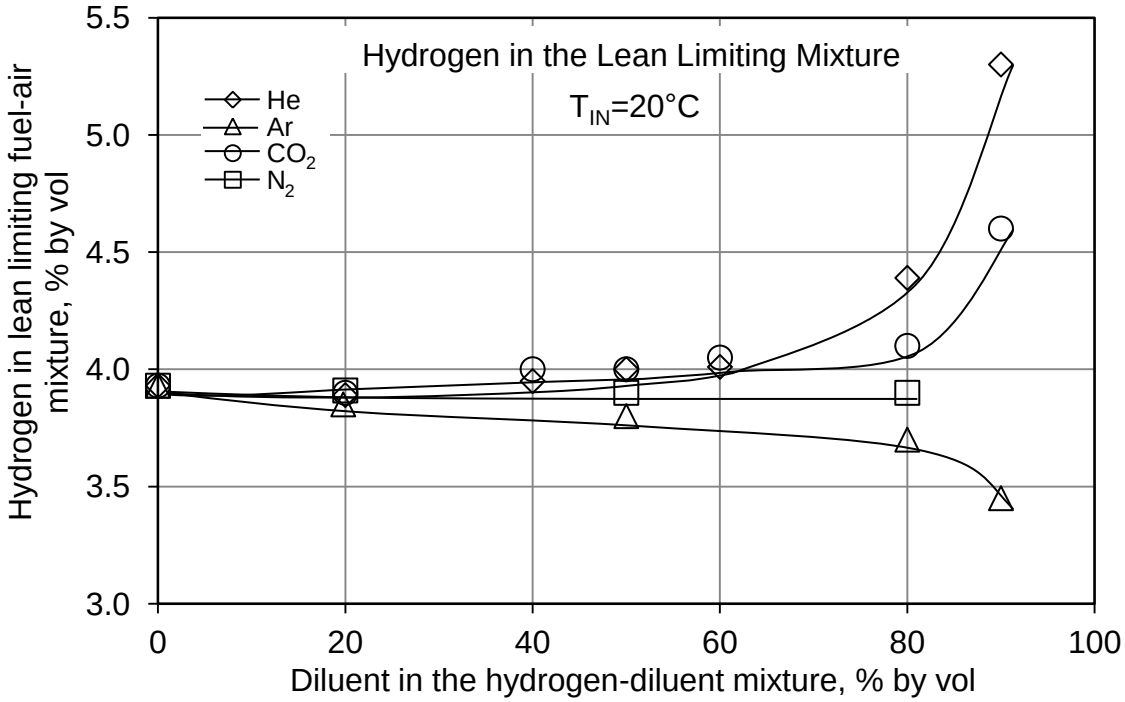

Figure 4.7. Hydrogen concentration in the lean limiting mixtures as a function of diluent in the fuel mixture

It can be seen that as increasing amounts of helium or argon are added to the fuel mixture, less oxygen is required within the rich fuel-air mixture to maintain flame propagation, with argon being slightly more effective. The addition of carbon dioxide to rich limiting mixture considerably increases the amount of oxygen required. The addition of nitrogen has minimal effect. In the case of the lean limiting mixtures, the addition of helium and carbon dioxide require increased hydrogen concentration within the fuel-air mixture to sustain flame propagation. The addition of nitrogen has a minimal effect on the amount of hydrogen that is required for flame propagation. In the case of argon as the diluent, when its concentration in the fuel mixture is increased, less hydrogen in the total mixture was required to sustain flame propagation

As noted earlier, the main focus of the investigation is to determine the effects of the presence of helium on the flammability limits of hydrogen and compare that to the effects of the presence of argon, carbon dioxide, and nitrogen. The addition of diluents to a fuel alters the physical properties of the resulting fuel mixture such as its specific heat capacity, thermal conductivity, diffusivity, and buoyancy. It may also affect the chemical behavior of the fuel. Some of the properties of the diluents used in this study are displayed in Table 4.6.

Table 4.6. Physical properties of the gases used in this investigation (at 25°C, 1atm)

Gas	Molecular Weight kg/kmol	Density kg/m^3	Heat Capacity kJ/kmol K	Thermal Conductivity W/m K	Diffusion Coefficient into N_2 m^2/s
Air (dry)	28.97	1.185	29.17	0.0263	
Hydrogen	2.016	0.08245	28.76	0.1706	0.773
Helium	4.003	0.1637	20.79	0.1501	0.696
Argon	39.95	1.634	20.79	0.01795	0.196
Carbon Dioxide	44.01	1.800	38.41	0.01653	0.169
Nitrogen	28.01	1.145	29.07	0.02475	

(Marrero, T.R., and Mason, E.A., 1972; Turns, S.R., 1996, Yaws, C.L., 1999; Poling B.E. et al., 2001)

The addition of a diluent to the fuel mixture changes the heat capacity of the total mixture. Helium and argon, as monatomic gases, have a relatively low heat capacity when compared to carbon dioxide and nitrogen and more importantly when compared to the heat capacity of hydrogen and air. As a diluent such as argon is added in increasing amounts to the fuel mixture, the heat capacity of the mixture will decrease. This mixture will require less energy to reach the threshold temperature in the flame front required for flame propagation. A lesser amount of fuel for the lean limit or oxidizer for the rich limit is thus required in the mixture, widening the flammable range. Conversely, the addition of carbon dioxide, which has a much higher heat capacity than hydrogen or air, will increase the overall heat capacity of the mixture, requiring more fuel or

oxidizer, for the lean and rich limit respectively, to be present for the temperature in the flame front to reach the threshold temperature. As nitrogen, the main component in air, has a very similar heat capacity to both air and hydrogen, it will not greatly alter the heat capacity of the mixture.

The change in heat capacity as diluents are added to the fuel-mixture agrees well with the trends observed for the rich limits of hydrogen-diluent mixtures. For the lean limit, the trends observed for the addition of argon, carbon dioxide and nitrogen agree well with the changing heat capacity of the mixture. The addition of helium to the lean limiting hydrogen-diluent mixtures requires more hydrogen to be present to maintain flame propagation even though the heat capacity of the total mixture will be decreasing. The flammability limits for the addition of helium to the lean limiting mixtures thus cannot be explained sufficiently on the basis of heat capacity alone.

The physical properties of helium differ considerably from the other diluents with a much higher thermal conductivity and diffusivity, but a much lower density. Kumar (1985) observed trends in the behaviour of hydrogen-helium mixtures similar to this study. He attributed this behaviour to the high thermal conductivity of helium. An increase in the thermal conductivity of a mixture would result in greater heat transfer from the flame front to the un-burnt mixture rates and heat loss to the surroundings from the flame front. Kumar found good agreement between the effects of thermal conductivity in addition to heat capacity for binary hydrogen mixtures with helium and argon. The rate of

diffusion of helium into nitrogen, which can be assumed to be similar to its diffusion into air, is significantly higher than that of the other diluents and much closer to that of hydrogen. Shebeko (1995) proposed that at the lean flammability limit, the high diffusivity of helium resulted in the preferential diffusion of helium to the flame front for hydrogen-helium mixtures in oxygen. However, this effect was reported to be more pronounced at low concentrations of helium, whereas, this study found that the effects of helium only become significant at very high concentrations. It has also been observed that methane flames propagating into helium atmospheres have lower than predicted flame speeds (Panlilio, J.P., 1981). It has been suggested that the low density of helium results in lower buoyant forces acting on the heated products. This effect would only be significant in mixtures with very large concentrations of helium.

Experiments were conducted with methane-diluent mixtures to see if the trends observed were similar to those observed for hydrogen-diluent mixtures. Methane mixtures containing 70% diluent concentration were tested. It was reported by Ale (1998) that methane mixtures with 80% carbon dioxide concentration were not flammable. The established lean and rich flammability limit values with methane as a fuel are listed in Table 4.7. For comparison, the corresponding values for hydrogen-diluent mixtures, obtained from Figures 4.1, 4.2, and 4.3 are also shown. The flammability limits obtained for methane, on its own in air, were 5.0% and 14.1% for the lean and rich limit respectively.

Table 4.7. Flammability limits of 30% methane - 70% diluent mixtures in air, for upward flame propagation

Diluent	Flammability limit of the fuel-diluent mixtures, % by vol.			
	Methane mixtures		Hydrogen mixtures	
	Lean Limit	Rich Limit	Lean Limit	Rich Limit
Helium	17.7	30.3	13.7	78.1
Argon	16.0	31.7	12.3	79.5
Carbon Dioxide	18.7	29.0	13.3	67.6

The experimental data shows that the addition of diluents to methane raises the value of the lean flammability limit. It appears that the greatest increase in the value of the rich limit of methane mixtures was caused by the addition of argon, followed by helium and carbon dioxide. This is a similar trend to that observed for the rich flammability limit of hydrogen-diluent mixtures. For the lean flammability limit of methane-diluent mixtures, the addition of helium to methane was less effective than carbon dioxide in raising the value of the lean flammability limit, which is a reversal of the trend observed in hydrogen mixtures. Similar to hydrogen-helium mixtures, the addition of helium to methane mixtures requires more methane to be present for flame propagation to occur, however this effect is less pronounced. The cellular nature of a very lean hydrogen flame could explain the increased effectiveness of helium in raising the value of the lean flammability limit of hydrogen mixtures when compared to methane mixtures. The large surface are to volume ratio of the cellular hydrogen flame could result in greater heat loss to the surroundings. As methane is much less diffusive than

hydrogen, the effect of preferential diffusion to the flame front would be far less significant. It is therefore likely that the high diffusivity of helium would much less significant for lean methane mixtures. The reduced buoyant forces in mixtures with large concentrations of helium would have similar influence for lean methane mixtures than hydrogen mixtures for upward flame propagation.

4.3 Flammability Limits of Hydrogen-Diluent Mixtures for Downward Propagation

It is well known that there is a significant difference between the flammability limits for upward and downward flame propagation of the highly buoyant hydrogen in air especially for lean mixtures. The lean flammability limit for downward flame propagation of hydrogen in air was determined to be 8.8%, while for upward flame propagation it is 3.9% hydrogen in air by volume. It was stated earlier that upward flame propagation is aided by buoyant convection of the heated products.

The flammability limit values determined for the downward propagation of hydrogen-helium and hydrogen-argon fuel mixtures are listed in Table 4.8 and shown in Figure 4.8 and 4.9. The flammability limits for upward propagation are also listed in Table 4.8 for comparison.

Table 4.8. Flammability limits of hydrogen-helium and hydrogen-argon mixtures in air, for downward flame propagation

Diluent in the fuel mixture, % by vol.	Flammability limit of the H_2-diluent mixtures, % by vol.							
	Helium				Argon			
	Upward		Downward		Upward		Downward	
	LL	RL	LL	RL	LL	RL	LL	RL
20	4.9	75.3	11.0	76.0	4.8	76.3	10.9	76.7
50	7.8	77.6	17.6	77.6	7.6	79.0	17.2	79.2
80	22.0	78.5	43.0	78.5	18.5	81.0	40.5	81.0
85	31.3*	78.8*	57.3	78.7	24.0*	81.7*	51.3	81.3

* Obtained from Figures 4.1 and 4.2

The flammable range for downward propagation is much narrower, as mixtures of 90% helium were unable to support flame propagation. The flammability limits for downward flame propagation for mixtures with argon were wider than those with helium, similar to the flammability limits for upward flame propagation. The rich flammability limits do not show a significant difference between upward and downward flame propagation for either hydrogen-helium or hydrogen-argon mixtures. This is likely due to the dominant effect of the properties of the excess fuel-diluent mixture compared to the effects of thermal buoyancy in rich mixtures. The effect of the addition of diluents on the hydrogen concentration in the limiting lean mixture for both upward and downward flame propagation is shown in Figure 4.10.

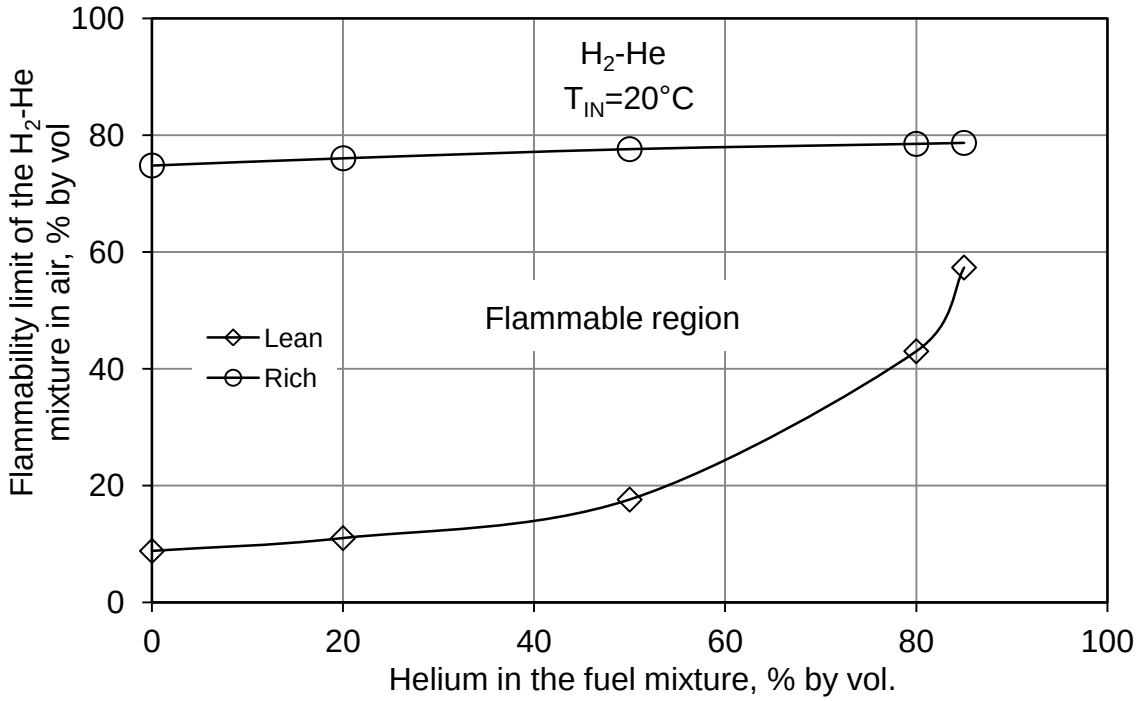

Figure 4.8. Flammability limits of hydrogen-helium mixtures in air as a function of helium concentration in the fuel mixture, for downward flame propagation

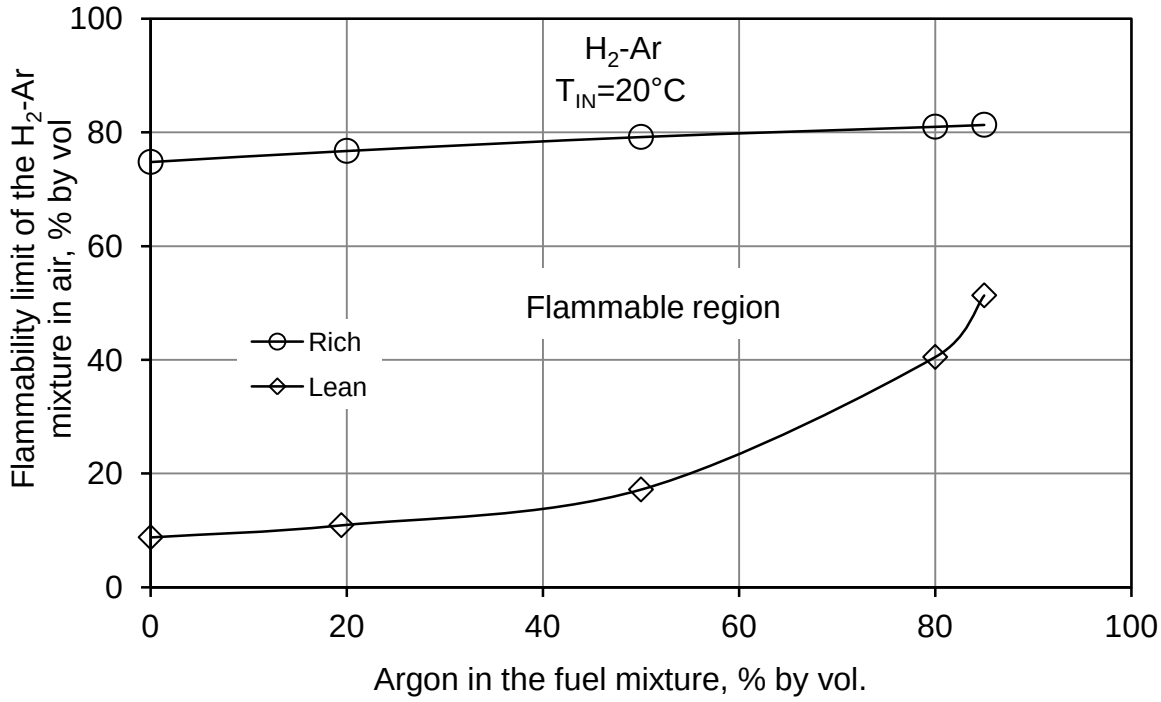

Figure 4.9. Flammability limits of hydrogen-argon mixtures in air as a function of argon concentration in the fuel mixture, for downward flame propagation

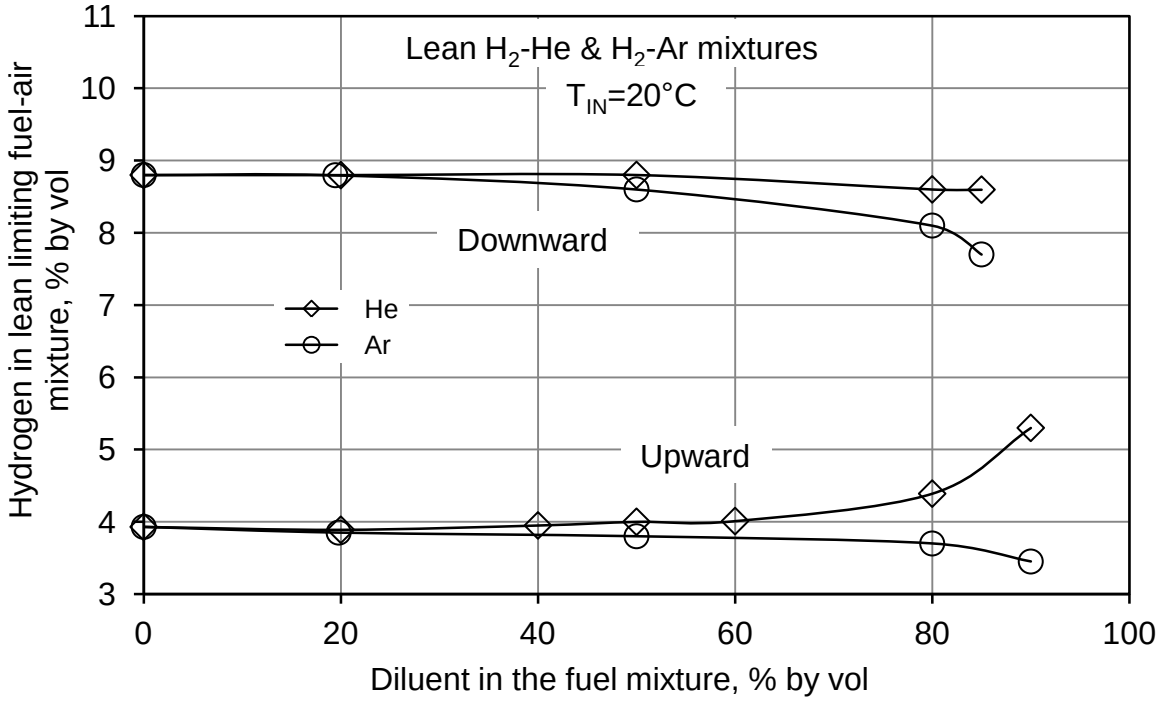

Figure 4.10. Hydrogen in the lean limiting fuel air mixtures as a function of diluent concentration in the hydrogen-diluent mixture

As expected, the addition of argon, which has a relatively low heat capacity, decreases the concentration of the hydrogen required in the total mixture for both the upward and downward flame propagation. The effect appears to be slightly more pronounced for downward flame propagation, likely due to the increased concentration of the fuel in the mixture. For downward flame propagation, the addition of helium to the fuel mixture slightly reduces the hydrogen concentration required, even at high concentrations of helium. Although the effect is minimal, this trend is very different from what was observed for upward propagation for both hydrogen and methane binary mixtures with helium as a diluent. The trend observed for fuel mixtures with helium for upward flame propagation could be

partly due to the low density of helium reducing buoyant forces on the heated products of combustion. The reduced buoyant forces should conversely produce relatively lower values for the lean limit of hydrogen-helium mixtures for downward propagation when compared to upward flame propagation. However, the values for the lean flammability limit of hydrogen-helium mixtures obtained for downward flame propagation are higher than those for hydrogen-argon mixtures. Kumar (1985) suggested that the temperature in the flame front of lean hydrogen mixture was more important for downward flame propagation than for upward flame propagation. The low heat capacity of helium would therefore raise the value of the lean limit for downward propagation less than for upward propagation. The relatively high thermal conductivity of hydrogen-helium mixtures could lead to higher rates of heat loss from the flame front to the un-burnt mixture, lowering the temperature in the flame front. The value of the lean flammability limit for hydrogen-helium mixture would be raised to a greater extent than for hydrogen-argon mixtures for downward propagation.

4.4 Effect of Increasing Initial Temperature on the Flammability Limits of Hydrogen-Diluent Mixtures

4.4.1 Flammability Limits of Hydrogen at Elevated Temperatures

The flammability limits for upward flame propagation for hydrogen fuel were obtained at initial temperatures of 20ºC, 50ºC, 100ºC, and 150ºC and are shown in Table 4.9. Values of the limits at initial temperatures of 200ºC and 300ºC are taken from Wang (2004) who employed the same apparatus and a similar procedure as in the present investigation. The results obtained in this investigation generally are in good agreement with those reported previously by Wang, although, the rich flammability limit value determined by Wang, was 0.6% higher at 74.7%, as compared to 74.1% in this investigation, for ambient initial temperature. It can be seen that there is a linear relationship between the increase in initial temperature and the widening of the flammable mixture zone (Figure 4.11).

Additionally, it was investigated whether the flammability limits of mixtures at slightly elevated initial temperatures can be predicted with the constant adiabatic flame temperature concept, as detailed in Appendix A. The adiabatic flame temperature was calculated using the experimental values of the flammability limits of hydrogen on its own in air at an initial temperature of 20°C. The adiabatic flame temperature at the lean flammability limit was calculated to be 618 K and the adiabatic flame temperature at the rich flammability limit was calculated to be 1168 K. These temperatures were assumed constant for

mixtures at the respective flammability limits for different initial temperatures. The predicted values of the flammability limits are also shown in Table 4.9 and Figure 4.11 for comparison.

Table 4.9. Flammability limits of hydrogen established at elevated initial temperatures

Initial Temperature (ºC)	Flammability limits of hydrogen, % by vol					
	Lean Limit			Rich Limit		
	Exp.	Calc.	Dev.%	Exp.	Calc.	Dev. %
20	3.9			74.1		
50	3.8	3.54	-6.8	74.5	74.93	0.58
100	3.6	2.95	-18.1	76.8	76.32	-0.63
150	3.3	2.35	-28.7	78.2	77.72	-0.61
200*	2.8	1.75	-37.5	80.3	79.12	-1.5
300*	2.4	0.52	-78.3	82.6	81.94	-0.80

* (Wang, Q., 2004), Relative deviation = $(L_{Calc}-L_{Exp})/L_{Exp}$

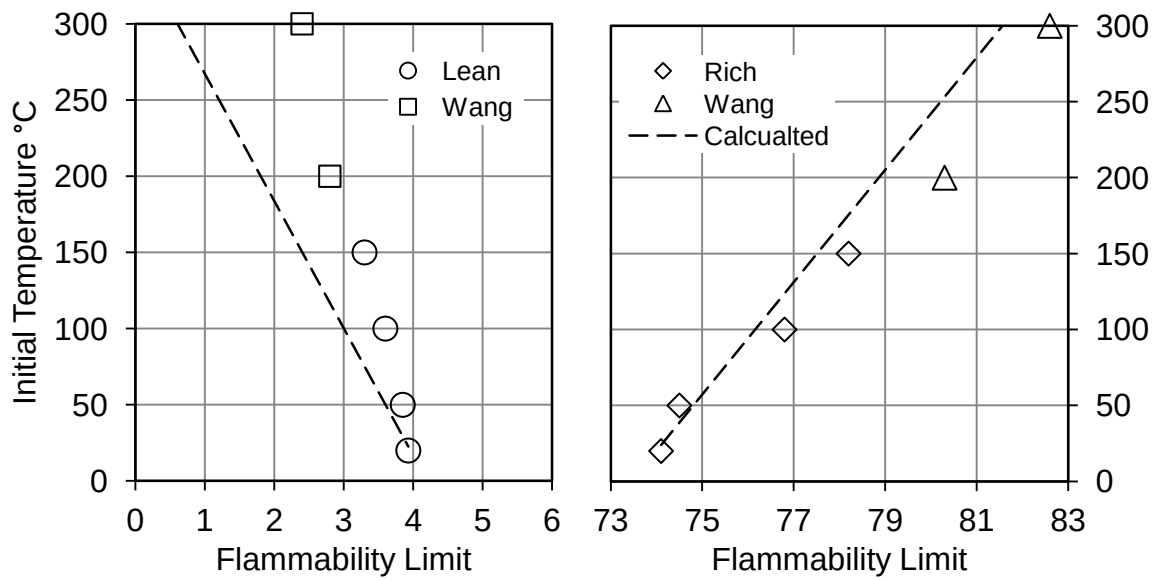

Figure 4.11. Flammability limits of hydrogen as a function of the mixture initial temperature

It can be seen that at initial temperatures of 20°C to 150°C that the rich limits are in good agreement with the corresponding experimental values with the deviation not exceeding 1.5%. However, the predicted values for the lean flammability limit deviate considerably from those experimentally observed. As explained earlier, very lean limits of hydrogen mixtures are driven in part by preferential diffusion of hydrogen to the flame front (Goldmann, F., 1929). The calculation based on the constant adiabatic concept flame temperature assumes the flame propagates in a planar fashion. The actual temperature within the less uniform flame front for lean hydrogen flames would be higher than calculated as the concentration at the flame front is higher than the in the overall mixture. Although an increase in initial temperature raises the enthalpy of the mixture, the diffusion of hydrogen to the flame front would still be required for the threshold temperature to be reached.

4.4.2 Flammability Limits of Hydrogen-Diluent Mixtures at Increasing Initial Temperature

The flammability limits of hydrogen-diluent mixtures containing 50% diluent were determined at elevated mixture temperatures up to 150°C and upward flame propagation as shown in Table 4.10 and Figure 4.12. The flammability limits of hydrogen-diluent fuel mixtures are compared to the values predicted from the constant adiabatic flame temperature concept. As helium and argon have the same heat capacity, the predicted limits for hydrogen-helium and

hydrogen-argon mixtures are the same. The predicted values of the rich flammability limit are in good agreement with those observed. However, as discussed in the previous section there is poor agreement between the experimental and calculated lean flammability limits for hydrogen, on its own in air, at an elevated initial temperature. Therefore, the adiabatic flame temperature was calculated on the basis of the experimentally determined lean limit of hydrogen on its own in air at each initial temperature. The calculated value was used then to predict the flammability limits of different hydrogen-diluent mixtures at this initial temperature. The comparison between the experimental and calculated values using this method is displayed in Figure 4.12.

Table 4.10. Flammability limits of hydrogen-diluent mixtures containing 50% diluent at elevated initial temperatures for upward flame propagation

Initial Temperature (°C)	Flammability limit of H2-diluent mixtures, % by vol.					
	Helium		Argon		Carbon dioxide	
	LL	RL	LL	RL	LL	RL
20	8.0	77.6	7.6	79.0	8.0	69.4
50	8.0	77.6	7.3	80.2	7.8	70.6
100	7.6	79.6	6.8	82.0	7.2	73.0
150	7.2	80.8	6.4	84.0	6.8	74.4

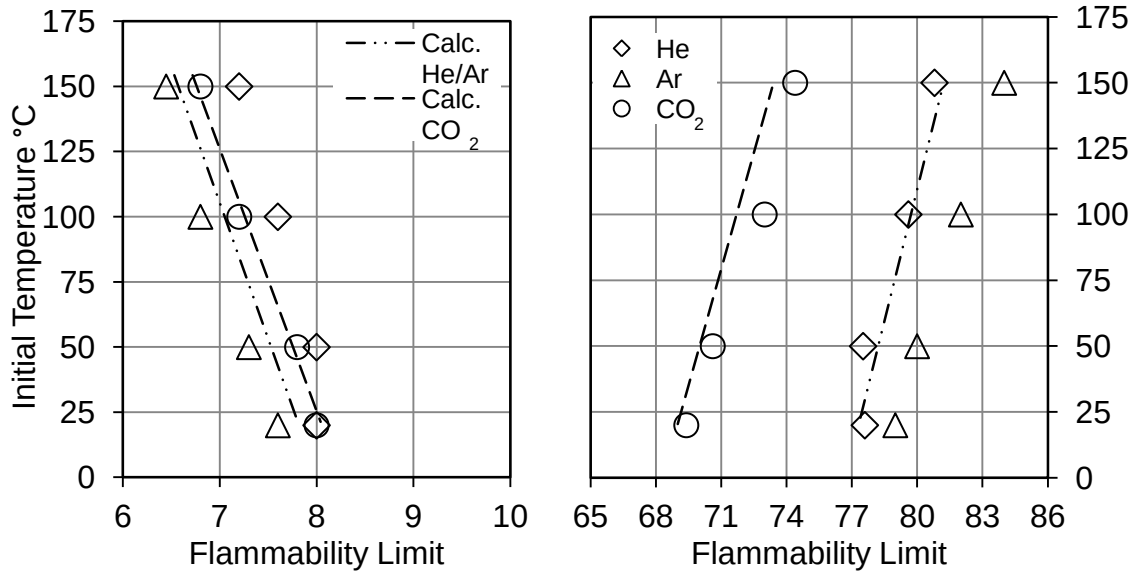

Figure 4.12. Flammability limits for upward flame propagation of hydrogen-diluent mixtures containing 50% diluent as a function of initial temperature

The predicted values are in generally much better agreement with the experimental values for the lean flammability limit of hydrogen-diluent mixtures compared to hydrogen on its own in air. The agreement is less accurate for hydrogen mixtures with helium. The predicted values of the rich flammability limit are in good agreement without performing the additional calculation step that was done for the lean limit. The experimentally determined rich flammability limits for hydrogen-argon mixtures appear to diverge slightly from the predicted limits at higher temperatures. However, sufficiently high temperature values were not reached in this investigation to confirm this divergence further.

CHAPTER 5

PREDICTION OF FLAMMABILITY LIMIT OF HYDROGEN-DILUENT MIXTURES

It has been shown previously and confirmed in this work that there is a linear correlation between the inverse of the flammability limit of a fuel mixture and the concentration of combustible gases in the fuel mixture (Bade Shrestha, S.O., 1992; Wierzba, I., et al., 1996; Bade Shrestha, S.O., et al., 2009). This can be seen by re-plotting the flammability data for upward and downward flame propagation for different hydrogen-diluent mixtures as shown in Figures 5.1 to 5.6.

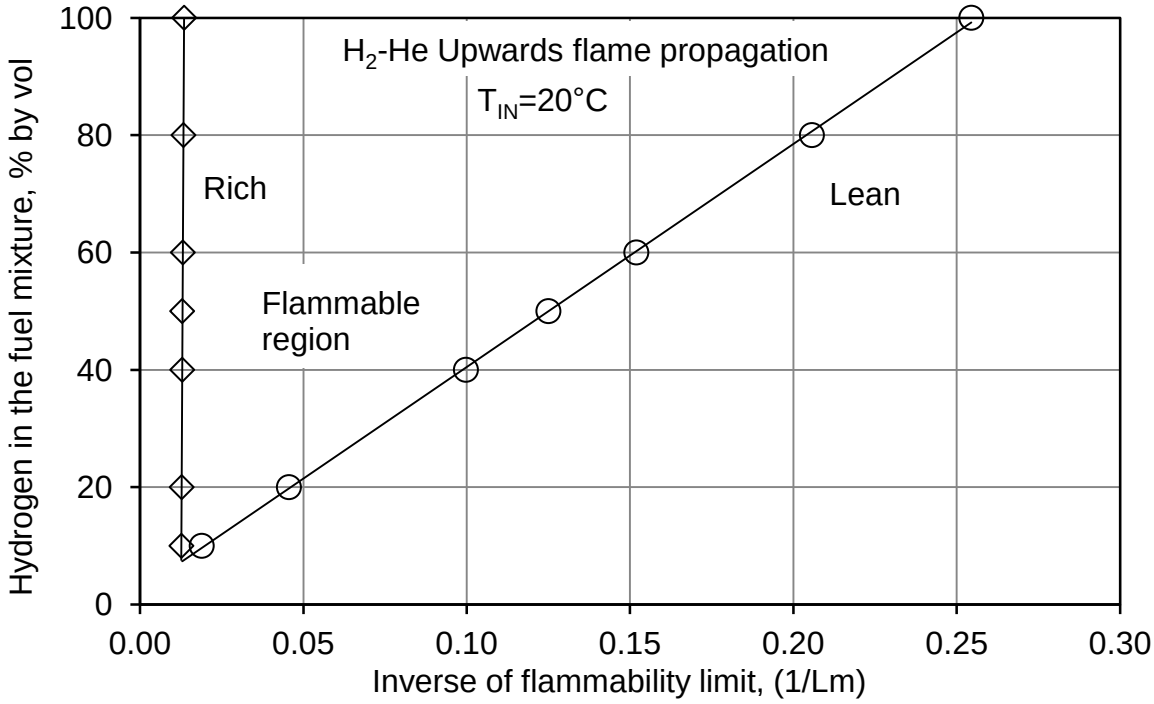

Figure 5.1. Inverse of the flammability limit of H_2-He mixtures in air for upward propagation as a function of hydrogen concentration in the fuel mixture

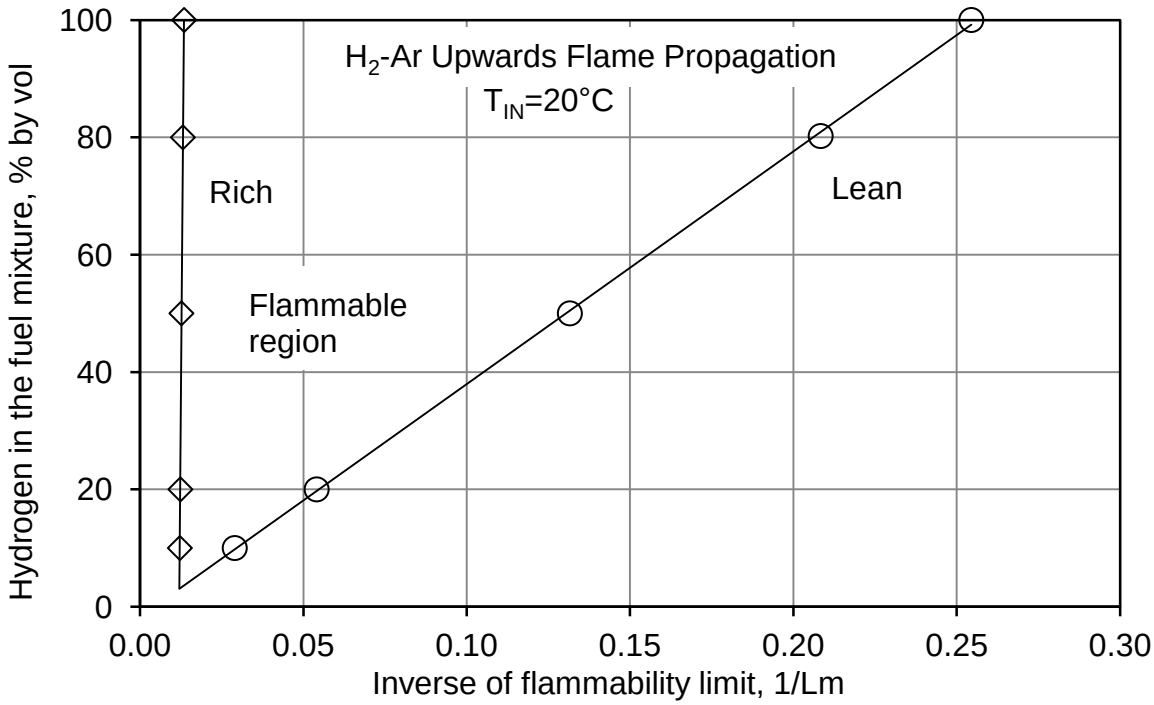

Figure 5.2. Inverse of the flammability limit of H_2-Ar mixtures in air for upward propagation as a function of hydrogen concentration in the fuel mixture

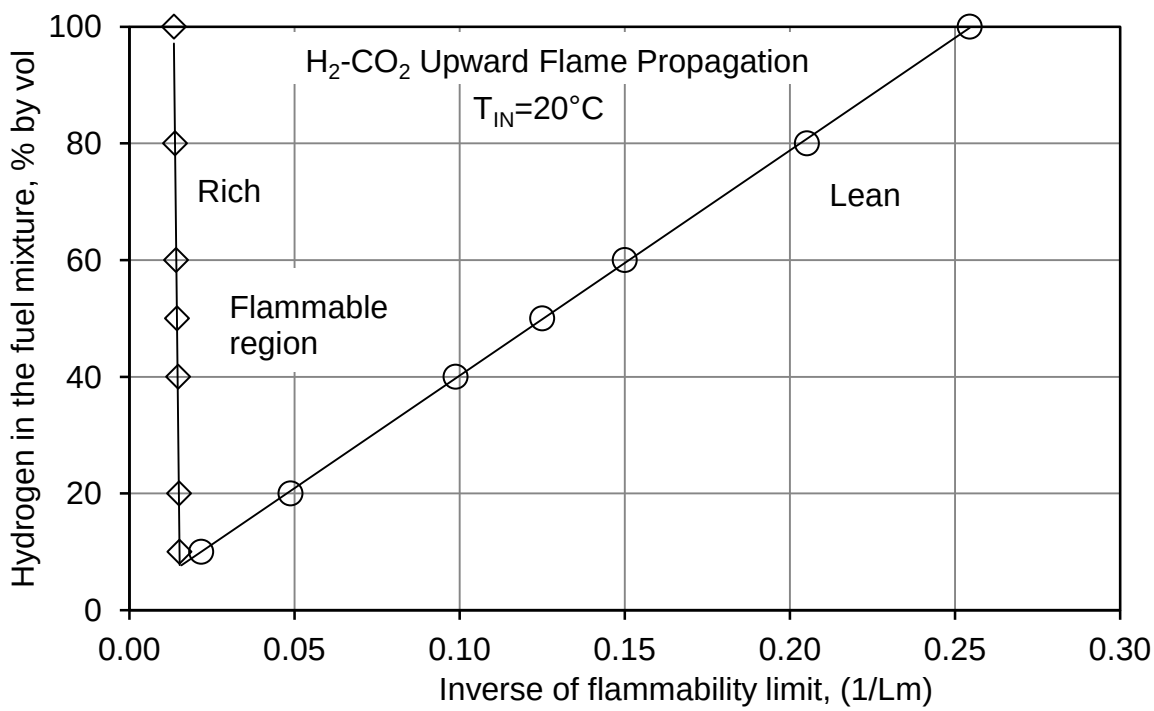

Figure 5.3. Inverse of the flammability limit of H_2-CO_2 mixtures in air for upward propagation as a function of hydrogen concentration in the fuel mixture

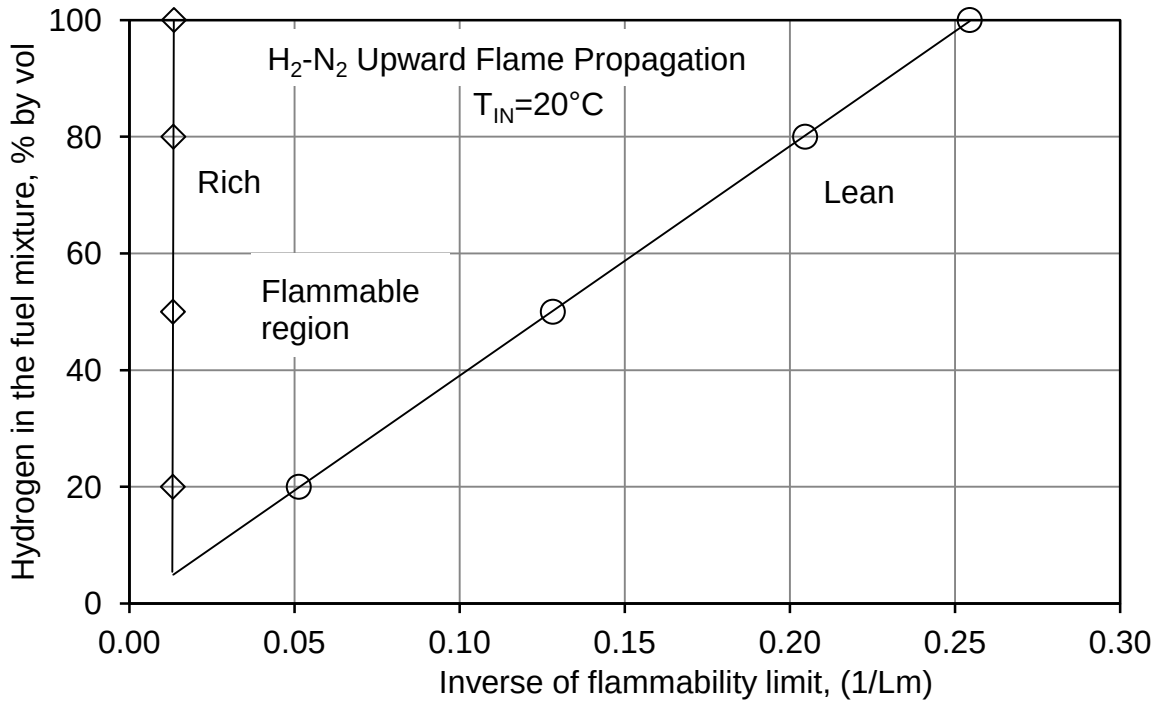

Figure 5.4. Inverse of the flammability limit of H_2-N_2 mixtures in air for upward propagation as a function of hydrogen concentration in the fuel mixture

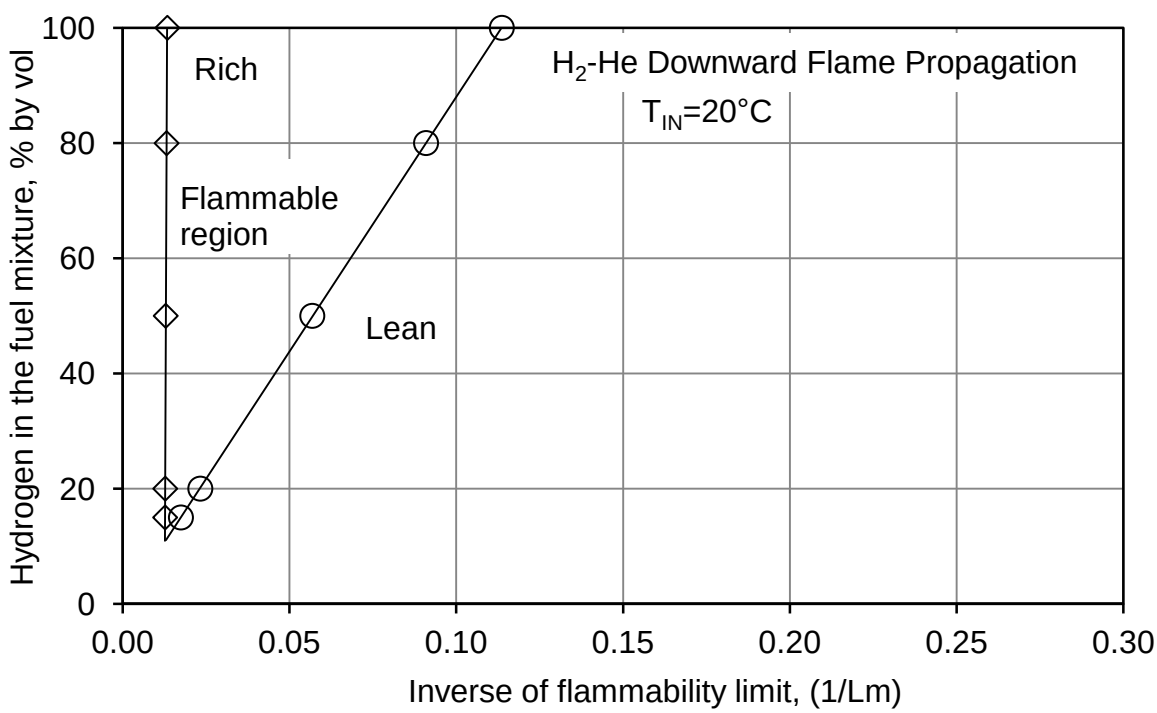

Figure 5.5. Inverse of the flammability limit of H_2-He mixtures in air for downward propagation as a function of hydrogen concentration in the fuel mixture

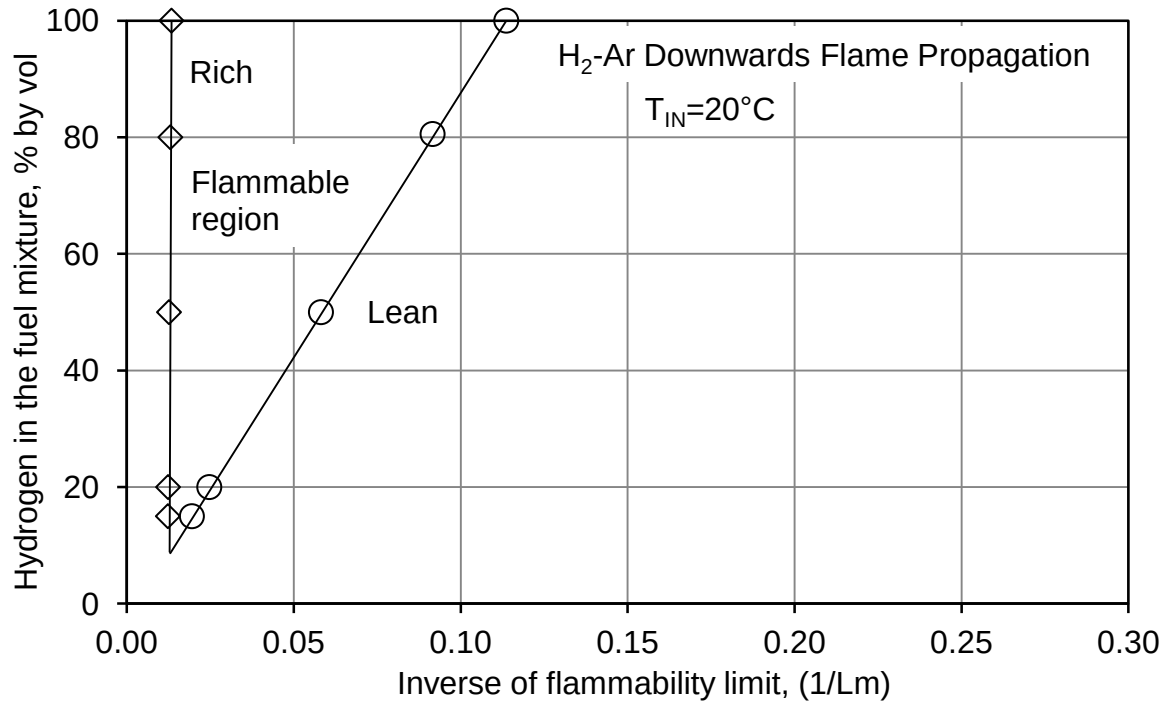

Figure 5.6. Inverse of the flammability limit of H_2-Ar mixtures in air for downward propagation as a function of hydrogen concentration in the fuel mixture

On the basis of these observed trends, the flammability limits of fuel-diluent mixtures can be calculated according to equations 5.1 and 5.2 for the lean and rich limits, respectively.

$$\frac{100}{L_{m,l}} = \frac{y_{f,l}}{L_{f,l}} + \alpha_l\left(100 - y_{f,l}\right) \qquad (5.1)$$

$$\frac{100}{L_{m,r}} = \frac{y_{f,r}}{L_{f,r}} + \alpha_r(100 - y_{f,r}) \qquad (5.2)$$

where,

$L_{m,l}$ and $L_{m,r}$ are the lean and rich flammability limits of the fuel mixture, % by vol.

$L_{f,l}$ and $L_{f,r}$ are the lean and rich flammability limits, of the pure fuel on its own in air, % by vol.

$y_{f,l}$ and $y_{f,r}$ are the concentration of combustible gas in the fuel mixture at the lean and rich flammability limit, % by vol.

α_l and α_r are the characteristic constants of the fuel mixture at the lean and rich flammability limit.

The characteristic constants 'α_l' and 'α_r' depend on the type of fuel and diluent, but can be considered independent of the diluent concentration in the fuel mixture. This correlation appears to predict well the flammability for a wide range of fuels and diluents (Wierzba, I., et al., 1994; Wierzba, I., et al., 1995; Bade Shrestha, S.O., et al., 2009). Once the flammability limit of the fuel on its own in air is known, it is computationally simple to determine the flammability limit of a fuel mixture with a known value of constant 'α'. The values of 'α_l' and 'α_r' can be determined experimentally for upward and downward flame propagation from determining the x-intercepts in Figures 5.1 to 5.6. These values are shown in Tables 5.1 and 5.2

Table 5.1.Experimental values of α_l and α_r for upward flame propagation

Diluent	Experimental		Calculated*	
	α_l	α_r	α_l	α_r
Helium	-6.54E-3	1.25E-2	3.08E-3	1.25E-2
Argon	4.26E-3	1.20E-2	3.08E-3	1.25E-2
Carbon dioxide	-4.05E-3	1.54E-2	-4.55E-3	1.60E-2
Nitrogen	7.91E-4	1.30E-2	8.80E-5	1.38E-2

Table 5.2.Experimental values of α_l and α_r for downward flame propagation

Diluent	Experimental		Calculated*	
	α_l	α_r	α_l	α_r
Helium	4.99E-4	1.26E-2	3.48E-3	1.28E-2
Argon	2.70E-3	1.21E-2	3.48E-3	1.28E-2

* (Bade Shrestha, S.O., 2009)

It can be seen that for very small values of 'α_l' for lean mixtures the second term in equation 5.1 may be approximated to zero. This is the case for lean hydrogen-nitrogen mixtures for upward flame propagation and lean hydrogen-helium mixtures for downward flame propagation,

When experimental data on the flammability limits of fuel-diluent mixtures are not available it was proposed to estimate the 'α_l' and 'α_r' constant using the constant adiabatic flame temperature concept (Wierzba, I., et al., 1994; Wierzba, I., et al., 1995; Bade Shrestha, S.O., et al., 2009) which is described in Appendix A. The agreement between the experimental and calculated values of α_r appears very good for the rich limit for both upward and downward flame propagation. However, the experimentally determined values of 'α_l' for the lean flammability limit deviate to various extents from the calculated values. The deviation between the experimental flammability limits and those predicted using 'α' are shown in Table 5.3, displaying generally good agreement for the majority of different hydrogen diluent mixtures. However, for mixtures containing very large amounts

of helium the experimentally obtained lean limit the deviates significantly (~15%) from that calculated.

Table 5.3. Calculated flammability limits for hydrogen-diluent mixtures at 20°C initial temperature

Diluent	%	Lean limit		Dev.* %	Rich limit		Dev.* %
		LL, Exp	LL, Cal		RL, Exp	RL, Cal	
Helium	20	4.9	4.9	0	75.3	75.2	-0.1
	50	8.0	7.8	-2.5	77.6	76.9	-0.9
	80	22.0	18.7	-15.0	78.5	78.7	0.3
Argon	20	4.8	4.9	2.1	76.3	75.2	-1.4
	50	7.6	7.8	2.6	79.0	76.9	-2.7
	80	18.5	18.7	1.1	81.0	78.7	-2.8
Carbon Dioxide	20	4.9	4.9	0.0	72.4	72.1	-0.4
	50	8.0	8.0	0.0	69.4	69.2	-0.3
	80	20.5	21.2	3.4	66.5	66.6	0.2
Nitrogen	20	4.9	4.9	0	75.1	73.8	-1.7
	50	7.8	7.9	1.3	75.8	73.4	-3.2
	80	19.5	19.6	0.5	76.0	73.0	-3.9

*Relative deviation = $(L_{Calc}-L_{Exp})/L_{Exp}$

This deviation for helium as a diluent can be seen in Figure 5.7. As the calculated value of α_l is determined on the basis of constant adiabatic flame temperature it is very much affected by the value of the heat capacity of the diluents. In the case of helium, this simplified model appears to be inadequate for concentrations of helium above 80% in the fuel mixture by volume.

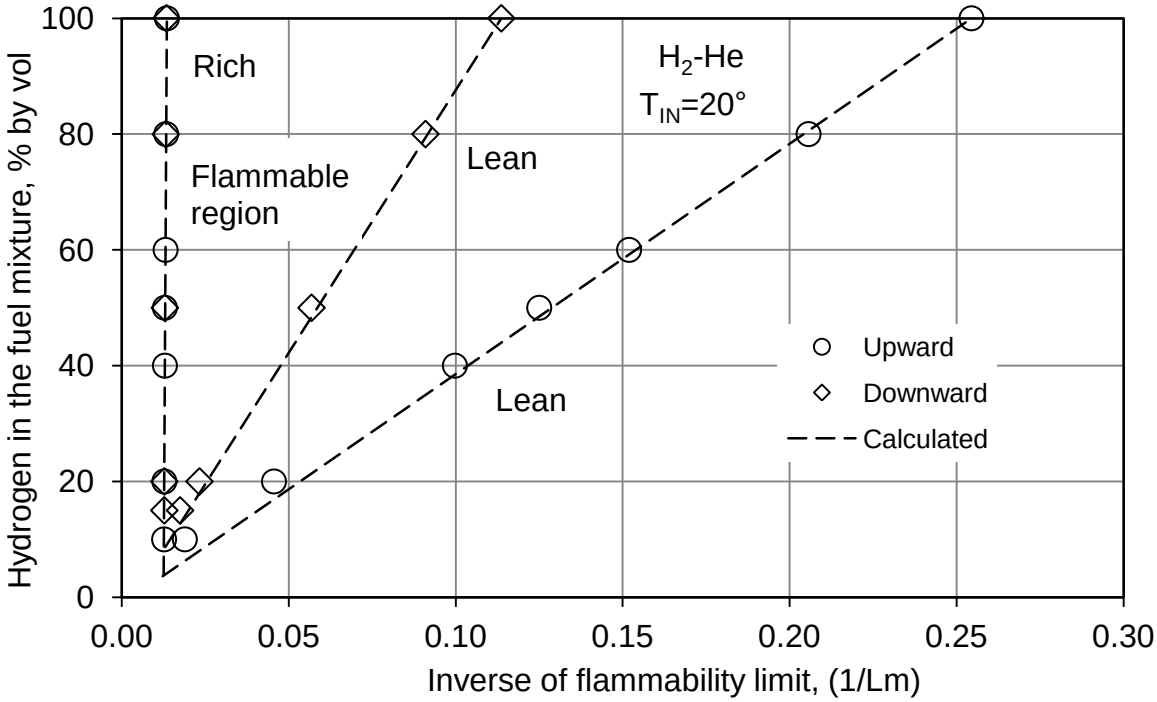

Figure 5.7. Inverse of the flammability limit of H_2-He mixtures in air compared to predicted values using the value of the calculated α as a function of hydrogen concentration in the fuel mixture

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

- Hydrogen-helium mixtures fail to propagate a flame at 92% helium in the fuel mixture under atmospheric pressure (Calgary, 89k Pa) and ambient temperature. Therefore, only a small percentage of the helium in dirigibles can be safely offset with hydrogen. This is in agreement with previously reported data.
- The lean flammability limits of hydrogen binary mixtures with argon, carbon dioxide, and nitrogen diluents in air for upward flame propagation appear to be very close to the limits predicted using the adiabatic flame temperature concept.
- The lean flammability limit for upward flame propagation in air for hydrogen-helium mixtures is increased as helium is added, requiring more hydrogen to be present in the limiting fuel-air mixture for the flame to propagate. The increase in the lean limit appears to be greater than that observed for carbon dioxide, which has a much higher heat capacity. This effect is most notable when the helium concentration in the fuel mixture exceeds 80%. It appears that other properties of helium, such as thermal conductivity and density, are responsible for the trends observed. As such, the flammability limits of

hydrogen-helium mixtures in air cannot be predicted well when using the constant adiabatic flame temperature concept.

- The values of the lean flammability limits for downward propagation in air are increased by the addition of helium and argon, with helium affecting the value of the lean limit more. The addition of helium has a minimal effect on the hydrogen required in the limiting fuel-air mixture for flame to propagate.
- The experimental rich flammability limits for upward flame propagation of hydrogen mixtures with helium, argon, carbon dioxide, and nitrogen appear to be in good agreement with the limits predicted by employing the adiabatic flame temperature concept. The diluents argon and nitrogen produce slightly wider limits than what is predicted.
- The flame propagation direction, upward or downward, does not affect significantly the values of the rich flammability limit.
- Increasing the initial temperature of the mixture widens the flammable zone linearly for hydrogen on its own and hydrogen binary mixtures with helium, argon, and carbon dioxide for upward flame propagation.
- For increased initial temperatures, the observed rich flammability limits appear to be in generally good agreement with the predicted limits using the constant adiabatic flame temperature concept. Mixtures with argon as a diluent appear to diverge slightly from the predicted results as the initial temperature increases.

- The constant adiabatic flame temperature concept predicts a much lower value of the lean flammability limit than what was observed for increased initial temperatures. Improved agreement may be achieved if the lean flammability limit of hydrogen, when on its own in air, is used to calculate the constant adiabatic flame temperature for lean limiting mixtures at the same corresponding initial temperature.
- The trends observed for the behavior of the limits with changes in the concentration of the diluents, initial temperature, and direction of flame propagation are the outcome of complex interactions between thermal, chemical, and physical factors. Further research is needed to establish reliably the basis of the observed effects.

6.2 Recommendations for Future Work

- The effect of the changes in the diameter of the flame tube on the flammability limit values determined for hydrogen-diluent fuel mixtures needs further investigation.
- The flammability limits of hydrogen-diluent fuel mixtures in air for horizontal flame propagation require investigation, as the effects of buoyancy are not present.
- The effect of the construction of the flame tube on the flammability limits of hydrogen-diluent mixtures warrants investigation. A flame tube constructed of quartz could be considered, which has a lower thermal conductivity and is

less prone to catalytic pre-ignition reactions than the stainless steel cylinder used.

- The precision of the instrumentation used to determine mixture composition could be improved, as sometimes the changes in the flammability limit occur within the estimated range of experimental error.
- The constant adiabatic flame temperature concept is a very simplified predictive approach and it has been found by Zlochower (2012), as well as in this investigation, that the calculated values of the flammability limits are often not in good agreement with experimentally determined values. The use of a more detailed predictive method aided by more recently available, albeit complex, programs that account for chemical kinetics could provide significant improvements.

REFERENCES

1 Ale, B.B., 1998, “Flammability Limits of Gaseous Fuels and Their Mixtures in Air at Elevated Temperatures”, Ph.D. Thesis, Department of Mechanical Engineering, University of Calgary.

2 Andrews, G.E. and Bradley, D., 1973, “Limits of Flammability and Natural Convection For Methane-Air Mixtures”, Fourteenth Symposium (International) on the Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp. 1119-1128.

3 Bade Shrestha, S.O., 1992, “Systematic Approach to Calculations of Flammability Limits of Fuel-Diluent Mixtures in Air”, M.Sc. Thesis, Department of Mechanical Engineering, University of Calgary.

4 Bade Shrestha, S.O., Wierzba I., Karim, G.A., 2009, “Prediction of the Extent of Diluents Concentrations in Flammability Limited Gaseous Fuel-Diluent Mixtures in Air”, Applied Thermal Engineering, Vol. 29, pp. 2574-2578.

5 Blanc, M.V., Guest, P.G., von Elbe, G. and Lewis, B., 1949, “Ignition of Explosive Gas Mixtures by Electric Sparks –III. Minimum Ignition Energies and Quenching Distances of Mixtures of Hydrocarbons and Ether with Oxygen and Inert gases”, Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp. 363-367.

6 Bone, W.A., Newitt, D.M. and Smith, C.M., 1928, “Gaseous Combustion at High Pressures”, Parts IX and XI, Royal Society Proceedings, pp. 553-576.

7 Boon, S.L., 1982, “An Experimental Study of the Lean Flammability Limits of Some Gaseous Fuels and Their Mixtures”, M.Sc. Thesis, Department of Mechanical Engineering, University of Calgary.

8 Boston, P.M., Bradely, D., Lung. F.K-K., Vince, I.M., and Weinberg, F.J., 1984, “Flame Initiation in Lean, Quiescent and Turbulent Mixtures with Various Igniters”, Twentieth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp. 141-149.

9 Britton, L.G., 2002, “Two Hundred Years of Flammable Limits”, Process Safety Progress, Vol. 22, No. 1, pp. 1-11.

10 Bunev, V.A., 1972, “Determination of the Concentration Limits of Flame Propagations at Elevated Temperatures”, Combustion, Explosion, and Shockwaves, Vol. 8, No.1, pp. 82-86.

11 Burgess, D.S., Furno, A.L., Kutcha, J.M., Mura, K.E., 1982, “Flammability of Mixed Gases”, US Bureau of Mines, Report of Investigation 8709.

12 Cashdollar, K.L., Zlochower, I.A., Green, G.M.,Thomas, R.A., Hertzberg, M., 2000, “Flammability of Methane, Propane, and Hydrogen Gases”, Journal of Loss Prevention in the Process Industries, Vol. 13, pp. 327-340.

13 Cheng, T.K.H., 1985, “An Experimental Study of the Rich Flammability Limits of Some Gaseous Fuels and Their Mixtures in Air”, M.Sc. Thesis, Department of Mechanical Engineering, University of Calgary.

14 Coward, H.F., and Jones, G.W., 1952, “Limits of Flammability of Gases and Vapors”, US Bureau of Mines, Bulletin 627, Pittsburgh, Pennsylvania.

15 Cussler, E. L., 1997, “Diffusion: Mass Transfer in Fluid Systems 2nd Edition”, New York, Cambridge University Press.

16 Fardisi, S., Karim, G.A., 2009, “Characteristics of Flammable, Buoyant Hydrogen Plumes Rising from Open Vertical Containers”, International Journal of Hydrogen Energy, Vol. 34, No. 15, pp. 6568-6579.

17 Goldmann, F., 1929, “Explosions with Para-Hydrogen”, Ztschr. Physikal Chem., Vol. B5, pp. 305-306. cited in ref. 14.

18 Harris, K.P., 1990, “The Effect of Low Temperatures on the Flammability Limits of Some Gaseous Fuels and Their Mixtures in Air”, M.Sc. Thesis, Department of Mechanical Engineering, University of Calgary.

19 Hertzberg, M., 1976, “The Theory of Flammability Limits Natural Convection”, US Bureau of Mines, Report of Investigation 8127.

20 Hustad, J.E. and Sonju, O.K., 1988 “Experimental Studies of Lower Flammability Limits of Gases and Mixtures of Gases at Elevated Temperatures”, Combustion and Flame, Vol. 71, pp. 283-294.

21 Jarosinski, J, Strehlow, R.A., Azarbarzin, A., 1982, “The Mechanisms of Lean Limit Extinguishment of an Upward and Downward Propagating Flame in a Standard Flammability Tube”, Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp.1549-1557.

22 Jarosinski, J. and Strehlow, R.A., 1986, “A Survey of Recent Studies on Flame Extinction”, Progress in Energy and Combustion Science, Vol. 12, pp. 81-116.

23 Karim, G.A. 2003, “Hydrogen as a Spark Ignition Fuel”, International Journal of Hydrogen Energy, Vol. 28, No. 5, pp. 569-577.

24 Kilchyk, V., 2000, “Flammability Limits of Carbon Monoxide and Carbon Monoxide-Hydrogen Mixtures in Air at Elevated Temperatures”, M.Sc. Thesis, Department of Mechanical and Manufacturing Engineering, University of Calgary.

25 Kondo, S., Takizawa, K., Takahashi, A., Tokuhashi, K., Sekiya, A., 2008, “A Study on Flammability Limits of Fuel Mixtures”, Journal of Hazardous Materials, Vol. 155, No. 3, pp. 440-448.

26 Kumar, R.K., 1985, “Flammability Limits of Hydrogen-Oxygen-Diluents Mixtures”, Journal of Fire Sciences, Vol. 3, pp. 245-262.

27 Kumar, R.K., Tamm, H., Harrison, W.C., 1983, “Combustion of Hydrogen-Steam-Air Mixtures near Lower Flammability Limits”, Combustion Science and Technology, Vol. 33, No. 1-4, pp. 167-178.

28 Law, C.K., and Egolfopoulos, F.N., 1990, “A Kinetic Criterion of Flammability Limits. The C-H-O-Inert System”, Twenty-Third Symposium (International) on Combustion, The Combustion Institute, pp. 137-144.

29 Law, C.K., and Egolfopoulos, F.N., 1992, “A Unified Chain-Thermal Theory of Fundamental Flammability Limits”, Twenty-Fourth Symposium (International) on Combustion, The Combustion Institute, pp. 137-144.

30 Levy, A., 1965, “An Optical Study of Flammability Limits”, Proceeding of the Royal Society (London), Vol. A283, pp. 134-144.

31 Lewis, B. and von Elbe, G., 1987, “Combustion, Flames, and Explosion of Gases”, Third Edition, Academic Press, Inc.

32 Lovachev, L.A., 1971, “The Theory of Limits on Flame Propagation in Gases” Combustion and Flame, Vol. 17, pp. 275-278.

33 Lovachev, L.A., Babkin, V.S., Bunev, V.A., V’yun, A.V., Krivulin, V.N. and Baratov, A.N., 1973, “Flammability limits. An Invited Review”, Combustion and Flame, Vol. 20, pp. 259-289.

34 Lovachev, L.A., 1979, “Flammability Limits: A Review”, Combustion Science and Technology, Vol. 20, pp. 209-224.

35 Macek, A., 1979, “Flammability Limits. A Re-Examination”, Combustion Science and Technology, Vol. 21, pp. 43-52.

36 Marrero, T.R., and Mason, E.A., 1972 “Gas Diffusion Coefficients”, Journal of Physical and Chemical Reference Data, Vol. 1, No. 1.

37 Mayer, E., 1957, “A Theory of Flame Propagation Limits Due to Heat Loss”, Combustion and Flame, Vol. 1, No. 4, pp. 438-452.

38 Panlilio, J.P., 1981, “Mass Transfer and Flame Propagation in Stratified Atmospheres Rich in Inert Gas” M.Sc. Thesis, Department of Mechanical Engineering, University of Calgary.

39 Peters, N. and Smooke, M.D., 1985, “Fluid Dynamics. Chemical Interaction at the Lean Flammability Limit”, Combustion and Flame, Vol. 60, No. 2, pp. 171-182.

40 Poling, B.B, Prausnitz, J.M., O’Connell, J.P., 2001 “The Properties of Gases and Liquids: 5th Edition”, McGraw Hill, New York.

41 Rivkin, S.L., 1988, “Thermodynamic Properties of Gases: 4th Edition, Revised”, Berlin, Hemisphere Publishing Corp.

42 Ronney, P.D., 1985, “Effect of Gravity on Laminar Premixed Gas Combustion II. Ignition and Extinction Phenomena”, Combustion and Flame, Vol. 62, pp. 121-133.

43 Ronney, P.D., and Wachman, H.Y., 1985, “Effect of Gravity on Laminar Premixed Gas Combustion I. Flammability Limits and Burning Velocities” Combustion and Flame, No. 62, pp. 107-119.

44 Satterly, J. and Burton, E.F., 1919, “Combustibility of Mixtures of Hydrogen and Helium”, Trans. Royal Soc. Canada, Vol. 13, sec 3, pp. 211-215. Cited by ref. 14.

45 Shebeko, Yu.N., Tsarichenko, S.G., Korolchenko, A.Ya., Trunev, A.V., Navzenya, V.Yu, Papkow, S.N., and Zaitzev, A.A., 1995, “Burning Velocities and Flammability Limits of Gaseous Mixtures at Elevated Temperatures and Pressures”, Combustion and Flame, Vol. 102, pp. 427-437.

46 Shebeko, Y.N., Fan, W., Bolodian, I.A., Navzenya, V.Yu., 2002, “An Analytical Evaluation of Flammability Limits of Gaseous Mixtures of Combustible-Oxidizer-Diluent”, Fire Safety Journal, Vol. 37, No. 6, pp 549-568.

47 Smedt, G.De., de Corte, F., Notele, R., Berghamns, J., 1999, “Comparison of Two Standard Test Methods for Determining explosion Limits of Gases at Atmospheric Conditions”, Journal of Hazard Materials, Vol. A70, pp. 105-113.

48 Spalding, D.B., 1957, “A Theory of Inflammability Limits and Flame-Quenching”, Proceeding of the Royal Society (London), Vol. A240, pp. 83-100.

49 Strehlow, R.A., Noe, K.A., and Wherley, B.L., 1986, “The Effect of Gravity on Premixed Flame Propagation and Extinction in a Vertical Standard Flammability Tube”, Twenty-first Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp. 1899-1908.

50 Takahashi, A., Uranu, I., Tokuhashi, K., Kondo, S., 2003, “Effect of Vessel Size and Shape on Experimental Flammability Limits of Gases”, Journal of Hazardous Materials, Vol. 105, No. 1-3, pp. 27-37.

51 Van den Schoor, F., and Verplaetsen, F., 2007, “The Upper Flammability Limit of Methane/Hydrogen/Air Mixtures at Elevated Pressure and

Temperatures" International Journal of Hydrogen Energy, Vol. 32, No. 13, pp. 2548-2552.

52 Van den Schoor, F., Verplaesten, F., Berghmans, J., 2008, "Calculation of the Upper Flammability Limit of Methane/ Air Mixtures at Elevated Pressures and Temperatures", Journal of Hazardous Materials, Vol. 153, No. 3, pp 1301-1307.

53 Vanderstraeten, B., Tuerlinckx, D., Berghmans, J., Vliegen, S., Van Oost, E., Smit, B., 1997, "Experimental study of the Pressure and Temperature Dependence on the Upper Flammability Limit of Methane/Air Mixtures", Journal of Hazardous Materials, Vol. 56, No. 3, pp. 237-246.

54 Vidal, M., Wong, W., Roger, W.J., Mannan, M.S., 2006, "Evaluation of Lower Flammability Limits of Fuel-Air-Diluent Mixtures Using Calculated Adiabatic Flame Temperatures" Journal of Hazerdous Materials, Vol. 130, pp. 21-27

55 Vince, I.M., Vovelle, C. and Weinberg, F.J., 1984, "The Effect of Plasma Jet Ignition on Flame Propagation and Sooting at the Rich Limit of Flammability", Combustion and Flame, Vol. 56, pp. 105-112.

56 Wang, Q., 2004, "Flammability Limits of Hydrogen-Carbon Monoxide-Methane Mixtures in Air at Elevated Temperatures", M.Sc. Thesis, Department of Mechanical and Manufacturing Engineering, University of Calgary.

57 White, A.G., 1925, "Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures Part III. The Effect of Temperature on the Limits", Journal of Chemical Society, Vol. 127, pp. 672-685.

58 Wierzba, I., Bade Shrestha, S.O., Karim, G.A., 1994, "A Thermodynamic Analysis of the Lean Flammability Limits of Fuel-Diluent Mixtures in Air", Journal of Energy Resources Technology, Vol. 116, pp. 181-185.

59 Wierzba, I., Bade Shrestha, S.O., Karim, G.A., 1995, "A Thermodynamic Analysis of the Rich Flammability Limits of Fuel-Diluent Mixtures in Air", Journal of Energy Resources Technology, Vol. 117, pp. 239-242.

60 Wierzba, I., Bade Shrestha, S.O., Karim, G.A., 1996, “An Approach for Predicting the Flammability Limits of Fuel-Diluent Mixtures in Air”, Journal of the Institute of Energy, Vol. 69, pp.122-130.

61 Yaws, C.L, 1999, “Chemical Properties Handbook”, McGraw Hill, New York

62 Zabetakis, M.G., 1965 “Flammability Characteristics of Combustible Gases and Vapors”, US Bureau of Mines, Bulletin 627, Washington.

63 Zabetakis, M.G., and Richmond, J.K., 1953, “The Determination and Graphic Representation of the Limits of Flammability of Complex Hydrocarbon Fuels at Low Temperatures and Pressures”, Fourth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp. 121-126.

64 Zlochower, I.A., 2012, “Experimental Flammability Limits and Associated Theoretical Flame Temperatures as a Tool for Predicting the Temperature Dependence of these Flammability Limits”, Journal of Loss Prevention in the Process Industries, Vol. 25, No. 3, pp. 555-560.

APPENDIX A

CONSTANT ADIABATIC FLAME TEMPERATURE CONCEPT

When the flammability limit of a fuel mixture is experimentally determined, its corresponding adiabatic flame temperature can be calculated. This is done through a first law energy analysis. For an idealized adiabatic reaction occurring at a constant pressure in the absence of work transfer, the following enthalpy balance can be made,

$$\left[\sum_i H_{i,reactant}\right]_{T_{IN}} = \left[\sum_i H_{i,product}\right]_{T_A} \quad (A.1)$$

$$H_{i,product} = \left(H_{i,T_A} - H_{i,T_o}\right) + \Delta H_{fi}^0 \quad (A.2)$$

$$H_{i,reactant} = \left(H_{i,T_{IN}} - H_{i,T_o}\right) + \Delta H_{fi}^0 \quad (A.3)$$

where for the '*i'th* species,

$H_{i,\,reactant}$ (kJ/kmol) is the enthalpy at the initial temperature T_{IN} (K)

$H_{i,\,product}$ (kJ/kmol) is the enthalpy at the adiabatic flame temperature T_A (K)

ΔH_{fi} (kJ/kmol) is the enthalpy change of formation reaction at a reference temperature T_0 (K).

The enthalpy of formation of elementary gases such as hydrogen, helium, argon and nitrogen is zero. The enthalpies of most gases were calculated from temperature dependant polynomial equations (Rivkin, S.L., 1988). Since the changes in the values of heat capacity of helium and argon over the expected temperature rise are small, a constant heat capacity was assumed for calculating their enthalpy change.

$$\int dH_i = Cp_i \int dT \qquad (A.4)$$

where, Cp is the heat capacity of the species

The ideal chemical reaction for the lean hydrogen-diluent limiting mixtures can be written as follows,

$$L_{m,l}\,(y_f\,H_2 + (1-y_f)D) + (1-L_{m,l})(0.21\,O_2 + 0.79\,N_2) \rightarrow$$

$$(L_{m,l}\,y_f)H_2O + (0.21(1-L_{m,l}) - L_{m,l}\,y_f/2)O_2 + L_{m,l}\,(1-y_f)D + 0.79(1-L_{m,l})N_2 \qquad (A.5)$$

the ideal chemical reaction for the rich hydrogen-diluent limiting mixture can be written as follows,

$$L_{m,r}\,(y_f\,H_2 + (1-y_f)D) + (1-L_{m,r})(0.21\,O_2 + 0.79\,N_2) \rightarrow$$

$$0.42(1-L_{m,r})H_2O + (L_{m,r}\,y_f - 0.42(1-L_{m,r}))H_2 + L_{m,r}\,(1-y_f)D + 0.79(1-L_{m,r})N_2 \qquad (A.6)$$

where,

$L_{m,l}$ is the lean limiting concentration of fuel in the mixture (by vol.)

$L_{m,r}$ is the rich limiting concentration of fuel in the mixture (by vol.)

y_f is the hydrogen fraction in the fuel (by vol.)

D represents the diluent in the mixture.

The energy balance for both lean and rich limiting reactant mixtures is as follows,

$$\left[\sum_i H_{i,react}\right]_{T_f} =$$

$$(L_m\,y_f)(H_{\mathrm{H_2},T_{IN}} - H_{\mathrm{H_2},T_0}) + 0.21(1-L_{m,l})(H_{\mathrm{O_2},T_{IN}} - H_{\mathrm{O_2},T_0}) +$$

$$0.79(1-L_m)(H_{\mathrm{N_2},T_{IN}} - H_{\mathrm{N_2},T_0}) + L_{m,l}\,(1-y_f)C_{p\mathrm{D}}(T_{IN} - T_0) \qquad (A.7)$$

the energy balance for both lean and rich limiting products of the reaction as follows,

$$\left[\sum_i H_{i,prod}\right]_{T_f,l} =$$

$$\left(L_{m,l}\, y_f\right)\left(H_{\mathrm{H_2O},T_A} - H_{\mathrm{H_2O},T_0} + \Delta H_{f\mathrm{H_2O}}\right) + 0.79\left(1 - L_{m,l}\right)\left(H_{\mathrm{N_2},T_A} - H_{\mathrm{N_2},T_0}\right) +$$

$$\left(0.21\left(1 - L_{m,l}\right) - L_{m,l}\, y_f/2\right)\left(H_{\mathrm{O_2},T_A} - H_{\mathrm{O_2},T_0}\right) + L_{m,l}\left(1 - y_f\right)C_{p\mathrm{D}}(T_A - T_0) \tag{A.8}$$

$$\left[\sum_i H_{i,prod}\right]_{T_f,r} =$$

$$0.42\left(1 - L_{m,l}\right)\left(H_{\mathrm{H_2O},T_A} - H_{\mathrm{H_2O},T_0} + \Delta H_{f\mathrm{H_2O}}\right) + \left(L_{m,l}y_f - 0.42\left(1 - L_{m,l}\right)\right) \times$$

$$\left(H_{\mathrm{H_2},T_A} - H_{\mathrm{H_2},T_0}\right) + 0.79\left(1 - L_{m,l}\right)\left(H_{\mathrm{N_2},T_A} - H_{\mathrm{N_2},T_0}\right) + L_{m,l}\left(1 - y_f\right)C_{p\mathrm{D}}\left(T_f - T_0\right) \tag{A.9}$$

As the enthalpies need to be evaluated at the unknown adiabatic temperature Newton's method was employed to iteratively calculated the adiabatic flame temperature.

$$f(T_n) = \left[\sum_i H_{i,product}\right]_{T_n} - \left[\sum_i H_{i,reactant}\right]_{T_{IN}} \tag{A.10}$$

$$f'(T_n) = \sum C_{p,product} \tag{A.11}$$

$$T_{n+1} = T_n - \frac{f(T_n)}{f`(T_n)} \tag{A.12}$$