University of California,

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DETERMINATION OF LOWER FLAMMABILITY LIMITS OF MIXTURES OF AIR AND GASEOUS RENEWABLE FUELS AT ELEVATED TEMPERATURES AND PRESSURES

Thesis

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by

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DEDICATION

Para mis padres, Victor David y Ruth Elisabeth

and to

Marisa

for their endless love and support

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ABSTRACT OF THE THESIS

Determination of lower flammability limits of mixtures of air and gaseous renewable fuels at elevated temperatures and pressures

By:

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Master of Science in Mechanical and Aerospace Engineering

University of California, Irvine, 2017

Professor G. Scott Samuelsen, Chair

Experimental studies of lean flammability limits (LFLs) for methane, hydrogen, carbon monoxide, in addition to mixtures of these gases (i.e. CH_4/H_2, H_2/CO, and CH_4/CO_2) were performed at temperatures up to 200° C and pressures up to 9 bar. ASTM Standard E918 (1983) provided the framework for tests at these elevated conditions, using a one-liter pressure-rated test cylinder in which the fuel-air mixtures were prepared and then ignited. Flammability is determined using a 7% and 5% pressure rise criterion per the ASTM E918 and European EN 1839 standards, respectively. The LFLs for each gas and gas mixture are found to decrease linearly with increasing temperature in the temperature range tested. The LFLs of hydrogen and mixtures containing hydrogen are observed to increase with an increase in the initial pressure, whereas the LFLs of all other mixtures exhibit a negligible dependence on pressure. For mixtures, predicted LFL values obtained using Le Chatelier's mixing rule are fairly consistent with the experimentally determined values near ambient conditions, however it is not recommended for use at elevated pressure and/or temperature. The purpose for characterizing the flammability limits for these gaseous mixtures is to extend the results to developing appropriate procedures for the safe industrial use of renewable gases, such as bio-derived methane, biogas composed mainly of methane and carbon dioxide, and renewably derived syngas which contains large quantities of hydrogen and carbon monoxide gas.

1 INTRODUCTION

1.1 MOTIVATION

1.1.1 Prevention of Fires and Explosions

While this thesis emphasizes renewable gaseous fuels, it is important to note that previous work in this area was motivated by ensuring safety associated with mining operations. Underground coal mines have long been associated with gas explosions and have motivated research in the area of loss prevention in the process industries. The worst mining tragedy in Australian history occurred in the Mount Kembla Mine in 1902 with 96 lives lost, while the deadliest coal mine explosion in human history occurred in 1942 at the Benxihu Colliery in China killing 1,549 people (Kundu et al. 2016). One does not have to explore too far back to find a recent example of these dangers that continue to threaten human life, as evidenced by the Xinxing Coal Mine disaster that took the lives of 92 coal miners in late 2009.

Figure 1: Rescuers go down the exploded coal mine in Hegang City, northeast China's Heilongjiang Province; November 21, 2009

Key research dedicated to preventing explosions of this nature were conducted by the U.S. Bureau of Mines in the form of the published Bulletins 503 and 627 (Coward & Jones 1952; Zabetakis 1965). These comprehensive studies are widely cited and are often considered the original standard for determining the flammable ranges of numerous combustible gases and vapors commonly associated with the metallurgical, petroleum, gas-manufacturing, and related industries. The first bulletin characterized these ranges for 155 substances, and was increased to more than 200 combustibles in the second bulletin. Although the data presented in these reports have been invaluable to many industrial applications, they are limited only to investigations of gas explosions occurring for non-renewable mixtures initially at standard atmospheric pressure and temperature conditions. The increased use of gaseous fuel mixtures at elevated operating conditions[1] in recent times, as well as industrial applications that already operate at elevated conditions, warrants research into characterizing the flammable properties at higher temperatures and pressures.

Certain events during the 2011 Fukushima nuclear emergency demonstrate an important application of flammability research in regards to accident prevention at elevated operating conditions. A build-up of explosive hydrogen gas – as occurred at Three Mile Island in the U.S. in 1979 – caused by nuclear fuel rods experiencing extremely high temperatures stripping the hydrogen out of the plant's steam, likely led to the destruction of four reactor buildings. The accumulation of the hydrogen gas in the reactor buildings likely reached an optimal composition at which point any small fire or spark of energy would have triggered the detonation. A better understanding of the flammable range of hydrogen-air mixtures at the elevated process conditions could have been helpful for preventing these hydrogen explosions.

[1] Elevated conditions in the context of this study refers to high temperature and high pressure environments

1.1.2 Increased Utilization of Renewable Fuels

In addition to industrial applications that involve the natural occurrence of flammable gas mixtures at elevated conditions of pressure and temperature, current flammable research in this area will facilitate the safe utilization of gaseous fuels produced by renewable technologies. Such technologies include the "recycling" of carbon already circulating in the environment by producing gas from waste feedstocks, as well as Power-to-Gas (P2G), which uses excess electricity from renewable sources to produce renewable hydrogen.

Fuel conversion from organic wastes such as biomass can be considered renewable. Examples of biomass include forestry and agricultural residues, urban wood waste, municipal solid waste, animal farm waste, sewage and others; unlike fossil fuels and other renewable energy resources, biomass generation is not limited to the specific geography (Hosseini & Wahid 2014). The resultant renewable fuels consist of landfill gas, biogas, syngas, renewable hydrogen, bio-derived methane, ethanol and biodiesel. Conversion of biomass to these biofuels can be grouped into two main types: thermochemical conversion such as pyrolysis and gasification, and biochemical conversion which includes fermentation and anaerobic digestion. The sources of biomass as well as the technologies to convert them to biofuels is well established. In 2014, California biomass power plants made up over 1000 MW of electric generation capacity, producing about 3% of total state electricity. The "recycling" of carbon can be best described by biomass waste being converted to fuel for electricity power generation, which produces carbon dioxide, which in turn is consumed by plants along with sunlight and water. Reducing the reliance on fossil fuels and their contribution to air pollution and greenhouse gas emissions is critical, and using renewably-produced gaseous fuels directly for industrial applications is a promising alternative.

Power-to-gas technology is another promising alternative for a renewable energy that promotes increased production and subsequent use of renewable gaseous fuels. When the electric power demand of a system is at a minimum, a challenge presents itself with respect to the storage of excess renewable electricity produced by wind and solar. P2G offers the opportunity of storing the excess power by converting water to hydrogen gas through electrolysis, and can be further coupled with CO_2 capture in order to upgrade the hydrogen to renewable methane. In this way, renewable electricity can be stored in the natural gas infrastructure, a benefit that is illustrated in the figure below (Jentsch et al. 2014).

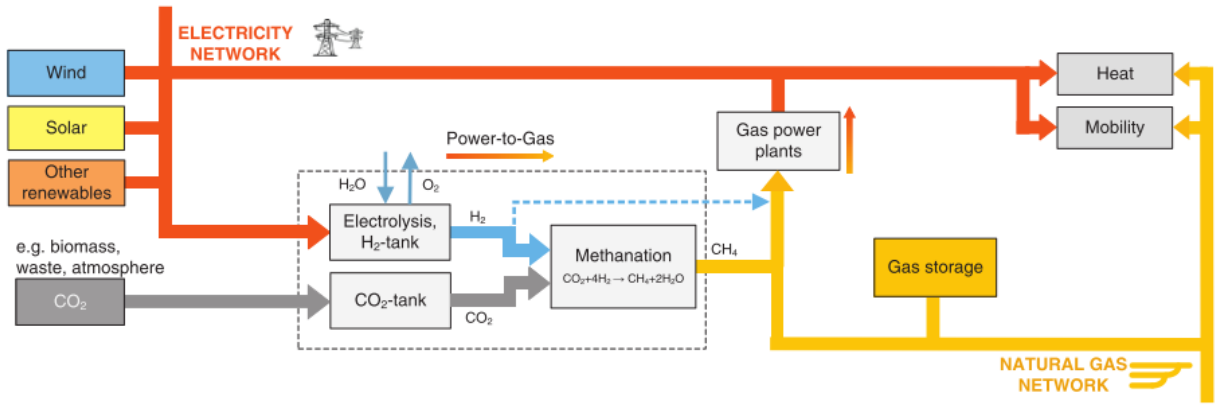

Figure 2: The storage concept P2G: storing renewable power as gas in the natural gas network for multiple use

Leveraging the existing natural gas (NG) pipeline infrastructure for massive-volume, long-term, distributed storage offers a possible solution to the challenge of energy storage. For comparison, batteries and flywheels offer rapid discharge and frequency management capabilities but are not suitable for long-term storage; while pumped hydro and compressed air energy storage offer longer-term storage, but are fundamentally limited by the requirement of favorable geographies. The renewable gases produced by P2G are either used directly in industry or transportation, or reformed to match the pipeline quality before introduction into the natural gas

network. For industrial use, an understanding of the flammable or "explosive" range of gaseous fuels at elevated conditions is critical for not only establishing appropriate safety standards and protocols, but also further improving the efficiencies of the power generation technologies that run on these fuels. For introducing renewable gases into the existing natural gas network for long term distributed energy storage, the key challenges include determining the safe amount of renewable gas (e.g. renewable hydrogen) that can be injected into the NG pipeline infrastructure while maintaining reliable and safe use of the gas for end users. Knowledge of the flammable ranges of these renewable gases, as well as mixtures of these gases, is pertinent to these issues related to the storage of renewable gas in the NG pipeline as well as direct industrial use of these gases.

The next section will provide the necessary definitions and terminology in order to understand how to address the aforementioned challenges as well as to help transition to the aim and scope of the present study.

1.2 KEY DEFINITIONS

Flammability limits, also called explosion limits, are the concentration limits of a combustible gas in a homogenous mixture of this combustible gas and an oxidizing gas within which a flame is able to propagate independently through the mixture. Gas mixtures are deemed flammable if and only if the concentration of the combustible gases lies between the lower flammability/explosion[2] limit (LFL/LEL) and the upper flammability/explosion limit (UFL/UEL). Inherently, the primary method for preventing a gaseous explosion is to prevent the formation of a flammable atmosphere. Therefore, knowing the flammability limits of a substance relative to an oxidizing agent is necessary. If possible, replacing the combustible component with a non-reacting

[2] Throughout this text, flammability limits and explosion limits will be used interchangeably to be consistent with the preferred terms used by each independent research study over the course of the past few decades

gas is ideal for preventing a possible gaseous fire or explosion; an example would be the substitution or general addition of nitrogen to act as a diluent. Another method for making sure the gaseous mixture is outside the flammable range is to decrease the concentration of the oxidizer gas (i.e. oxygen). The *limiting oxygen concentration* (LOC) is the maximum concentration of oxygen in a homogenous mixture of fuel, air and inert gas at which this mixture is nonflammable.

These flammability characteristics, among others, can be summarized in a flammability diagram as shown in Figure 3. *Flammability diagrams* show the regimes of flammability in mixtures of fuel, oxygen and an inert gas, such as nitrogen. These mixtures are often depicted in a ternary plot due to the typical composition of three gases. As can be seen in the figure below, the LEL for methane in air[3] is approximately 5% by volume, and the UEL is about 15% by volume, at standard atmospheric pressure and temperature. An increase in the concentration of methane corresponds to a shift in the diagram towards the upper vertex of the triangular diagram. An increase in the oxygen concentration would mean shifting towards the bottom-left vertex, and an increase in nitrogen concentration follows a shift towards the bottom-right vertex. It is important to note that the flammable range for methane increases greatly as the inert gas is replaced by a higher oxygen concentration, with the UEL reaching a value of 61% for pure oxygen versus the UEL of 15% for air. Knowledge of the flammability envelope of a combustible is thus useful for preventing flammable atmospheres, however, if this cannot be avoided it is necessary to isolate the gaseous mixtures from possible sources of ignition.

[3] The air composition here is assumed to be 79% nitrogen, 21% oxygen

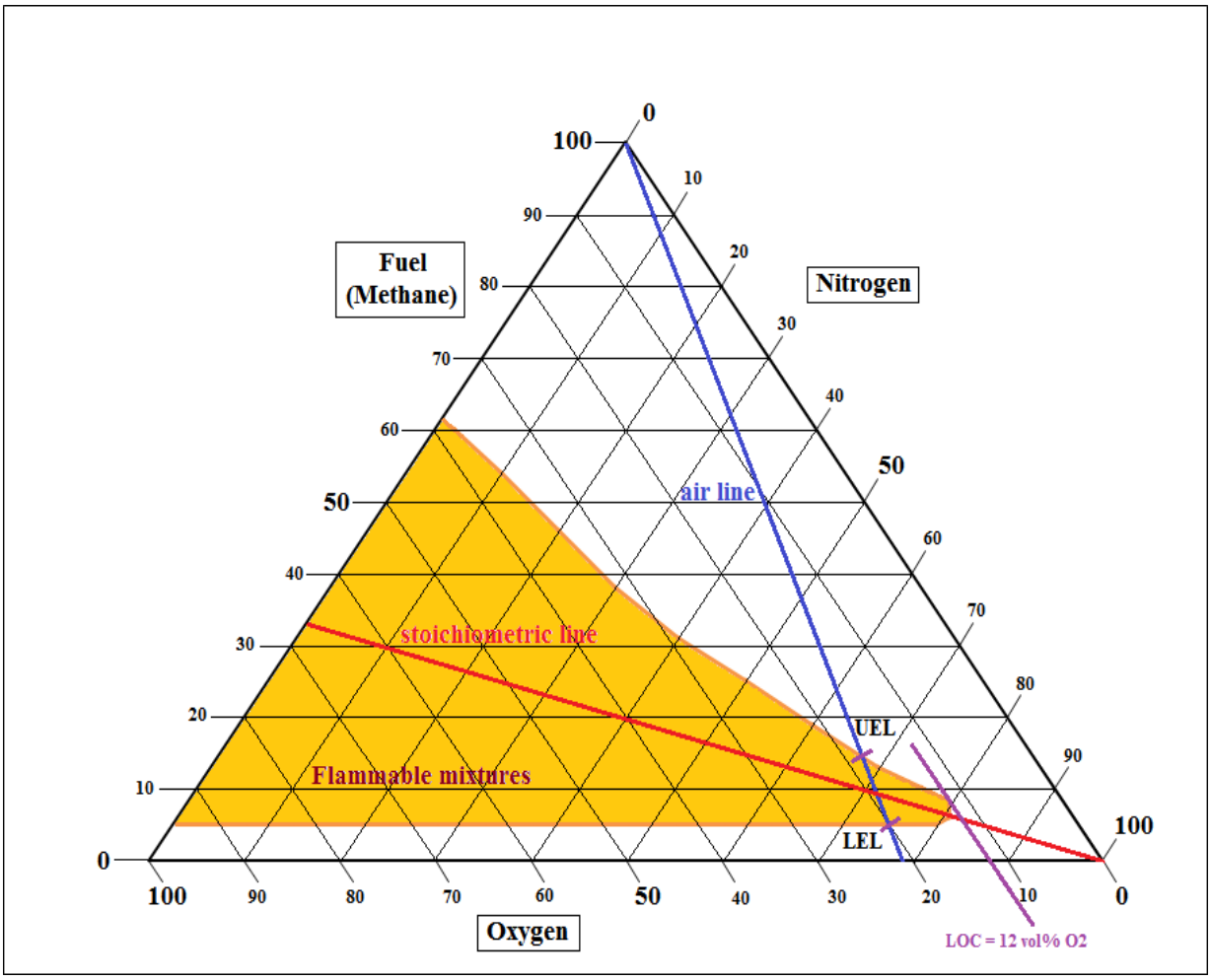

Figure 3: Flammability ternary plot for methane at ambient pressure and temperature

Ignition sources can be in the form of an open flame, a spark energy, or even the presence of a high enough temperature. The *auto-ignition temperature* is the lowest temperature at which a substance will produce hot-flame ignition in air at atmospheric pressure, provided a sufficient amount of time (10 minutes per ASTM E659) has passed and without the aid of an external energy source (ASTM E659 2005). Therefore, gas explosion prevention requires the isolation of possible flammable mixtures from ignition sources of these types. Finally, it is important to characterize the *explosion pressure* as the maximum pressure obtained during an explosion, as this will play a significant role as a criterion for ignition when determining the flammability limits of a

combustible mixture. The previously mentioned terminology and terms will be crucial for establishing an effective method for the determination of flammability limits, which will be covered in more detail in Chapters 2 and 4.

1.3 RESEARCH SCOPE, GOAL AND OBJECTIVES

The scope of this study involves determining and characterizing the flammability limits of gases and mixtures of gases in air at elevated initial temperatures and pressures. These limits are well established at ambient temperature and pressure, as evidenced by the work by the U.S. Bureau of Mines (Coward & Jones 1952; Zabetakis 1965) as well as extensive, albeit inconsistent, literature data. Flammability data at elevated conditions are limited, however, as is literature on the flammability of different gaseous mixtures. Section 2.3 of this text provides a full summary of the literature related to the determination of flammability limits for single and multiple-component gas mixtures at both standard and elevated conditions. Studies that investigate the dependence of both pressure and temperature on the flammability limits are minimal, and only two authors also investigated mixtures of gases (Ale et al. 1981; Van den Schoor 2007). The present work is motivated to not only validate previously published flammability data at elevated pressure and temperature conditions, but to also remark on the application of the flammability limits of gas mixtures in promoting the increase of renewable gas use for industrial applications.

The **goal of this research** is to:

- Determine the lower flammability limits of methane, hydrogen, carbon monoxide, in addition to mixtures of these gases (i.e. CH_4/H_2, H_2/CO, and CH_4/CO_2) in air; and confirm the dependence of initial temperature and pressure on these flammability limits.

The main objectives to achieve this goal are:

1. Develop a test apparatus. A suitable device that best matches those found in pertinent standards and other flammability studies is necessary for use in the determination of lower flammability limits (LFLs) of combustible mixtures at elevated initial conditions.
2. Determine LFLs experimentally. The lower flammability limits of varying mixtures of methane/hydrogen (CH_4/H_2), methane/carbon dioxide (CH_4/CO_2) and hydrogen/carbon monoxide (H_2/CO) at initial pressures up to 9 bar and initial temperatures up to 200 °C will be found experimentally using the test apparatus.
3. Determine LFLs numerically. Laminar flame propagation will be modeled in CHEMKIN in order to simulate limits of flammability for the experimental test parameters, and the numerical results will be compared with the experimental results.
4. Validate results with literature data. Available flammability data for the previously mentioned pure fuels and renewable gaseous fuel mixtures at elevated temperature and pressure will be compared with the flammability data determined in this study; also, flammability limits calculated using predictive methods (e.g. Le Chatelier's Law) will also be evaluated.
5. Propose revised standard. An optimal test apparatus and ignition criterion, inter alia, for the determination of flammability limits at elevated conditions will be suggested consistent with the conclusions from this study.

2 BACKGROUND

Numerous parameters influence flammability limits, but the three main factors include: the conditions of use (e.g. pressure, temperature, composition of mixture), the test apparatus, and the ignition criterion. This chapter will seek to address these factors with respect to their role in the development of methods for determining flammability limits of combustible gas mixtures.

2.1 THEORETICAL BACKGROUND

Establishing a theoretical basis for the influence of pressure and temperature on the limits of flammability will be useful as it can allow for a more logical interpretation of the results presented through the experimental and numerical methods in the following chapters. An active researcher of the effects of elevated initial conditions on the limits of flammability is F. Van den Schoor (2006; 2007; 2008; 2009). In his 2007 study in particular, various aspects of flame propagation and their dependence on pressure and temperature are comprehensively derived and summarized. Table 1: Summary of the pressure and temperature dependence of the variables important in flame propagation, with $n < 2$, $0 < m < 1$, $1.5 < a < 2$ and $1.5 < b < 2$ (Van den Schoor 2007)Table 1 provides a concise reference of the results for the variables in question, and the following is a brief discussion of the importance of each in the context of the flammable range.

2.1.1 Influence of Pressure and Temperature on Flame Propagation

Adiabatic Flame Temperature

Assuming isobaric flame propagation, and that the specific heat capacity at constant pressure is independent of temperature, a relationship for the adiabatic flame temperature can be derived from the governing energy balance:

$$T_{f,ad} = T_1 + \frac{-\Delta H_r(T_1)}{C_p} \quad (1)$$

The variable ΔH_r denotes the heat of reaction and T_1 represents the initial temperature.

	Pressure dependence	**Temperature dependence**
$\boldsymbol{T_{f,ad}}$	Slightly increases	Increases
$\boldsymbol{\dot{\omega}}$	$\sim p^n$	$\sim \exp\left(-\frac{E_a}{RT}\right)$
$\boldsymbol{\nabla \cdot \overrightarrow{q_r}}$	$\sim p^m$	$\sim a_{p,i}(T) \cdot T^4$
$\boldsymbol{T_f}$	Slightly increases	Increases
$\boldsymbol{\alpha}$	$\sim 1/p$	$\sim T^a$
$\boldsymbol{D}$	$\sim 1/p$	$\sim T^b$
$\boldsymbol{S_u}$	$\sim p^{\frac{n-2}{2}}$	$\sim \left[\exp\left(-\frac{E_a}{RT_f}\right)\right]^{\frac{1}{2}}$
$\boldsymbol{\delta}$	$\sim p^{-\frac{n}{2}}$	$\sim \left[\exp\left(-\frac{E_a}{RT_f}\right)\right]^{-\frac{1}{2}}$
$\boldsymbol{S_f}$	$\sim p^{\frac{n-2}{2}}$	$\sim \left[\exp\left(-\frac{E_a}{RT_f}\right)\right]^{\frac{1}{2}} \frac{T_f}{T_u}$
$\boldsymbol{\mathcal{L}K}$	Decreases	?
$\boldsymbol{v}$	Slightly increases	Decreases
$\boldsymbol{\Delta\Phi}$	Independent	(Nearly) Independent

Table 1: Summary of the pressure and temperature dependence of the variables important in flame propagation, with $n < 2$, $0 < m < 1$, $1.5 < a < 2$ *and* $1.5 < b < 2$ (Van den Schoor 2007)

A direct result of equation (1) shows an increase in the **initial temperature** causes an increase in $T_{f,ad}$. However, it should be noted that this increase is smaller than the increase in initial temperature due to the resultant chemical energy release. With respect to **initial pressure**, an

increase in pressure causes a decrease in product dissociation. The adiabatic flame temperature increases with increasing pressure as a result of the endothermic nature of dissociation reactions.

Chemical Reaction Rate

The rate of reaction $\dot{\omega}$ for an arbitrary reaction, $A + B \rightarrow C + D$ can be described by the law of mass action, namely:

$$\dot{\omega} = kC_A C_B \tag{2}$$

This law states that the reaction rate is proportional to the product of the concentrations of the reacting species. This constant of proportionality is given by

$$k = AT^{\frac{1}{2}} \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

with A defined as the pre-exponential factor. A generalized form of equation (2) can be combined with the ideal gas assumption and the fact that C_{A_i} is directly proportional to pressure, to find the relationship of the reaction rate to the **initial pressure**:

$$\dot{\omega} \sim p^n \tag{4}$$

where $n = \sum \nu_i'$ represents the order of the reaction, which is determined by the total number of reactants through the stoichiometric coefficient ν. Therefore, increasing pressure will mostly increase the reaction rate, especially if the chain propagating and branching steps are the most important.

A combination of equations (2) and (3) can be used to confirm the reaction rate dependence on **initial temperature**:

$$\dot{\omega} \sim \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

Overall, since the propagating and branching steps generally have a higher activation energy than the terminating steps, the overall reaction rate will increase exponentially with temperature.

Radiation Heat Transfer

Energy transferred from the reaction products to the surroundings via heat radiation can be summarized by:

$$\nabla \cdot \overrightarrow{q_r} = 4a_p(T,p)\sigma T^4 \tag{6}$$

which is an expression for the divergence of the radiant energy q_r under the assumption that only emission is considered. The total Planck mean absorption coefficient a_p can be calculated from the specific coefficients of each radiating species:

$$a_p(T,p) = \sum p_i a_{p,i}(T) \tag{7}$$

with p_i representing the partial pressure of each species. It can be easily shown by combining equations (6) and (7) that the net outflow of radiant energy from a unit volume is directly proportional to pressure:

$$\nabla \cdot \overrightarrow{q_r} = 4\left(\sum p_i a_{p,i}(T)\right)\sigma T^4 \sim p \tag{8}$$

It is important to note this result is only valid under the emission approximation. If absorption cannot be neglected, the total radiation heat loss will be lower than in the emission approximation. Therefore, the dependence on **initial pressure** of the radiant heat transfer is concisely:

$$\nabla \cdot \overrightarrow{q_r} \sim p^m \tag{9}$$

with $m = 1$ if no absorption is present and $0 < m < 1$ otherwise. The dependence on initial temperature is clearly shown in equation (8) as well, and radiation heat loss generally increases with **initial temperature**.

Flame Temperature

Considering radiation heat loss, it can be assumed that the actual flame temperature T_f will be less than the adiabatic flame temperature $T_{f,ad}$. An overall balance between the reaction rate $\dot{\omega}$ and the heat loss rate $\nabla \cdot \overrightarrow{q_r}$ will determine the extent of the decrease in temperature. Although there may be a difference in the reaction order n and the characteristic exponent m of equation (9), the flame temperature will only be slightly dependent on **initial pressure**, similar to the adiabatic flame temperature. Also comparable to the adiabatic case, the flame temperature will increase with **initial temperature**.

Thermal and Mass Diffusion

The commonly used quantities of thermal diffusivity and mass diffusivity are well known to be inversely proportional to **pressure**:

$$\alpha \sim 1/p \tag{10}$$

$$D \sim 1/p \tag{11}$$

It can also be stated that the Lewis number $Le = \frac{\alpha}{D}$ is independent on pressure. The relationship of these diffusivities to **temperature** are also known:

$$\alpha \sim T^a \tag{12}$$

$$D \sim T^b \tag{13}$$

where the value of a and b range from 1.5 - 2. The quotient of these quantities gives the Lewis number and in this case the temperature dependence is minimal.

Burning Velocity and Flame Thickness

The burning velocity S_u as well as the flame thickness δ can be determined by the following derived expressions:

$$S_u \sim \left(\frac{\alpha\dot{\omega}}{\rho}\right)^{\frac{1}{2}} \tag{14}$$

$$\delta \sim \frac{\alpha}{S_u} \tag{15}$$

Substituting equations (4) and (10) into equation (14) gives:

$$S_u \sim p^{\frac{n-2}{2}} \tag{16}$$

For the burning velocity, given an overall reaction order of 2 or less, an **increase in pressure** would see a decrease in the velocity of the flame front. In similar steps, the pressure dependence of the flame thickness can be found to be:

$$\delta \sim p^{-\frac{n}{2}} \tag{17}$$

Given the overall reaction order n is mostly positive, the flame thickness will decrease with **increasing pressure**. The **temperature** dependence for both the burning velocity and the flame thickness can be found in a similar manner, and can be shown to be:

$$S_u \sim \left[\exp\left(-\frac{E_a}{RT_f}\right)\right]^{\frac{1}{2}} \tag{18}$$

$$\delta \sim \left[\exp\left(-\frac{E_a}{RT_f}\right)\right]^{-\frac{1}{2}} \tag{19}$$

Flame Speed

The flame speed is defined as the velocity of the flame front with respect to a fixed frame, whereas the burning velocity was defined relative to the velocity of the unburned gases. A relationship between the two is provided for a spherically expanding isobaric flame:

$$S_f = S_u \left(\frac{\rho_u}{\rho_b}\right) \tag{20}$$

where ρ is the density of the unburned/burned gases. Using the isobaric relation $\frac{\rho_u}{\rho_b} \sim \frac{T_f}{T_u}$, it is clear the influence of **pressure** is the same for the flame speed as the burning velocity:

$$S_f \sim p^{\frac{n-2}{2}} \tag{21}$$

The **temperature** dependence of the flame speed under the aforementioned conditions is found:

$$S_f \sim \left[\exp\left(-\frac{E_a}{RT_f}\right)\right]^{\frac{1}{2}} \frac{T_f}{T_u} \tag{22}$$

Therefore, the flame speed increases with increasing temperature due to the exponential term dominating over the fractional term.

Natural Convection

The effects of natural convection become relevant to the propagation of a flame in a one-g environment. Derived from the momentum equation, the upward velocity v of a spherical flame kernel with neglect of the drag force is given by:

$$v = \frac{\left(\frac{\rho_u}{\rho_b} - 1\right) gt}{4\left(1 + \frac{1}{2}\frac{\rho_u}{\rho_b}\right)} \tag{23}$$

The dependence of the upward velocity on **pressure** can be found by differentiation of the above equation with respect to the density ratio. The result is that the upward velocity increases with the density ratio, which also means that the velocity slightly increases with pressure. The isobaric relation $\frac{\rho_u}{\rho_b} \sim \frac{T_f}{T_u}$ shows the inverse relationship between **temperature** and the density ratio. Therefore, the upward velocity decreases with an increasing temperature.

Preferential Diffusion

The main effect of preferential diffusion, namely the shift in composition, is given by:

$$\Delta\Phi \sim \Phi\left(\frac{1}{Le_c} - \frac{1}{Le_o}\right) \tag{24}$$

where the subscript c refers to the combustible concentration and the subscript o refers to the oxidizer concentration. As previously mentioned when discussing thermal and mass diffusivities, the Lewis number is independent of **pressure**. Therefore, the compositional shift $\Delta\Phi$ is independent of pressure as well. It was also mentioned that the dependence on **temperature** is minimal, therefore, $\Delta\Phi$ is (nearly) independent on temperature.

2.1.2 Influence of Pressure and Temperature on Flammability Limits

Limiting combustion phenomena occur when the rate of heat developed by chemical transformation equals the rate of heat lost to the surroundings (Penner & Mullins 1959). Not only is it important to consider this competition between heat production and heat loss when studying flammability theory, but it is also important to delve more into the competitive nature of the chemical reactions during heat production. A few of the characteristic variables of flame propagation discussed in the previous section will be elaborated now in order to offer insight into a fundamental theory behind the *pressure and temperature dependence of the flammability limits*.

Chemical Kinetics

As the concentration of a mixture nears the flammability limits, flame extinction mechanisms will govern the chemical reactions. It is important to emphasize the competition between chain branching and chain terminating reactions in particular. Near-limit mixtures are removed from the optimal stoichiometric mixture, therefore flame temperature is generally lower. The reaction rate of the branching reactions are more sensitive to temperature than the reaction rate of the terminating reactions. Along with a decrease in chain carriers due to a decrease in the reaction rate of the chain branching reactions, it is clear the reaction rate is the decisive factor for evaluating pressure and temperature dependence.

As mentioned previously, the reaction rate $\dot{\omega}$ varies with **pressure** through equation (4), therefore the reaction order n establishes the effect of pressure. As the reaction order is mostly positive, the lower (upper) flammability limit will tend to decrease (increase) with pressure which results in a wider flammable range. It is important to note that n can assume negative values and therefore, an increase in pressure would have the opposite effect (Law 2006). The **temperature** dependence is given by equation (5) which shows the reaction rate generally increases exponentially with temperature. Therefore, similar to pressure, the lower (upper) flammability limit will tend to decrease (increase) with temperature.

Heat Production vs Heat Loss

Flame extinction will also result from the competition between heat production (i.e. reaction rate) and the heat loss rate. The foregoing discussion regarding heat loss rate included assumptions of only radiant emission, as well as neglecting conduction and convection heat loss as flame propagation is assumed to be removed sufficiently from notable boundaries.

When considering the determining factors with respect to increased pressure or temperature, it is important to recall and compare the dependence of the reaction rate and heat loss rate to these elevated conditions. Comparison of equations (4) and (9) demonstrate that the determining factor will depend on how the reaction order *n* compares with *m*. The reaction order is usually a positive value, and $m = 1$ if no absorption is present; however, *m* can take on a value between 0 and 1 which means the heat loss rate will be lower than the emission-only approximation. The overall flammable range (decrease of lower limit, increase of upper limit) will increase with increasing **pressure**, assuming $n > 1$.

The temperature dependence for the reaction rate was given by equation (5) and the temperature dependence of the radiant heat loss rate was given by equation (8). Comparison of these two expressions shows that the determining factor is the exponential dependence of the temperature for the reaction rate, when compared with the T^4 relationship for the radiant heat loss rate. Therefore, the overall flammable range (decrease of lower limit, increase of upper limit) will also increase with increasing **temperature**.

2.1.3 Summary

The preceding sections provide a brief yet valuable, theoretical foundation for the existence of flammability limits and their dependence on pressure and temperature. Various aspects of flame propagation were introduced and extended in the context of the mechanisms of flame extinction. The framework indicates not only the existence of lower and upper flammability limits, but the general increase of the flammable range (decrease of lower limit, increase of upper limit) with increasing pressure and temperature. It should be noted that various assumptions were taken such as neglecting heat loss due to conduction or convection, as well as assuming a reaction order *n* greater than unity. It is also important to mention that this very dependence on reaction order *n*

also predicts a decrease in the flammable range (increase of lower limit, decrease of upper limit) with negative overall reaction orders, as were found for lean hydrogen/air mixtures (Law 2006).

The theoretical framework is not sufficient for the determination of the flammability limits, however it provides a basis for evaluating and validating experimental data. The following sections cover a brief history of flammability research, the development of widely used standards for the determination of the limits of flammability, and a literature review of the current state of research in this area.

2.2 DEVELOPMENT OF STANDARDS

Flammability limit data for many gaseous fuels have been published extensively. However, the inconsistency of the published data as well as the lack of attention given to elevated temperature and pressure conditions of fuels and fuel mixtures are the impetus for this study. The following discussion will summarize the details that led to the development of standards for the determination of flammability limits for combustible mixtures, will introduce terminology widely associated with these standards and used extensively in the literature, and will offer clarification as to why published data are inherently inconsistent.

2.2.1 American Standards

Some of the earliest reports on flammability data were conducted as a collaboration between the Safety in Mines Research Board of Great Britain and the Bureau of Mines, United States Department of the Interior. Bulletin 503 was published by Dr. H. F. Coward of Sheffield, England and G. W. Jones of the Bureau of Mines, and presented a comprehensive study on the limits of flammability of gases and vapors (Coward & Jones 1952). The particular edition of the bulletin referenced in this study provides a summary of the flammability limits in air and in oxygen

of 155 substances, compared to 26 substances in the original edition. With a similar goal in mind of the prevention of disastrous gas explosions and overall mine safety, a supplemental bulletin was provided by M. G. Zabetakis in 1965. Bulletin 627 reports available limit of flammability, auto-ignition, and burning rate data for more than 200 combustible gases and vapors (Zabetakis 1965). Although these reports are thorough and widely referenced, the data are limited to the atmospheric conditions the tests were conducted under, which means they cannot be applied directly to applications under elevated pressure and temperature conditions. Zabetakis addresses this concern despite suggesting the empirical rules and graphs presented can be used to predict similar data for other combustibles under a variety of conditions. It is made clear that although suitable approximations can be made to permit a realistic evaluation of the hazards associated with the process being considered, it is no substitute for flammability data obtained at the elevated process conditions.

For many years, the U.S. Bureau of Mines bulletins were treated as the standard for which to measure the limits of flammability of combustible gases and vapors. For this reason, the experimental methods provided by these reports will be the first to be characterized with respect to the three main parameters that influence the flammability limits: the **test apparatus**, the **ignition criterion** and the **conditions of use**.

The test apparatus first introduced by Coward & Jones (1952), and used extensively by Zabetakis (1965) and others, is a vertical flame propagation tube made of glass, with a diameter of about 50 mm. and a length of 1.5 m. Mixtures are ignited at the bottom end of the tube using an electric spark from an induction coil or by drawing a flame across an aperture in the observation vessel. The ignition criterion for this experimental setup is visual flame propagation over the length of the tube (1.5 m.). As tests are conducted, the overall limits of flammability are established as

halfway between the largest concentration that is not flammable and smallest concentration that is flammable (lower limit), and halfway between the largest concentration that is flammable and the smallest concentration that is not flammable (upper limit). Finally, as previously mentioned, the conditions of use for the U.S. Bureau of Mines "standard" are largely atmospheric conditions with some insight to effect of elevated initial temperatures, and primarily flammability data of pure gases and vapors.

An effort to standardize test methods for the determination of flammability limits was developed by the American Society for Testing and Materials (ASTM) in the early 1980's. ASTM E681 was developed as the standard test method for the concentration limits of flammability of chemicals at ambient conditions, while ASTM E918 became the standard practice for determining limits of flammability of chemicals at elevated temperature and pressure (ASTM E681 1985; ASTM E918 1983). The test apparatus discussed in the ASTM E681 standard is a glass sphere ($V = 5\ L, D = 222\ mm$) which differs greatly from the propagation tube introduced by the U.S. Bureau of Mines. The test apparatus presented by ASTM E918 is characteristically unique as it is one of the only standards intended for use at elevated conditions. The test vessel is prescribed to be a steel cylinder with a volume no less than 1 L, and a minimum inside diameter of 76 mm. The ignition for both of these standards is provided by a fuse wire extended into the vessel, with supply energy provided at approximately 500 VA. The ignition criteria differs for both of these standards due to their differing conditions of use. The ignition criterion for ASTM E681 is visual flame propagation observed over 0.2 m. while the criterion for ASTM E918 requires a pressure rise of 7% of the initial pressure. The criterion for the former is similar to that of the Bureau of Mines study, however it is no surprise that the flammable range determined by ASTM E681 is less conservative due to the shorter distance of flame propagation imposed. The pressure rise criterion

for ASTM E918 is necessary as visual flame propagation may not be possible due to the large initial pressures to be tested. The choice for a 7% pressure rise was chosen as it corresponds to an increase of 1 psia (0.007 MPa) per atmosphere of initial pressure. Further discussion of this choice will demonstrate whether it is a suitable criterion or if another value may be superior at determining the flammability limits. The definition for the limit of flammability offered by the ASTM standards is consistent with the U.S. Bureau of Mines as halfway between the flammable and non-flammable point. Finally, the conditions of use for ASTM E681 is pressures up to ambient (1 atm) and temperatures up to 150 °C, while for ASTM E918 the conditions are initial pressure up to 13.8 bar (200 psia) and temperatures up to 200 °C. For this reason, it is important that the vessel used in accordance to ASTM E918 is rated to withstand explosion pressures up to 206.8 bar (3000 psi). Only ASTM E681 mentions applicability of limits found using the test standard to determining limits of known mixtures using Le Chatelier's law, however it references Bulletin 627 (1965) of the Bureau of Mines for further calculation details.

2.2.2 European Standards

The first notable European standard was developed around the same time as the ASTM standards, namely DIN 51 649 (1986). The test apparatus adopted by this standard is similar to the flammability tube described by the U.S. Bureau of Mines, however its length is shorter and diameter is slightly larger ($D = 60\ mm, L = 0.3\ m$). Also similar is the source of the ignition energy through a spark. Whereas, DIN 51 649 specifies the amount of energy to be provided as 5 Joules over a period of 0.5 seconds, the American standards do not provide this information. The ignition criterion for this standard is by far the least strict, with the only requirement being any visual flame detachment at the location of the spark. Another clear distinction between the American and European standards is the definition of the flammability limit. DIN 51 649 states

the flammability limits as the fuel concentrations beyond which the mixtures are not ignitable (De Smedt et al. 1999). This can be a significant difference as limits determined by European standards do not include mixtures that can sustain flame propagation, while American standards allow this possibility. Finally, the conditions of use for the determination of flammability limits of pure combustibles are atmospheric initial pressures and temperatures up to 200 °C, which agree with the conditions of use of the U.S. Bureau of Mines studies.

The new European standard EN 1839 (2003) is based on the DIN 51 649 standard, but also incorporates an additional test apparatus in order to reflect the two most accepted and employed experimental configurations. The first vessel type is used for tests according to the "tube" method, while the second vessel type corresponds to the "bomb" method, both per EN 1839. The first vessel adopts a similar glass cylinder as DIN 51 649 and the U.S. Bureau of Mines flammability tube, however its dimensions are more similar to that of the former European standard ($D = 80\ mm, L = 0.3\ m$). The second vessel is prescribed as either a sphere or cylinder with a diameter to length ratio between 1 and 1.5, and a volume no less than 5 L. The ignition source for the tube method is from a spark located at the bottom end of the tube, similar to both the European and American standard; however the ignition energy differs slightly as 2 Joules provided over a period of 0.2 seconds. The ignition source for the bomb method is described as a fuse wire (NiCr) located at the center of the vessel, and providing between 10 and 20 Joules of ignition energy. The ignition criterion for the tube method is visual flame propagation over 0.1 m, which is the largest variation from DIN 51 649, but still not as long as the Bureau of Mines criterion. The criterion for the bomb method is a 5% pressure rise of the initial pressure, similar to ASTM E918 as neither prescribed vessel allow for observation of flame propagation. Consistent with the European standard, the definition of the flammability limit for both methods of EN 1839 is also given at the characteristic

non-flammable points rather than halfway between flammable and non-flammable points. Finally, the conditions of use for both the tube and bomb method of EN 1839 are exactly the same as DIN 51 649 (atmospheric pressure, temperatures up to 200 °C, pure fuel-air mixtures); interestingly, despite the similarities between the bomb method of EN 1839 and ASTM E918, the pressure resistant test "bomb" is not prescribed for use in determining the flammability limits at elevated pressures.

2.2.3 Comparison and Review of Terminology

A summary of the previous discussion regarding the various American and European standards for the determination of flammability limits is found in Table 2. Although the data collected by using these standards can be consistent, a side-by-side comparison of the test apparatus, ignition criterion and conditions of use for each standard display the lack of true "standardization" amongst the different flammability limit determination test methods. The test apparatus for each standard is unique and there is hardly any overlap that would allow for straightforward comparison of data collected using each method. The ignition criterion is either visual or by means of a pressure rise, but there is disagreement in the exact distance of flame propagation necessary for confirming flammability as well as in the percentage of pressure rise of the initial pressure. The most significant similarity between the aforementioned methods is the conditions of use for which they apply; nearly all are valid at ambient conditions and ASTM E918 is the only standard capable of testing at elevated conditions.

	Method	Test Apparatus	Ignition Criterion	Conditions of Use
American Standards	U.S. Bureau of Mines	Vertical glass tube $D = 50\ mm$; $L = 1.5\ m$	Visual flame propagation over 1.5 m	Atmospheric pressure, Atmospheric temperature
	ASTM E681	Glass sphere $V = 5\ L$; $D = 222\ mm$	Visual flame propagation over 0.2 m	Atmospheric pressure, Ambient temperature up to 150 °C
	ASTM E918	Steel cylinder $V \geq 1\ L$; $D \geq 76\ mm$	Pressure rise of 7% of initial pressure	Pressures less than 13.8 bar (200 psia) Ambient temperature up to 200 °C
European Standards	DIN 51 649	Vertical glass tube $D = 60\ mm$; $L = 0.3\ m$	Visual flame detachment	Atmospheric pressure, Ambient temperature up to 200 °C
	EN 1839 - Tube	Vertical glass tube $D = 80\ mm$; $L = 0.3\ m$	Visual flame propagation over 0.1 m	Atmospheric pressure, Ambient temperature up to 200 °C
	EN 1839 - Bomb	Pressure resistant sphere/cylinder $V \geq 5\ L$; $\frac{D}{L} = 1 - 1.5$	Pressure rise of 5% of initial pressure	Atmospheric pressure, Ambient temperature up to 200 °C

Table 2: Comparison of current standards for the determination of flammability limits

Due to the discrepancies found in these standards, it should be apparent that published literature data are inherently inconsistent. Many studies use the experimental configurations specified in the above standards while others use vessels of different shapes and sizes. Ignition criteria can include temperature rise or analysis of combustion products, in addition to visual flame propagation and/or percent pressure rise. Flammability data at elevated temperatures and pressures, as well as data specific to different gaseous mixtures, are scarce and require validation as well as further investigation. The following section examines the state of research in these areas in order to achieve a perspective that will help to further develop the aim and scope for this study.

2.3 LITERATURE REVIEW

The foregoing evaluation of the standards for determining the flammability limits of gaseous fuels served to group the numerous parameters that influence these limits into three main categories: the test apparatus, the ignition criterion, and the conditions of use (e.g. pressure, temperature, gas composition). Each study will be grouped into one or more of these three categories, and will be evaluated with respect to the relative significance of their contributions.

2.3.1 Test Apparatus Dependent Studies

Some of the earliest studies regarding the determination of flammability limits for combustibles were consistent with respect to the test apparatus used, mostly due to the fact that some of the only available "standards" at the time were the bulletins provided by the U.S. Bureau of Mines. Considering these tests were being performed at atmospheric conditions, understandably the glass tube apparatus referenced in these bulletins was used extensively.

Karim et al. (1984) investigated the lean flammability limits of methane, hydrogen, and carbon monoxide determined using a vertical tube apparatus as suggested by the Coward & Jones

(1952). De Smedt et al. studied the explosion limits of methane, ethane, propane and butane, and also used a glass tube test vessel (De Smedt et al. 1999). By this point in time, however, European standards were well established (DIN 51649 and EN 1839) and provided a similar glass tube standard for flammability limit determination. Also by this point in time, determination of flammability limits using pressure resistant vessels was strongly suggested and standardized as an alternative to the well-accepted "flammability tubes". The flammability data obtained by De Smedt et al. were collected not only using the aforementioned glass tube, but also a 20-liter sphere per dust explosion standard VDI 2263. Comparison of data found using different vessels suggested by established standards was also investigated by Schröder & Molnarne for hydrogen, ethylene, methane and ammonia in air (Schröder & Molnarne 2005). Specifically, they determined the explosion limits using the tests vessels identified in two European standards (DIN 51649, EN 1839 Tube and Bomb) as well as the American standard ASTM E681. Both of these studies that compare flammability data obtained using different standard apparatus are important for evaluating their practical use and potentially improving the original test methods and procedures.

The dependence of the test vessel volume on the flammability limits was investigated extensively, in order to provide insight as to the optimal size for standard testing. The flammability study conducted by Cashdollar et al. used an assortment of test chambers including an 8-liter, 120-liter and 25,500-liter (25.5 m^3) pressure resistant vessel (Cashdollar et al. 2000). Remarkably, this study concluded that there is minimal dependence on the explosion limits due to the size of the test vessel, especially when determining the lower flammability limit.

A report on the experimentally determined explosion limits of methane, hydrogen and propylene included a comparison of flammability data found using different sized test vessels (Holtappels 2006). Figure 4 shows that an increase in volume of the test vessel from approximately

2.8-liters up to 20-liters has little to no effect on the lean flammability of methane-air mixtures. Miao et al. also commented on the volume dependence on the flammability limits of methane and hydrogen in the literature (Miao et al. 2011). Studies that are covered in this paper performed tests in vessels as small as 2.7-liters and as large as 25.5 m^3. It should be noted that the lower flammability data presented in this study vary significantly, however, it is clear that the size of the vessel is not the main factor. For example, the lean limits for methane vary from 3.8 vol. % to 5.3 vol. %. These values are a result of the type of ignition criterion used – a summary of the various types of criteria used in the literature will be discussed in the next section.

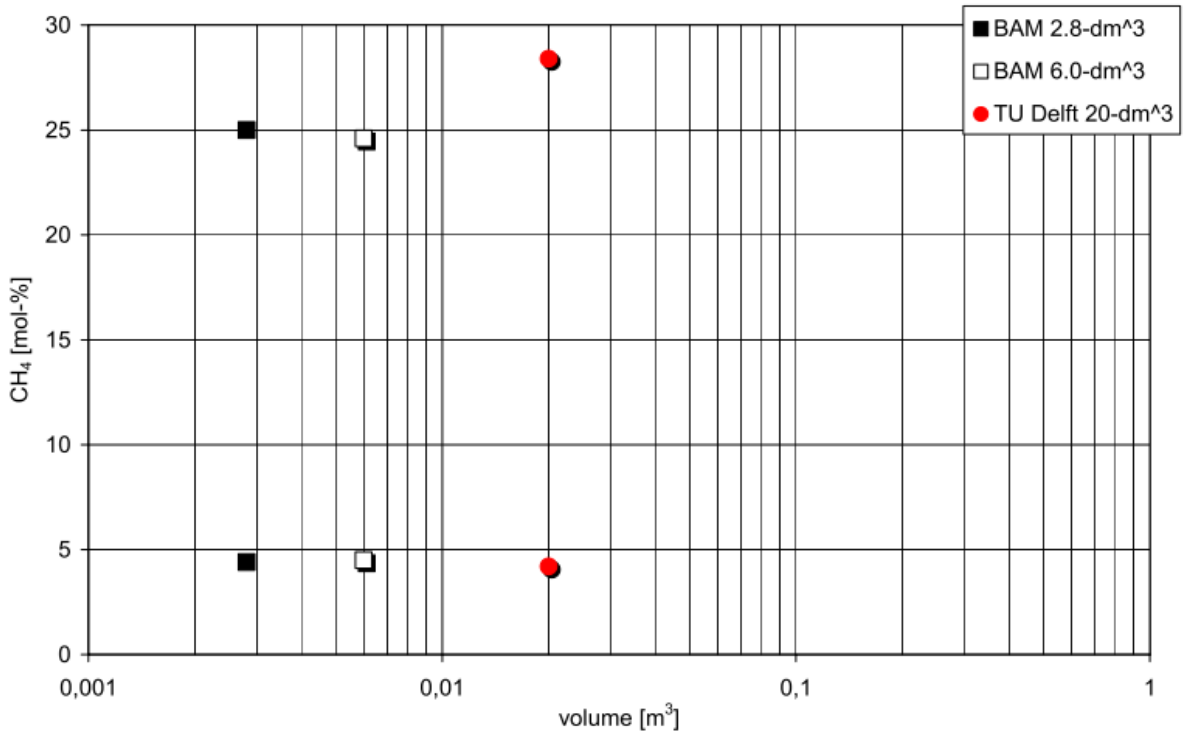

Figure 4: Volume dependence of the explosion limits of methane/air mixtures at P = 10 bar; T = 200 ◦C (Holtappels 2006)

2.3.2 Ignition Criteria Dependent Studies

De Smedt et al. (1999) along with Cashdollar et al. (2000) are also significant studies in that they investigated the effect of different ignition criteria on the flammability data. De Smedt et al. initially used a pressure rise criterion of 7% to validate the data, as suggested by the standard ASTM E918, but when comparing the results from both the glass tube and the pressure resistant vessel, ultimately concluded that a 2% pressure rise allowed for an agreement of the flammability data collected. Cashdollar et al. also compared different ignition criteria in addition to different sized test vessels. It was shown that the lean flammability limits for methane and propane were consistent, regardless of which ignition criterion was used (e.g. visual flame propagation, 3% pressure rise, 7% pressure rise); however, the results for hydrogen varied significantly based on a different criterion.

Miao et al. (2011) presented a comprehensive review of published flammability data for pure methane and pure hydrogen, making sure to include the details of the apparatus size, type and ignition criteria. Conclusions drawn from this study were similar to that of Cashdollar et al. in that the variations in the lower flammability limits for methane varied due to different choice of ignition criteria – albeit minimal – and that the lean limits for hydrogen were highly dependent on the ignition criterion. Most recently, Tschirschwitz et al. studied the influence of different ignition criteria on the explosion limits for methane, propane, n-butane, hydrogen, ammonia and acetone at non-atmospheric conditions (Tschirschwitz et al. 2015). Different ignition criteria are mentioned, such as temperature rise, analysis of typical reaction products, and mathematical analyses of the pressure-time curve; however, Tschirschwitz conducted tests using the most commonly cited criteria, namely flame detachment, flame propagation and percent pressure rise. This study is one of several key studies concerning the determination of flammability limits at

elevated conditions and provide useful data that will be evaluated directly in this study, but the lack of insight provided for the effect of different mixture compositions confirms the motivation for the aim and scope of the current study.

2.3.3 Conditions of Use Dependent Studies

The previously mentioned studies investigate the first two main parameters that influence the limits of flammability, however, the resulting data are largely relevant for only ambient conditions. Flammability studies that address elevated conditions are limited, and ones that also investigate mixtures of two or more combustibles even more so.

Mixtures at Ambient Pressures and Temperatures

Karim et al. investigated the effect of hydrogen addition on the flammability limits of carbon monoxide, methane, propane and ethane (Karim et al. 1985). In this study, the influence of initial temperature was also investigated, however, for the sake of relevance to the current study, the temperatures investigated were below ambient and therefore do not meet the "elevated" condition. The motivation for the Karim study was to understand the effect of fuel mixture composition on the flammability limits, an area of interest that would greatly benefit from further examination. Pahl measured the lower and upper flammability limits of methane/hydrogen/air mixtures in a closed cylindrical bomb (Pahl 1994), while Liao et al. studied the flammability limits for methane and natural gas mixtures in air (Liao et al. 2005). These two studies were motivated by the diversity of possible future fuels that are composed of two or more components. Hydrogen addition is a prevalent research area of interest, especially when treating it as a supplement for low-BTU methane or natural gas mixtures.

In addition to alternative fuels that include hydrogen, it is common to encounter combustibles such as methane or natural gas that are "contaminated" with diluents such as carbon dioxide (CO_2). Gant et al. addresses this contamination of hydrocarbon fuels and seeks to characterize the influence of CO_2 addition to hydrocarbon mixtures (Gant et al. 2011). Hu et al. investigates the flammability limits of oxy-methane mixtures, with the goal of characterizing the flammability range for mixtures that effectively replace nitrogen in the air with another diluent, CO_2 (Hu et al. 2014). Removing nitrogen from the oxidizer during combustion can be vital for decreasing the amount of nitrogen oxides produced from typical industrial use of fossil fuels. Another reason for studying the effects of diluent concentration when determining flammability limits is to support measures for explosion suppression. Wang et al. specially address this issue and determine the explosion characteristics of methane and air mixtures with increasing concentrations of N_2/CO_2 (Wang et al. 2014).

The following subsections summarize the literature most relevant to the current study, as they explore the flammability characteristics of various fuels and fuel mixtures at elevated initial temperatures and pressures.

Pure Fuels at Elevated Pressures and Temperatures

Relevant studies corroborate the distinct dependence of temperature and/or pressure on the flammability limits of common combustibles. Zlochower investigated the flammability limits of methane, ethylene, dimethyl ether and carbon monoxide individually, with respect only to temperature dependence up to 100 °C (Zlochower 2012). The expected result of the widening of the flammable range (increase of upper limit, decrease of lower limit) is confirmed. Other studies show the dependence of both temperature and pressure on the limits of flammability, but only across a small range of values. Liu & Zhang investigated the influence of initial pressure and

temperature on the flammability limits of hydrogen, however the maximum pressures and temperatures were only 4 bar and 90 °C, respectively (Liu & Zhang 2014). Their investigation confirmed the decrease of the lower flammability limits of hydrogen with increasing initial temperature and pressure. Mitu et al. characterized the flammability range of ethane-air mixtures at elevated conditions by studying the normal burning velocity and propagation of speed in the mixture (Mitu et al. 2015). Similar to the Liu study, the maximum initial pressure and temperature are miniscule, 1.3 bar and 150 °C, respectively. Two more studies that investigate the influence of pressure and temperature on the flammability limits are Pekalski & Pasman who determine the flammability limits of *n*-butane-oxygen and C1-C2-oxygen at pressures up to 16 bar, and temperature up to 230 °C (Pekalski & Pasman 2009); as well as Tschirschwitz et al. (2015) who studied the flammability limits of methane-air and hydrogen-air mixtures, with pressures up to 175 bar, and temperatures up to 150 °C. This study presented an increase (decrease) of the lower (upper) explosion limit for methane-air mixtures with increasing pressure, contrary to related literature and the developed theoretical hypotheses.

The SAFEKINEX (SAFe and Efficient hydrocarbon oxidation processes by KINetics and Explosion eXpertise) program supported by the European Union published a comprehensive report on explosion limits of methane, hydrogen and propylene at elevated pressures up to 20 bar and temperatures up to 200 °C (Holtappels 2006). This report provides valuable data for comparison with flammability data of the current study for single fuel-air mixtures (e.g. methane-air, hydrogen-air). Similar to Tschirschwitz (2015), Holtappels confirms the increasing trend of the lower flammability limit with increasing initial pressure, especially for hydrogen-air mixtures. Van den Schoor has actively researched the influence of pressure and temperature on flammability limits, including a study on the upper explosion limit of lower alkanes and alkenes at elevated

pressures up to 30 bar and temperatures up to 250 °C (Van den Schoor & Verplaetsen 2006). The insight regarding the effect of elevated conditions on the upper flammability limit provided by Van den Schoor will be beneficial as it can be also be extended to the lower flammable limits associated with the current study.

Mixtures at Elevated Temperatures

The literature review of this subsection are pertinent to understanding the effects of increasing only the initial temperature for determining the flammability limits of certain mixtures of gases. It is evident that the data in this area are scarce due to the few key studies available up to the time of the writing of this review.

Hustad studied the temperature dependence on the lower flammability limits of methane, butane, hydrogen, carbon monoxide, in addition to mixtures of these gases, performed at temperatures up to 450 °C (Hustad 1988). The limits for each gas were found to decrease linearly with increasing temperature as expected, and a mixing rule for estimating the flammability limits of the mixtures was suggested. Wierzba has conducted multiple studies on the flammability limits of gas mixtures at elevated temperatures, especially those involving hydrogen. Wierzba & Ale investigated the rich flammability limits of fuel (methane, ethylene, propane) mixtures involving hydrogen at elevated temperatures up to 350 °C (Wierzba & Ale 2000). Le Chatelier's Rule for estimating the flammability limits of multi-component gases agreed well at elevated temperatures, however, it was not accurate if the hydrogen concentration exceeded 70%. The following year, Wierzba & Kilchyk published a study on the flammability limits of hydrogen-carbon monoxide mixtures at moderately elevated temperatures (Wierzba & Kilchyk 2001). A key result in this study showed that the lean flammability limits of the mixtures in question obeyed Le Chatelier's Rule over the entire range of temperature considered when the corresponding individual limit values of

the components were employed; however, the rich flammability limits deviated very significantly from the corresponding values calculated using this rule, especially for mixtures containing small concentrations of hydrogen. The results regarding the effect on hydrogen concentration on the accuracy of Le Chatelier's Rule for estimating the flammability limits was also substantiated further in a later study for mixtures containing hydrogen, carbon monoxide and methane in air at initial temperatures up to 300 °C (Wierzba & Wang 2006).

In addition to the motivation of flammability studies to support safe utilization of alternative fuels at elevated operating temperatures, explosion prevention of these gas mixtures as they may occur in industrial applications is also of particular importance. Van den Schoor et al. determined the flammability limits of hydrogen/carbon monoxide/nitrogen/air mixtures at elevated temperatures up to 200 °C (Van den Schoor et al. 2009). The upper limits of flammability decreased with increasing amount of nitrogen, which is expected as it is a diluent, however the influence of added diluent on the lower flammability data was inconclusive. Grune et al. studied the flammability limits for multi-component (CO-H_2)-O_2-(H_2O-CO_2-N_2) mixtures at elevated temperatures of 170 °C and 250 °C (Grune et al. 2015). Similar to the previous study, an increase of the inert gases such as nitrogen and water vapor decreased the flammable range of the hydrogen/carbon monoxide mixtures, however, this study limited the hydrogen concentration to a maximum of 3% which may not be useful for comparisons with the present study.

Mixtures at Elevated Pressures and Temperatures

The aforementioned flammability studies conducted at elevated pressures and temperatures provide important knowledge as well as a foundation for the current study; however, none of these studies provided flammability data for gas mixtures at these elevated conditions. Two notable studies were found that determined the limits of flammability for gas mixtures at elevated

temperatures and pressures. It is clear that further investigations are necessary in order to support and complement the scarce, yet significant contributions in this area of research.

The first of these studies was conducted by Ale et al. and was motivated by the possibility of explosion hazards at process conditions when the atmosphere was affected by trace mixtures of ammonia, hydrogen and methane (Ale et al. 1981). These experiments were conducted at initial temperatures up to 150 °C, which is lower than most elevated temperature studies, and initial pressures up to 175 bar, much higher than the majority of elevated pressure studies. The paper concluded that the flammable regions found at these elevated conditions did not vary much from a previous study for mixtures of ammonia and hydrogen, yet the range was remarkably wider than for ammonia alone (Figure 5). The author contributes this deviation as having to do more with the inclusion of hydrogen at the elevated conditions.

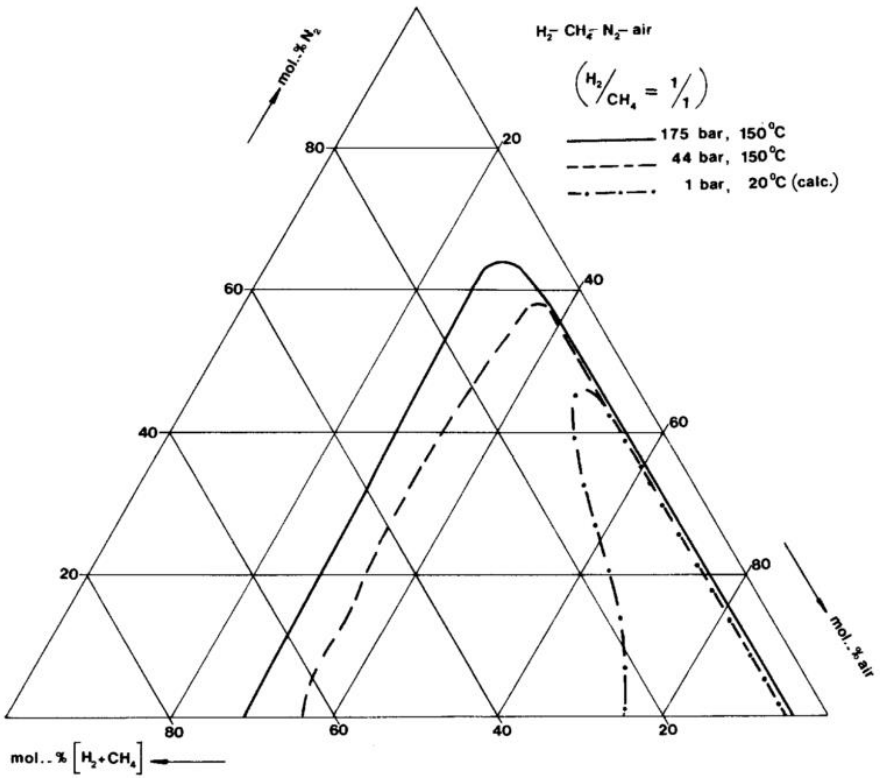

Figure 5: The limits of flammability of a mixture of H2 and CH4 = 1/1 in air and nitrogen, under atmospheric conditions, and at 150 C, and 4 and 175 bar (Ale et al. 1981)

The second study was conducted by Van den Schoor and was motivated by the fact that many industrial processes involve mixtures of combustible gases with oxidizing gases at elevated pressure and temperatures (Van den Schoor 2007). In this report, the author provided a comprehensive theoretical background for the determination of flammability limits and the experimental methods used for obtaining the data presented. Methane, ethane, propane, n-butane, and hydrogen were the gases studied, and methane/hydrogen was the only gas mixture for which flammability data was reported. Van den Schoor focuses primarily on the influence of temperature and pressure on the upper explosion limit and so the data provided for gas mixtures are for various concentration of methane/hydrogen at initial temperatures up to 200 °C and initial pressures up to 10 bar. As hypothesized and as shown in Figure 6, the upper explosion limit increased with increasing concentrations of hydrogen, as well as with increasing initial pressures and temperatures.

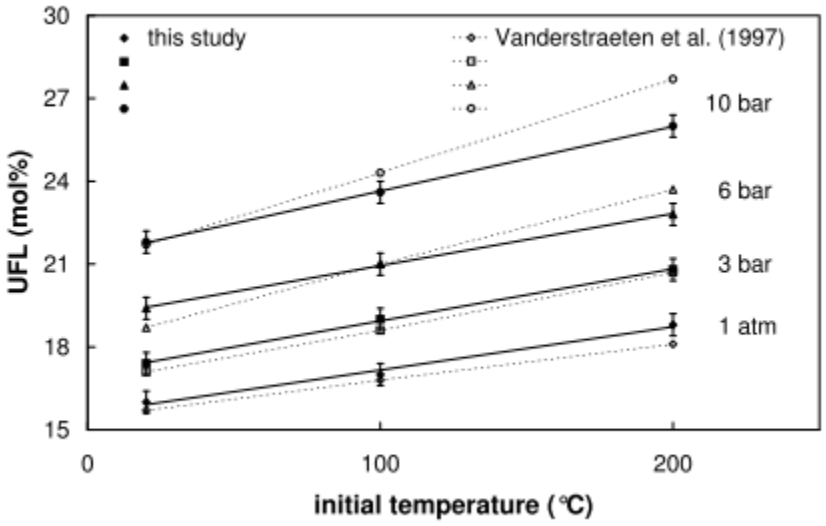

Figure 6: Temperature dependence of the UFL of methane/air mixtures (Van den Schoor 2007)

2.3.4 Summary

Although the standardization provided by the U.S. Bureau of Mines, DIN 51649, ASTM E681 & E918, and EN 1839 have allowed for a significant amount of flammability data to be collected, there is still a lack of agreement over an ideal apparatus and suitable ignition criterion. It is significant to note that ASTM E918 remains the only reliable standard for the determination of flammability limits at elevated conditions, however it is not as widely referenced in the literature due to a lack of studies performed at elevated temperatures and pressures. The majority of flammability data are found at atmospheric conditions therefore it cannot be applied to combustibles at elevated initial conditions. Le Chatelier's law provides a rule for estimating the flammability limits of gaseous mixtures, however experimental data show deviation at elevated conditions and for mixtures containing significant amounts of hydrogen. The literature review presented is representative of the limited amount of flammability studies at elevated conditions for gaseous mixtures, although the available experimental results at these conditions provide important data for validation of the experimental methods in the current study. The purpose of this thesis research is to address this lack of flammability data at elevated conditions of temperature and pressure for various gaseous mixtures, as well as to definitively determine the effect of these conditions of use on the lower limit of flammability. The next section will outline in more detail the approach and key objectives necessary for achieving this purpose.

3 APPROACH

Before proceeding, it is important to revisit the research scope and objectives with the benefit of the background and context provided in Chapter 2, and outline the tasks, each of which maps to one of the objectives for the study.

3.1 TASK 1: DEVELOP A TEST APPARATUS

A suitable device that best matches those found in pertinent standards and other flammability studies is necessary for use in the determination of lower flammability limits (LFLs) of combustible mixtures at elevated initial conditions.

This first objective is supported by the choice of a vessel that has been used considerably in the literature, and/or is standardized as an appropriate experimental setup for the determination of the flammability limits of gaseous mixtures. In the preceding chapter, the various shapes and sizes of test vessels as well as different ignition criteria were summarized as they appear in the literature. The first thing to note is how the conditions of use affect the choice of the test apparatus. It is widely suggested that using a visual flame propagation criterion is the most reliable for the determination of the limits of flammability, and this is the criterion widely chosen for "flammability tube" experiments (Schröder & Molnarne 2005; Tschirschwitz et al. 2015). As studies investigate the limits of flammability at elevated conditions, pressure resistant test vessels are necessary to use and a pressure rise ignition criterion is used as visual flame propagation is often not possible or practical. Standards such as ASTM E918 (1983) and EN 1839 (2003) suggest metal pressure vessels or "bombs" that are rated to withstand high temperatures and large explosion pressures. The experimental setup developed for the current study is initially based on the setup proposed by the American standard ASTM E918 (1983), as E918 is the only current standard that specifies elevated temperature and pressure testing conditions. A detailed description

of the process for choosing the test apparatus, as well as the features of the final experimental setup can be found in Chapter 4: Methods.

3.2 TASK 2: DETERMINE LFLS EXPERIMENTALLY

The lower flammability limits of varying mixtures of methane/hydrogen (CH_4/H_2), methane/carbon dioxide (CH_4/CO_2) and hydrogen/carbon monoxide (H_2/CO) at initial pressures up to 9 bar and initial temperatures up to 200 °C will be found experimentally using the test apparatus.

This second objective follows directly after the development of the experimental setup. First, a matrix of all test parameters will be developed, based on existing elevated flammability data, which will describe the various combinations of binary fuel mixtures, initial test pressure and initial test temperature. Second, an ignition criterion will be necessary to establish the limits of flammability; however the choice of a suitable ignition criterion is not straightforward as it varies from study to study as well as from standard to standard. With respect to percent pressure rise of the initial mixture pressure, ASTM E918 advises use of a 7% pressure rise criterion, while EN 1839 B suggests a 5% pressure rise; comparison of these unique criteria is necessary. Previous studies have compared different pressure rise criteria (e.g. 1%, 2% and 3%), and have also attempted to determine a relationship with visual flammability data (Van den Schoor 2007; De Smedt et al. 1999; Cashdollar et al. 2000). Lower values for percent pressure rise have been preferred over higher values in terms of consistency, especially the ASTM E918 value of 7%, and so the current study will evaluate the variation in flammability data collected and will comment on the influence of the specific criterion. It should be noted that most of the studies that suggest certain ignition criteria, although important to consider, may not be applicable as they were conclusions from flammability tests performed exclusively at ambient conditions. With the test

parameters and choice of ignition criterion in place, lower flammability tests are performed and the measured data are collected and processed. Chapter 4: Methods provides a detailed review of the test procedure while Chapter 5: Results and Discussion summarizes the lower flammability data collected experimentally.

3.3 TASK 3: DETERMINE LFLS NUMERICALLY

Laminar flame propagation will be modeled in CHEMKIN in order to simulate limits of flammability at the experimental test parameters, and the numerical results will be compared with the experimental results.

In parallel with Task 2, this objective will be met by calculating the flammability limits numerically for the same experimental test parameters that are investigated. This task involves solving the fundamental energy equation as well as including the chemical kinetics involved with the relevant reaction mechanisms for the fuel mixtures. With the help of CHEMKIN combustion simulation software, a premixed laminar flame speed model is set up that can calculate the flame speed at different equivalence ratios, which is used to determine flammability limits based on the convergence of a solution to the governing equations. The benefits of a numerical analysis are increased when these results are evaluated alongside the results from the experimental approach. Numerical simulations in this manner not only allow for the determination of the flammability limits at the previously mentioned test parameter combinations, but can also be extended beyond the constraints of the experimental setup as well as the time constraints associated with experimental procedures. Although these results may seem exact or accurate, they are only significant when considered in the same context of the acquired experimental results. Similar to Task 2, a detailed review of the procedure for calculating the limits of flammability numerically is

provided in Chapter 4: Methods, while a summary and discussion of the resultant flammability data can be found in Chapter 5: Results and Discussion.

3.4 TASK 4: VALIDATE RESULTS WITH LITERATURE DATA

Available flammability data for the previously mentioned pure fuels and renewable gaseous fuel mixtures at elevated temperature and pressure will be compared with the flammability data determined in this study; also, flammability limits calculated using predictive methods (e.g. Le Chatelier's Law) will also be evaluated.

This objective serves to evaluate the overall accuracy of the flammability data collected in Tasks 2 and 3, and also is necessary for confirming the temperature and pressure dependence on the flammability limits observed in the current study relative to past studies. Two of the three key experimental studies that were referenced when determining the experimental parameters provide flammability data for pure methane and/or pure hydrogen at elevated temperatures and pressures (Holtappels 2006; Tschirschwitz et al. 2015). The third of these studies also investigated the flammability limits of CH_4/H_2 mixtures at elevated conditions, however lower flammability data for these mixtures were not made available (Van den Schoor 2007). All other studies discussed in Section 2.3: Literature Review offer flammability data for either only pure fuels or fuel mixtures at atmospheric conditions, or for gas mixtures at elevated temperatures only. These published values will be important for defining the lower flammability limits for each test mixture at atmospheric conditions, as well as for conditions of elevated temperatures.

With respect to the flammability testing of gaseous mixtures, pertinent literature typically suggests the use of Le Chatelier's law as a predictive method for the determination of these limits. This rule has been used extensively in the literature and has been confirmed to be accurate,

however, only at standard conditions for temperature and pressure. Additionally, it has been suggested by many authors that the presence of hydrogen in a gaseous mixture causes deviation in the effectiveness of Le Chatelier's law, and so this area of study will be important to comment on (Ale et al. 1981; Wierzba & Kilchyk 2001; Law 2006). Along with all experimental and numerical results of the current study, Chapter 5: Results and Discussion will also include a comparison of these results with published flammability data as well as comments regarding the accuracy of determining the lower flammability limit using simulation and predictive methods.

3.5 TASK 5: PROPOSE A REVISED STANDARD

An optimal test apparatus and ignition criterion, inter alia, for the determination of flammability limits at elevated conditions will be suggested consistent with the conclusions from this study.

Finally, this objective concludes the study by proposing revisions to the standard for the determination of the limits of flammability that was initially used as a basis for choosing the experimental setup in Task 1 (ASTM E918 1983). Suggestions for changes will concern the test vessel size, ignition criterion, specific auxiliary components, amount of ignition energy, as well as other minor modifications. This effort will not directly support the goal of this research, but will seek to promote the reliability of published flammability data in the scope of this study by addressing inconsistencies across the existing standards and recommending an optimal experimental approach for determining the limits of flammability. The revised ASTM E918 standard is proposed in more detail in Section 6.3: Recommendations.

4 METHODS

The next section will introduce the specific experimental and numerical methods used to determine the lower flammability limits of methane, hydrogen, carbon monoxide, in addition to mixtures of these gases (i.e. CH_4/H_2, H_2/CO, and CH_4/CO_2) in air, at elevated initial temperatures and pressures. In order to support the key research objectives presented in Chapter 3: Approach, each method will include a description of how the experimental/numerical setup was developed, as well as the test procedures that were used for collecting the results.

4.1 EXPERIMENTAL METHODS

4.1.1 Experimental Setup

The experimental setup used in this study was initially modeled after the suggested setup and conditions provided by ASTM E918 (1983). The test vessel chosen is required to have a volume of no less than 1 liter and a minimum inside diameter of 76 mm (3 in.). The apparatus also needs to be rated to a maximum pressure of 20.68 MPa (3000 psi) in order to be used for mixtures at initial pressures up to as much as 1.38 MPa (200 psia). The specific test vessel chosen was a HOKE sampling cylinder constructed of 304 stainless steel, with a 3.5 in. diameter and equipped with two ½" female NPT connections. Variations to the suggested experimental setup provided by ASTM E918 were considered in order to simplify the procedure for flammability testing while ensuring consistent results. The standard recommends adding three ½" NPT female pipe connections in addition to the two existing ones, but it was decided to only add one (for the spark ignitor) for the above reasons. It is important to compare the comment on the shape and size of the test vessel chosen with those from similar studies. The vessel chosen for this study is again based on the ASTM E918 standard. The standard states that measured limits of flammability are influenced by flame-quenching effects of the test vessel walls. The vessel described in the standard

is suitable for use with most mixtures at elevated temperatures and pressures. However, for certain amines, halogenated materials, etc., which have large ignition-quenching distances, tests may need to be conducted in larger diameter vessels (ASTM E918 1983). Studies such as Liao et al. (2005) and Miao et al. (2011) used relatively small pressure resistant vessels (1.57 L and 5.34 L) while also comparing their results with flammability data of larger vessels and different ignition criteria. Holtappels (2006) concluded there is minimal volume dependence on flammability limits, especially at the lean explosion limit. With respect to the stated research objectives of this study, the test vessel chosen is suitable for the determination of the lower flammability limits of the gaseous mixtures in question.

The spark ignitor was chosen according to the ASTM E918 standard as a Champion FI21501 spark plug that would be fitted in the lower half of the cylinder and extending inside to reach the vertical centerline of the test apparatus. The spark ignitor receives power from a Jefferson/Magnetek M9409 ignition transformer, type single spark. ASTM E918 suggests that energy to the ignitor should be supplied by an isolating transformer rated at 500VA at 115 V. This recommendation is flexible as some ignitors may be rated at slightly different voltages and power capacities. The Jefferson/Magnetek ignition transformer used for this experimental setup is rated at 250 VA with 120 V and 60 Hz on the primary side, and 10,000 V and 23 mA on the secondary side directly connected to the ignitor. The key parameter for determining the amount of ignition energy provided would be the amount of time the transformer is energized, as that would determine the amount of Joules provided to the fuel-air mixture. ASTM E918 does not specify an amount of time to energy the transform but the standard for atmospheric standards (ASTM E681 1985) specifies spark duration to be between 0.2 and 0.4 seconds. For these time intervals, and considering the rating of the transformer in this standard to be approximately 450 VA, the range

of energy provided is 90 – 180 Joules. Although the European standard EN 1839 is only for flammability testing at atmospheric conditions, for comparison, the amount of ignition energy suggested is in the range of 10 – 20 Joules (EN 1839 2003). Various studies reference this standard and use this range for ignition energy including Van den Schoor (Van den Schoor & Verplaetsen 2006; Van den Schoor et al. 2009) who specify providing 10 Joules in 40 ms, and Cashdollar (Cashdollar et al. 2000) who provide ignition energy at around 17 Joules. The ranges of ignition energy provided by ASTM E681 and EN 1839, although significantly different, fall above the threshold for ignition source strength dependence as discussed in US BOM Bulletin 627. Below approximately 1-2 Joules, the limits of flammability are reduced to limits of ignitibility which are dependent on the amount of ignition energy provided. For example, a 0.2 mJ spark is inadequate to ignite even a stoichiometric mixture at atmospheric pressure and 26°C (Zabetakis 1965). Considering the literature only specifies amount of ignition energy for the foregoing atmospheric studies, a range for ignition energy can be independently suggested for flammability testing at elevated temperature and pressure conditions. To consistently avoid approaching the region of ignitibility limits rather than flammability limits at the various pressures investigated in the current study, the suggested amount of ignition energy strength was chosen to more closely match with the American ASTM E681 standard. Spark duration was kept consistently in the range of 0.4 and 0.8 seconds to ensure an ignition energy strength range of 100 – 200 Joules at the rated ignition transformer power of 250 VA.

The thermocouple chosen for temperature measurements was an Omega TJ36-CAIN type-K thermocouple with a diameter of 1/16” inch in order to provide a more rapid response. The choice of an accurate pressure transducer was key as the initial ignition criterion to be used was a small percentage pressure rise with respect to the initial mixture pressure. For the atmospheric

testing, it was beneficial to have a transducer with an accurate resolution at lower pressures. The Phidget 1140 absolute air pressure sensor was chosen for its range of 20 kPa (2.9 psia) to 400 kPa (58 psia) and 413 Pa (0.06 psia) resolution. The Phidget transducer operates in-line with an Arduino UNO board to allow for data acquisition and logging. Each gas component (i.e. air, methane, nitrogen) is added manually using the method of partial pressures to prepare each test mixture.

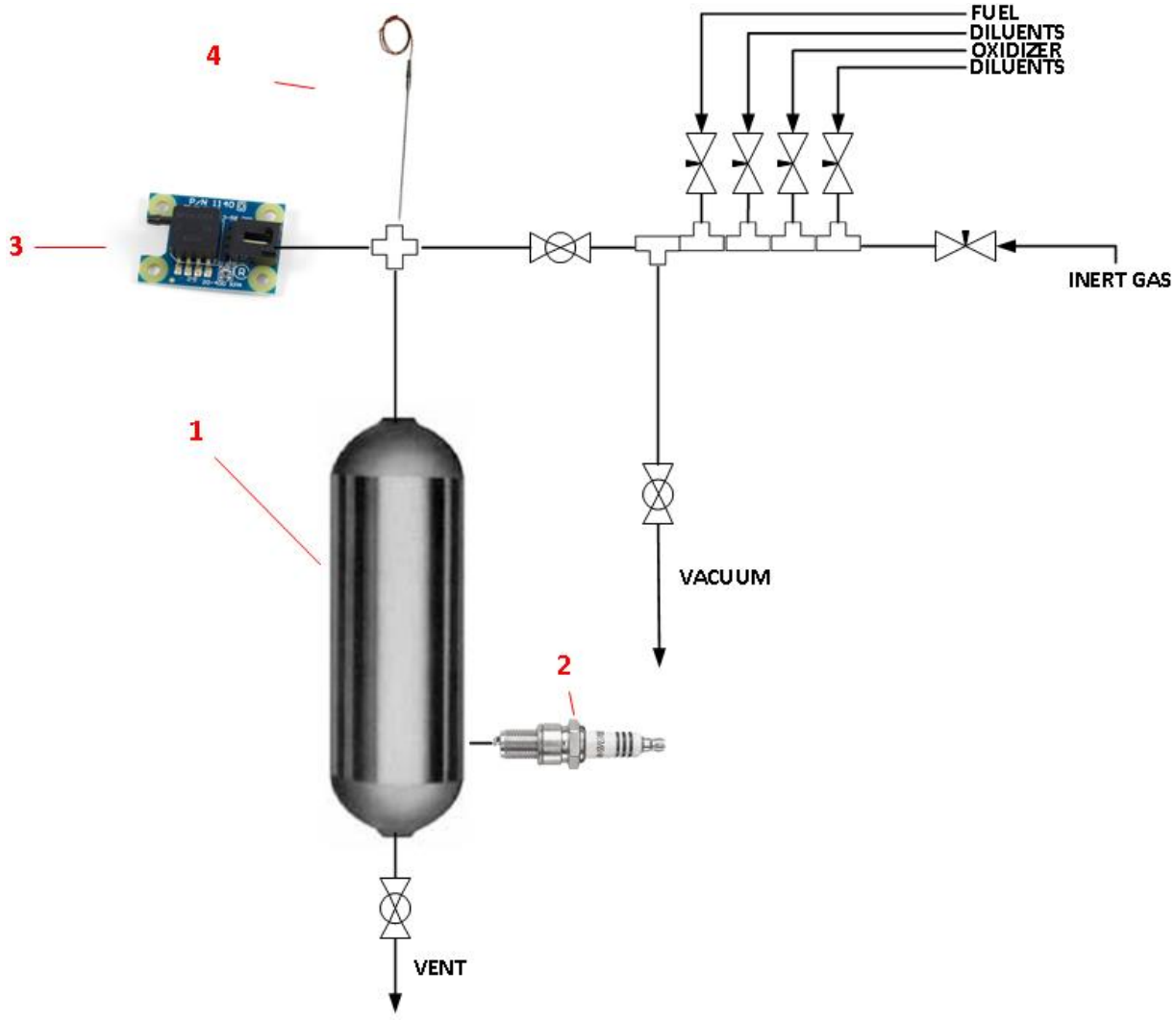

Figure 7: Preliminary experimental setup for atmospheric testing including (1) One-liter stainless steel cylinder; (2) Champion spark plug; (3) Phidget pressure transducer; (4) Type-K thermocouple

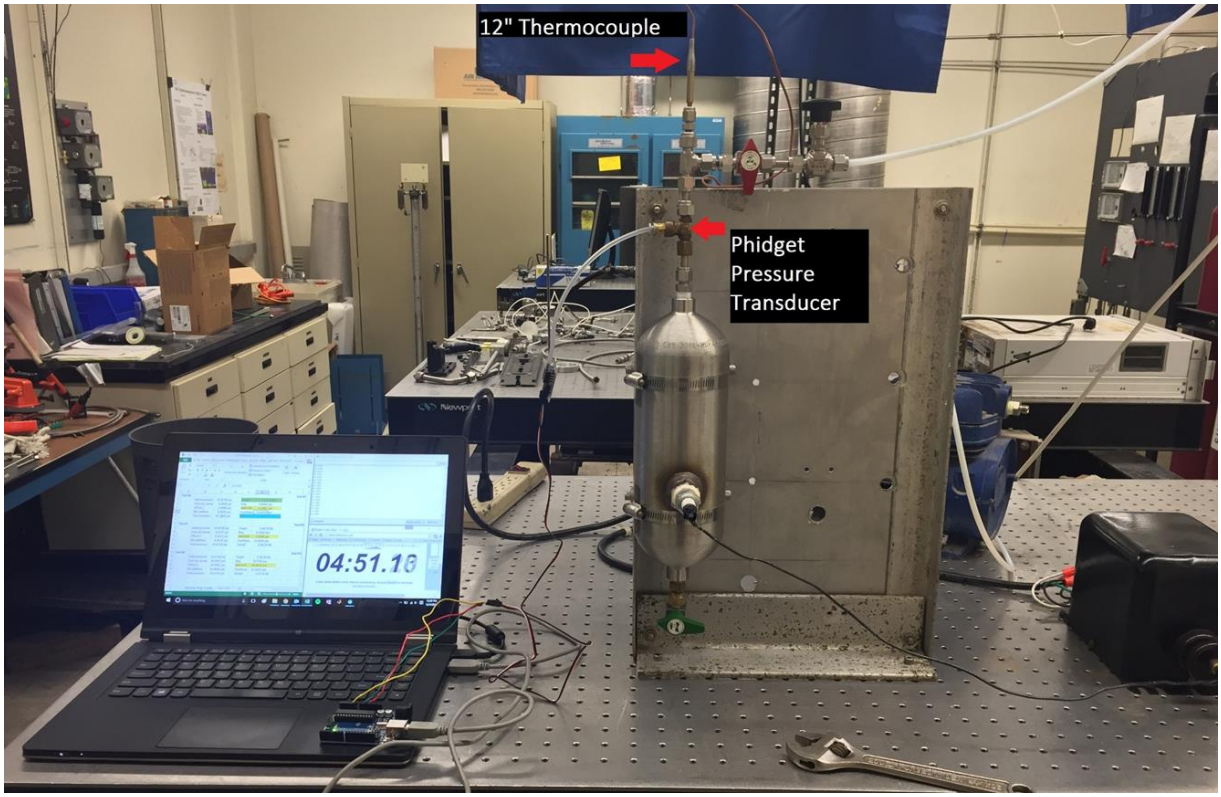

Figure 8: Preliminary setup for the determination of flammability limits at atmospheric conditions

Altogether, these first components were assembled and were used to provide the baseline testing under atmospheric conditions. Figure 7 and Figure 8 shows the atmospheric setup which was used to confirm the preliminary lower flammability limits for natural gas and methane, individually and separately.

According to ASTM E918 (1983), a combustion reaction that produces at least a 7% rise of the initial absolute pressure is said to have propagated a flame. The 7% rise in pressure corresponds to 1 psia (0.007 MPa) per atmosphere of initial pressure. Many studies have used this ignition criterion, but usually only for comparison with other values for percent pressure rise or different ignition criteria (De Smedt et al. 1999; Cashdollar et al. 2000; Liao et al. 2005). The bomb method discussed in EN 1839 (2003) suggests a pressure rise of 5%, while a study such as

De Smedt et al. (1999) concludes an even smaller pressure rise of 2% is more suitable with respect to matching flammability data determined by a pressure rise criterion and data determined using a visual propagation criterion. Tschirschwitz et al. (2015) claims the 7% pressure rise criterion suggested by ASTM E918 corresponds the least with flame detachment, and therefore gives impractical flammable ranges. While the optimal value for percent pressure rise seems to be less than 5%, Schröder & Molnarne (2005) maintain use of a pressure rise criterion of 2% or lower is too sensitive and difficult to interpret, because the ignitor does not only cause a pressure increase itself by heating the surround gas, but also by triggering local burning of the mixture. Despite this argument, Van den Schoor & Verplaetsen (2006) use a 1% pressure rise ignition criterion as they conclude that the pressure increase caused by the ignitor is important only at low pressures. For the current study and considering the stated research objectives, the lack of agreement on a suitable ignition criterion suggests further investigation and comparison of common values for percent pressure rise. Limited flammability data available at elevated conditions as well as the difficulty of using a test vessel to observe flame propagation will provide a challenge when seeking an optimal ignition criterion; however, the importance of using various ignition criteria and commenting on the resultant effects on the lean flammability limit should not be overlooked an is discussed further in the following test procedure section.

Modifications were necessary to prepare the experimental setup for possible conditions of use up to 13.8 bar (200 psia) and 200 °C. In order to allow the complete system to tolerate the high pressure testing, the pressure transducer was replaced with an Omega high pressure (HP) PX41T0 0-300 psig (~20.7 bar) pressure transmitter. A LabVIEW virtual instrument (VI) program was developed to display measurements and collect data from both the Omega thermocouple and now the Omega HP transmitter.

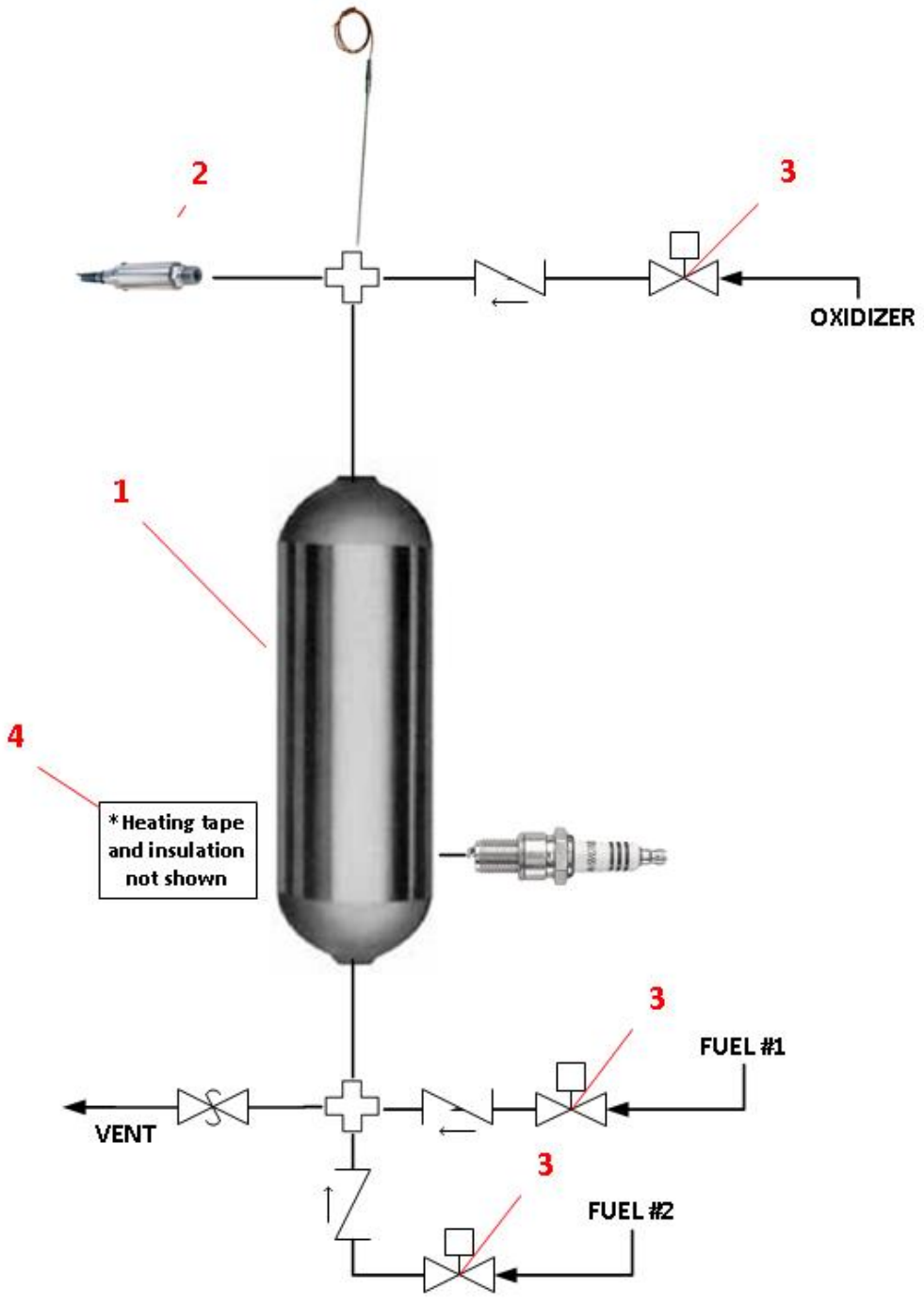

Figure 9: Modified experimental set up for elevated conditions (1) One-liter stainless steel cylinder; (2) Omega high pressure transmitter; (3) Powered solenoid valves; (4) Silicone rubber heating tape

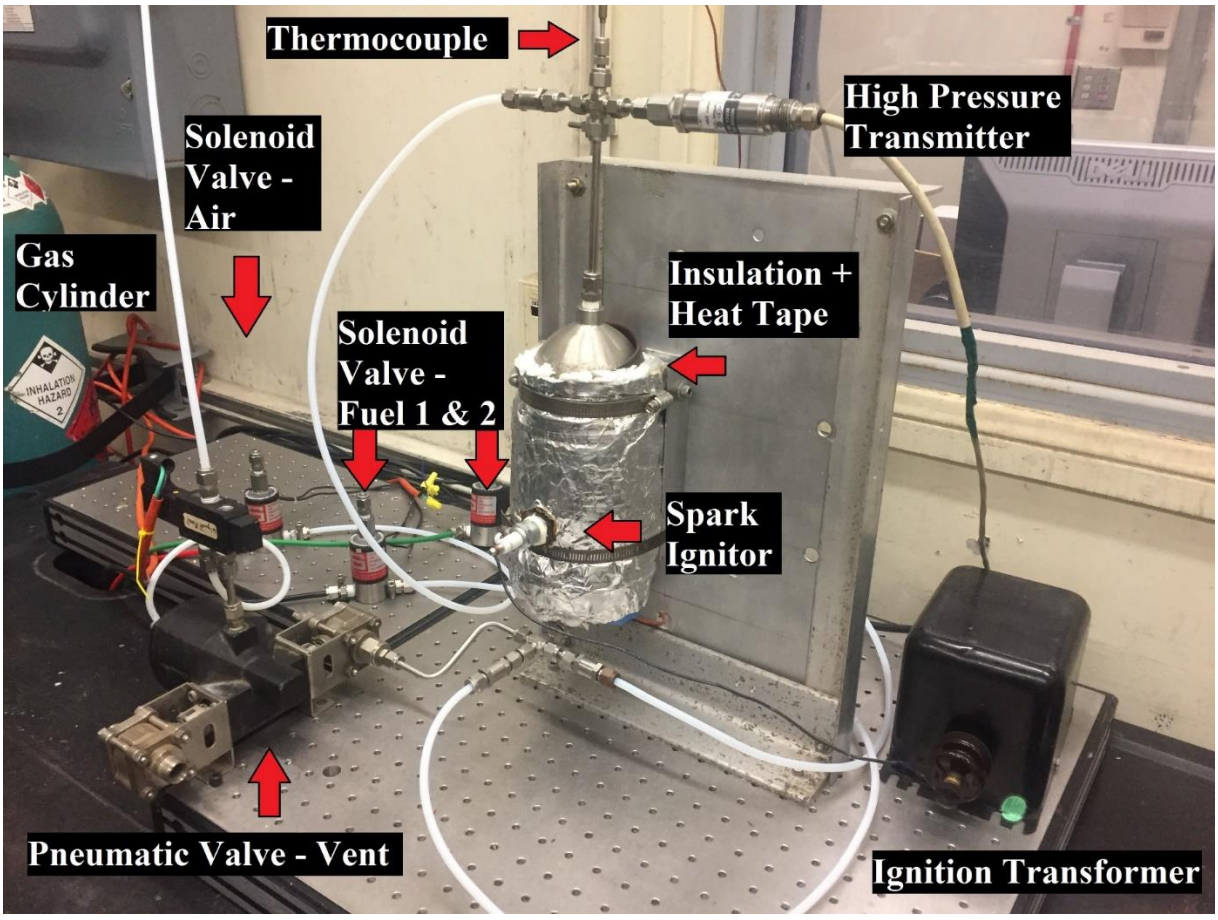

Figure 10: Final setup for the determination of flammability limits at elevated temperatures and pressures

Instead of the manual addition of the gas components, it was determined to use Schrader solenoid valves to ensure remote yet accurate partial pressure addition. The desire to operate the valves remotely is to ensure safety during each test, especially for higher pressure procedures. The addition of remote ignition of the cylinder was also considered not only to also ensure safety but to also be able to quantify the amount of ignition energy provided. It was necessary to add a check valve after the installation of each solenoid valve (one for the first fuel component, one for the second fuel component, and one for air) so as to prevent the backflow of gaseous components during partial pressure addition. Finally, BriskHeat BS0 silicone rubber heating tape was chosen as it was suitable for electrical conductive surfaces such as this application, and would allow for

maximum exposure temperatures up to 230°C. The final experimental setup for elevated conditions can be seen in the schematic above (Figure 9) and photograph above (Figure 10).

4.1.2 Experimental Fuels and Fuel Blends

After final modifications, the experimental setup was ready for testing to determine the lower flammability limits of various fuels and mixtures of fuels. The pure fuels in question were primarily methane and hydrogen. Initially, natural gas was considered as an alternative or additional fuel, however, the variability of the concentration was an undesirable factor which led to its exclusion in the current study. The rationale for testing pure methane and pure hydrogen was that these gaseous fuels are the most common fuels derived from biomass or other renewable resources. The first fuel blend is a varying mixture of methane and hydrogen, often referred to as hydrogen-enriched methane or hythane. The other two fuel blends are referred to as biogas (methane/carbon dioxide, CH_4/CO_2) and syngas (hydrogen/carbon monoxide, H_2/CO); to emphasize, these simulated biogas and syngas fuels refer to fuel mixtures that are derived from renewable resources.

The pure fuels and fuel blends tested for the experimental investigation of the lower flammability limits were prepared using gas cylinders of at least 99.3% purity. The supply of hydrogen (H_2) was Pre-Purified Grade 4.0 with a purity of 99.99%, while methane (CH_4) was chemically pure (CP) Grade 2.5 with a purity of 99.5%, and finally carbon monoxide (CO) was CP Grade 2.3 with a purity of 99.3%.

4.1.3 Experimental Test Parameters

Defining the test parameters for the experimental approach required investigating typical compositions of biogas and syngas derived from renewable sources (Table 3), as well as

consolidating existing flammability data at elevated conditions and noting the typical range of temperature/pressure test conditions that were studied.

Biogas		Syngas	
CH_4	50-75%	CO	30-60%
CO_2	25-50%	H_2	25-30%
N_2	0-10%	CH_4	0-5%
H_2	0-1%	CO_2	5-15%

Table 3: Typical renewable gas composition; Source: www.netl.doe.gov

The above table summarizes the usual composition for both renewably-derived biogas and syngas, and mainly shows that the majority of each fuel mixture is made up of only two fuel components. For the sake of consistency when comparing all fuel blends discussed in the current study and related literature, all three fuel blends are binary fuel mixtures, that is they are composed of only two fuel components. For biogas, this simplification results in only considering methane and carbon dioxide, while syngas is "simulated" using varying amounts of hydrogen and carbon monoxide.

Table 4 summarizes the various fuel blend compositions considered for experimental testing. The binary fuel blends varied by 20% per case and extended from 0% to 100%. The red text indicates text mixtures that were not considered for one of two reasons: (1) the fuel blend mixture was redundant, or (2) the fuel test mixture was outside the scope of the typical renewable gas composition from Table 3. For example, the 100/0 case for syngas (H_2/CO) is already addressed in the 0/100 case for hydrogen-enriched methane (CH_4/H_2), while biogas compositions beyond 60% carbon dioxide are much more diluted than gaseous mixtures found naturally from biomass resources.

Methane/Hydrogen		Syngas		Biogas	
CH_4	H_2	H_2	CO	CH_4	CO_2
100%	0%	100%	0%	100%	0%
80%	20%	80%	20%	80%	20%
60%	40%	60%	40%	60%	40%
40%	60%	40%	60%	40%	60%
20%	80%	20%	80%	20%	80%
0%	100%	0%	100%	0%	100%

Table 4: Final test parameters for gas fuel mixture composition

UFL data
from Van den Schoor, F., 2007

Fuel: 100% Methane

P vs. T	20 C	100 C	200 C
1	16.0	17.0	18.8
3	17.4	19.0	20.8
6	19.4	21.0	22.8
10	21.8	23.6	26.0

Fuel: 80% Methane - 20% Hydrogen

P vs. T	20 C	100 C	200 C
1	20.2	21.4	22.8
3	22.0	24.2	26.0
6	25.0	27.6	29.8
10	28.8	32.2	33.6

Fuel: 60% Methane - 40% Hydrogen

P vs. T	20 C	100 C	200 C
1	25.6	27.2	29.6
3	28.6	31.2	34.6
6	33.2	37.0	40.2
10	38.0	42.8	44.8

LFL data
from Holtappels, K., 2006

Fuel: Hydrogen*

P vs. T	20 C	100 C	200 C
1	3.90	3.80	4.00
5	4.60	4.19	3.90
10	4.91	4.64	4.30

LFL data
from Tschirschwitz, R., 2015

Fuel: Methane*

P vs. T	20 C
1	4.90
2	5.00
5	5.30
10	5.40
20	5.40

Figure 11: Sample flammability data from key studies at elevated pressure and/or temperature conditions

Determining the test parameters for pressure and temperature required examining key literature and using the cited range of test conditions as an initial outline. Figure 11 provides a sample of some of the few flammability data available in the literature. Holtappels provided flammability limits for only pure fuels such as methane and hydrogen, and tested various test vessels at conditions of pressure up to 10 bar and temperature up to 200 C (Holtappels 2006). Tschirschwitz et al. only provided flammability data for methane at room temperature, however this study was able to investigate higher pressures up to 20 bar (Tschirschwitz et al. 2015). Van den Schoor exclusively investigated the upper flammability limit, although this study did investigate fuel mixtures (hydrogen-enriched methane only) at pressure up to 10 bar and temperatures up to 200 C (Van den Schoor 2007). Based on the elevated flammability data, the dependence of temperature on the limits of flammability is distinct but minimal in small increments. The decision was made to consider two temperature conditions which would confirm the anticipated dependence on temperature to widen the flammability limits. Regarding the choice for pressure, in order to be able to evaluate the flammability data obtained in the current study against data as shown in Figure 11, five pressure were chosen from 1 bar to 9 bar in increments of 2 bar which would be easy to compare. The final tests parameters regarding elevated conditions for a given fuel mixture for the current study are summarized in Table 5.

Pressure vs. Temperature	25 C	200 C
1 bar		
3 bar		
5 bar		
7 bar		
9 bar		

Table 5: Final test parameters for conditions of use (elevated pressure and temperature)

4.1.4 Experimental Test Procedure

The general procedure for flammability tests at atmospheric conditions was initially adopted per ASTM E918 and subsequently modified to suit the current study. Each test began by flushing each line that would carry a gas component, and also by evacuating the test vessel and manifold. A vacuum pump was used to evacuate the test vessel to a sub-ambient pressure of about 4 psia. The partial pressures method was used for the addition of the gaseous components into the experimental setup. Since these tests were in search of the lean flammability limits, the fuel component was always the first introduced into the test vessel as it was the smallest component. For example, when testing for the lower flammability limit of methane, the amount of methane added would be approximately 5% of absolute atmospheric pressure (0.735 psia) with the remaining component being the oxidizer (air). The addition of air as the last and largest component would be restricted to less than 15 seconds per ASTM E918, in order to achieve appropriate homogeneity of the test mixture. After these steps, it is important to ensure the valves nearest to the test vessel are closed as to reduce dead volume in tubing, and that the gas mixture is allowed 2 minutes to equilibrate to test conditions. Use of gas analyzers for early tests was necessary to ensure the procedure provided accurate mixtures of fuel concentration in air. The Horiba FIA-510 flame ionization detector and the Horiba FTIR gas analyzer were both used to confirm that the mixture composition procedure was completed accurately. In addition to these analyzers, a comprehensive pressure-time history would be recorded during the addition of components by partial pressures, and so post-processing of these measurements would allow for a reduction of error when adjusting the mixture concentrations. After the mixture has been allowed to mix for the prescribed amount of time, the ignition transformer is activated and spark ignition is attempted. The pressure measurements should indicate an expected pressure rise corresponding to the concentration of the test mixture, and if ignition was not successful, further ignition was attempted

and noted for further analysis. After each test, the test vessel is vented through the exhaust valve and purged with air. In this manner, the fuel concentration is decreased for every successive test until the lean flammability limit is achieved using the previously mentioned pressure ignition criteria.

The general test procedure for elevated initial pressure and temperatures was first proposed to be identical to the above procedure for the preliminary atmospheric determination of the flammability limits, although the use of the LabVIEW program allowed for a more sophisticated method of recording pressure and temperature data while also displaying real time graphs for the benefit of the researcher performing the tests. The addition of this tool has permitted an increase in accuracy when adding components by partial pressures, and has also decreased the amount of time per flammability test which is beneficial to gathering more useful data. Finally, an advantage with testing at elevated pressures includes not needing to evacuate the vessel with a vacuum pump, as well as the added benefits of safety due to separating the operator from the test vessel by use of solenoid valves. The final experimental test procedure for the flammability tests conducted at elevated conditions is given below in more detail for the experimental setup of the current study:

1. Prepare gas cylinders for fuels to be used in the tests by adjusting pressure regulators to desired pressure addition settings. Open main high pressure airline (maximum in-house capacity of 150 psia ≈ 10 bar) to 1 bar greater than the intended initial test pressure. Ensure power supply to pressure transmitter is connected. Connect and turn on high temperature heating tape 1-2 hours prior to testing if testing conditions require elevated temperatures.
2. In the control room, open LabVIEW program (see Figure 12) and ensure power is supplied to remote switches for fuel solenoid valves, pneumatic exhaust valve, and spark ignitor.
3. Before each test, evacuate the test vessel and manifold, and purge with air.

4. Select the test fuels and set the percentage split of fuel mixture to be tested, specify the target fuel concentration to be tested, and specify the desired initial test pressure. Ensure the “Record Data” button is selected and initiate the LabVIEW program to begin taking temperature and pressure time histories.
5. After one minute, closed the pneumatic exhaust valve and use the remote fuel switches to add to the test vessel the first fuel component. Add the second component up to the desired pressure after if the test fuel is a binary mixture. Obtain mixing of gas in the test vessel by adding the largest component (air) last and at high velocity. It is suggested to add air in less than 15 seconds.
6. Allow the test gas mixture to equilibrate to test conditions, waiting a minimum of two (2) minutes.
7. Attempt ignition of the gas mixture by energizing the ignition transformer using the remote switch for the ignitor. Note: Spark duration should be approximately 0.4 - 0.8 seconds.
8. If pressure rise is observed, allow recording of measurements to continue for an additional minute. If no pressure rise is observed, attempt ignition a second time after one more minute to allow the mixture to equilibrate.
9. Deselect the “Record Data” button on LabVIEW to stop recording; each test will produce a text file with all temperature and pressure recordings. Vent the test vessel through the exhaust valve.
10. Repeat Steps 3 – 9 while varying the fuel concentration as required to find the minimum concentration that gives flame propagation and the maximum concentration that does not give flame propagation. Repeat the analysis and test on fuel concentrations near the lean flammability limit to confirm repeatability.

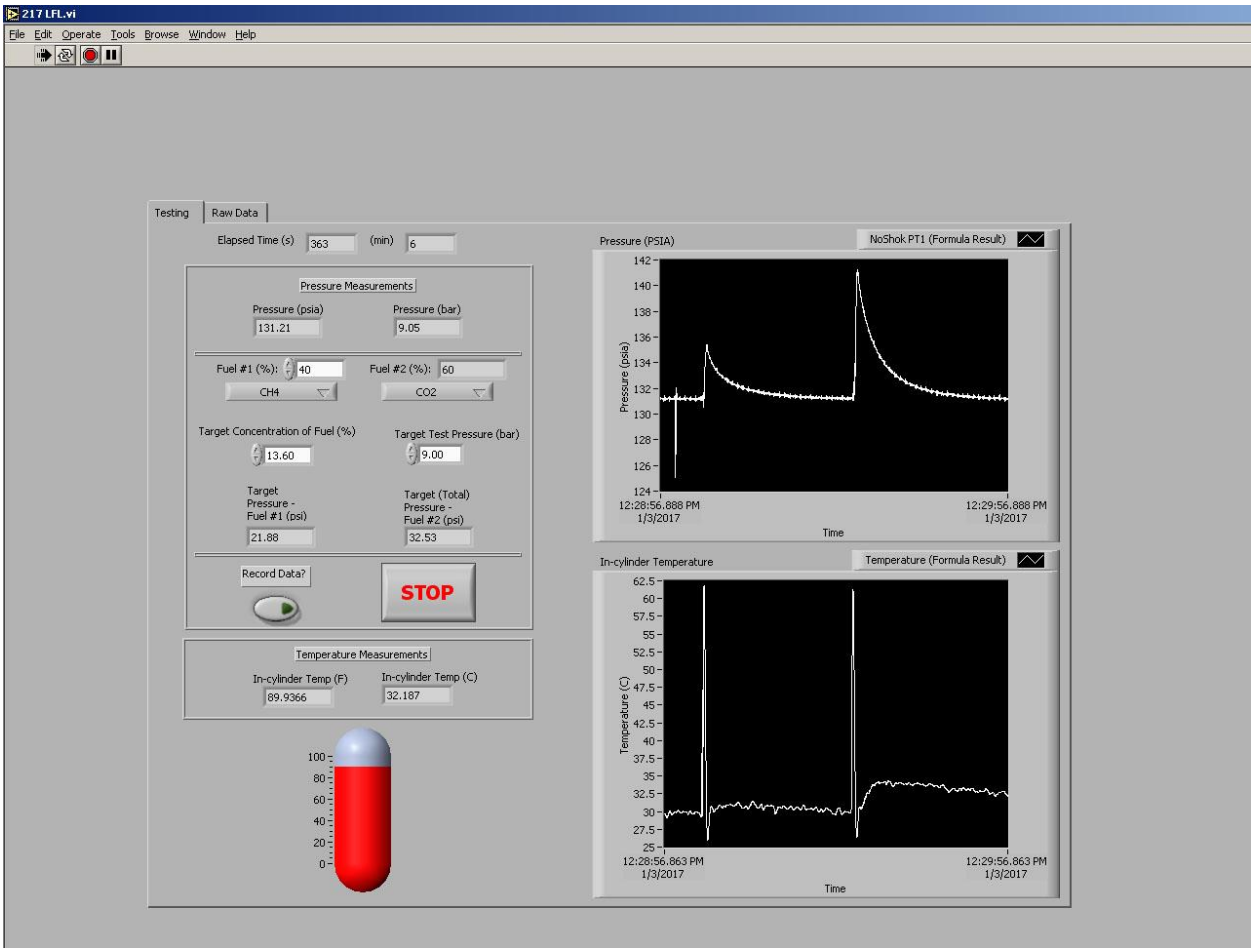

Figure 12: Real-time LabVIEW user interface for lower flammability limit testing

4.1.5 Le Chatelier's Law

In addition to validating all experimental results of the current study with available literature data, flammability limit results for the methane/hydrogen (CH_4/H_2), methane/carbon dioxide (CH_4/CO_2) and hydrogen/carbon monoxide (H_2/CO) fuel blends will also be compared for accuracy with LFL estimates found by using Le Chatelier's Law:

$$LFL_{mix} = \frac{1}{\sum \frac{x_i}{LFL_i}} \tag{25}$$

With respect to the flammability testing of gaseous mixtures, pertinent literature typically suggests the use of Le Chatelier's law as a predictive method for the determination of these limits. This rule has been used extensively in the literature and has been confirmed to be accurate, however, these studies are conducted primarily at standard conditions for temperature and pressure. The standard for the determination of flammability limits at elevated temperature and pressure conditions, ASTM E918, does not explicitly mention Le Chatelier's law as a valid method for estimating the lean flammability limit; however, ASTM E681 suggests that lower flammability limits of known mixtures may be estimated from known lower flammable limits of the mixture components using Le Chatelier's law (ASTM E918 1983; ASTM E681 1985). An LFL estimation using equation 25 for a natural gas with the composition below (Table 6) gives the following result:

$$LFL_{mix} = \frac{1}{\sum \frac{x_i}{LFL_i}} = \frac{100}{\frac{80}{5.30} + \frac{15}{3.22} + \frac{4}{2.37} + \frac{1}{1.86}} = 4.55\%$$

Fuel Component	Composition (%)	LFL (% vol)
Methane	80	5.30
Ethane	15	3.22
Propane	4	2.37
Butane	1	1.86

Table 6: Sample natural gas composition for Le Chatelier example

The benefits of a simple calculation to predict the LFL of various types of gaseous mixtures are of great interest to the current study, however, it is important to compare these estimates with experimental results in order to assess the conditions for the safe and efficient use of Le Chatelier's law to estimate LFLs. Discussion of the LFL results for methane/hydrogen (CH_4/H_2), methane/carbon dioxide (CH_4/CO_2) and hydrogen/carbon monoxide (H_2/CO) gas mixtures in comparison to estimates using Le Chatelier's law can be found in Chapter 5, while a more detailed description of the Le Chatelier analysis used in the current study can be found in Appendix 0.

4.2 NUMERICAL METHODS

4.2.1 Literature Review

In parallel with the experimental determination of the flammability limits, numerical methods for the determination of the flammability limits of certain gaseous fuels and gaseous fuel mixtures were also considered. A review of available literature concerning the numerical determination of the flammability limits yields various approaches and methods. Unique approaches include a study conducted by Liaw et al. who propose a criterion for determining if a mixture is flammable by using a Fourier transform infrared spectroscopy (FTIR) gas sensor to analyze the post-combustion products of the fuel/air sample (Liaw et al. 2016). Giurcan et al. also investigate a unique method for determining the flammability limits of hydrocarbon fuels by using experimental pressure versus time curves to extrapolate and predict the flammability limits (Giurcan et al. 2015).

The most common approach for numerical calculation of the flammability limits however is by solving the energy equation through an enthalpy balance of the reactant fuel-air mixtures to complete combustion products, either directly using tabulated values or with the help of a computer model or "flame code". Hu et al. compared the flammability limits of $CH_4/CO_2/O_2$ mixtures at atmospheric conditions determined experimentally as well as through theory calculations (Hu et al. 2014). For their numerical model (theory calculations), the temperature of the mixture was arbitrarily set to be 1650 K in order to ensure the complete combustion of the fuel; overall, this method of numerical calculation is expected to differ greatly from experimental values however Hu et al. demonstrated satisfactory agreement with the flammability limit values determined using their glass tube apparatus. Mendiburu et al. also use an elevated flame temperature assumption equal to the auto-ignition temperature of the fuel for their estimation of the lower flammability

limits of C-H compounds in air at atmospheric pressure (Mendiburu et al. 2015). In particular, the two aforementioned studies were able to determine numerical flammability limits that agreed well with values determined experimentally, however these studies did not extend into the effect of elevated temperatures and pressures. Di Benedetto introduced a numerical method for determination of the flammability limit by assuming zero heat loss and defining the determining limits as "adiabatic" flammability limits (AFLs) (Di Benedetto 2013). These AFLs grossly overestimated the flammable range but this result was intended as this "adiabatic" flammable range was more appropriate for the determination of safe flammability limits dependent only on the fuel type. The results provided in this study at elevated conditions confirmed an increase in the flammable range (decrease of LFL, increase of UFL) with increasing temperature and pressure, in agreement with the theoretical background of the current study. Wan et al. reached the same conclusion with their study into the theoretical estimation of the lower flammability limit of fuel-air mixtures at temperatures up to 1200 K and pressures up to 100 atm (Wan et al. 2015). Despite the many successful numerical methods for determining the limits of flammability mentioned above, the current study takes advantage of an existing computer model or "flame code" to simulate the flammability of many fuels and provides a brief yet significant comparison of data with the results from the experimental methods. The following section provides a detailed description of the numerical model that was chosen and a sample procedure for the determination of the flammability limits for the gaseous fuels and gaseous fuel mixtures in question at elevated temperatures and pressures.

4.2.2 CHEMKIN Flame Speed Model

A premixed laminar flame speed model developed by ANSYS and included in their Chemkin-Pro® Software was the basis of the numerical model for the determination of

flammability limits in the current study. This model acts as a laminar flame speed "calculator" and simulates a freely propagating flame which makes it ideal for use in the determination of flammability limits of various fuels at various conditions, as the general procedure for determining flammability limits experimentally involves the confirmation of flame propagation after an ignition attempt. A diagram view of the freely-propagating laminar flame speed model is shown in Figure 13.

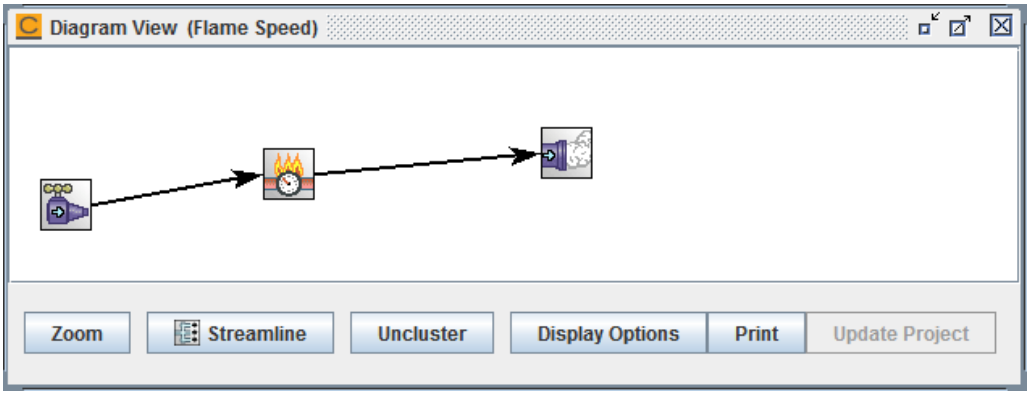

Figure 13: CHEMKIN laminar flame speed model diagram view

The test parameters investigated are identical to the experimental parameters discussed in Section 4.1.3 with the addition of intermediate pressures as the computational power afforded time to run additional cases. The pressures tested varied from 1 bar to 10 bar with an interval of 1 bar, and the temperature remained at the two initially determined cases ($T = 25°C$ and $T = 200°C$). The use of this flame speed model for the numerical determination of the flammability limits benefited from the simplicity of the fuels investigated in this study (i.e. CH_4/H_2, CH_4/CO_2, and H_2/CO). CHEMKIN models utilize various chemistry sets to perform the necessary calculations and optimizations, and it was important to first determine an appropriate chemistry set (or reaction mechanism) for the desired combustion reactions and also compare the effect of each different set on the flame speed results. The software was initially equipped with the widely used GRI-Mech version 3.0 mechanism which was originally developed from work conducted by the Gas Research

Institute. This relatively well-tested reaction mechanism, consisting of gas-phase chemistry, thermodynamic, and transport data, contains 5 elements, C, H, O, N and Ar, 53 chemical species, and 325 reactions. Another mechanism investigated for comparison is the mechanism from the Center for Energy Research (CER) at the University of California, San Diego. It consists of 46 species and 235 reactions, and the elements constituting the species are N, H, C, O, Ar, and He. These two mechanisms were primarily used for the methane/hydrogen/air and methane/carbon dioxide/air mixtures. For the hydrogen/carbon monoxide/air (syngas/air) mixtures, a reaction mechanism developed by the National University of Ireland Galway was utilized as it was specialized for use in hydrogen and syngas combustion. More detail for all three of the mechanisms investigated in the current study can be found in Appendix C.

Overall, the CHEMKIN laminar flame speed model was chosen for its similarity to flammability studies that determined the limits of flammability using the most accurate and widely cited ignition criterion – visual flame propagation. Initially, a closed homogenous reactor was chosen as the numerical model, however, this model simulates combustion chemistry without flame propagation and therefore is not suitable for studying the limits of flammability. The premixed laminar flame speed model is designed to provide flame speed measurements specifically, however, the range of operating conditions for which a flame speed solution is convergent would closely resemble the flammability range of the fuel-air mixture being tested. The general approach for determining the lower flammability limit was to specify the appropriate initial fuel-air test mixture, initial conditions of temperature and pressure, and vary the simulation for various equivalence ratios (EQR, ϕ). The equivalence ratios for which a laminar flame speed solution was convergent could then be easily converted to mol % or vol % to fully characterize the

flammable range of the test mixture. The following section describes in more detail the test procedure for the numerical determination of the lower flammability limits in the current study.

4.2.3 Numerical Test Procedure

Generally, the CHEMKIN laminar flame speed model is used for determining the characteristic flame speed of a certain fuel-air mixture at specific initial conditions of temperature, pressure, etc. The flame speed in this context is defined as the inlet velocity (velocity of unburned gas moving towards the flame) that allows the flame to stay in a fixed location. To assist in the solution of this freely propagating flame problem, this numerical method uses continuations to successively refine the domain and grid of the solution until a desired accuracy and grid-independence is achieved. The continuations would be performed for every combination of test parameter, decreasing in fuel-air equivalence ratio until the mixture became too lean to sustain flame propagation. This lean limit would determine the lower flammability limit, and a lower flammability limit would be determined at every test pressure and temperature and finally compared with experimental flammability data from the current study. The numerical test procedure for the flammability tests conducted at elevated conditions using the aforementioned flame speed model is given below in more detail[4]:

1. Open CHEMKIN and select new project file; from the Models tab, select the Premixed Flame-speed Calculation reactor, and inlet and an outlet and connect in series.
2. Before being able to run any flame speed calculations, the Pre-Processer must be run; select the Pre-Processing option under the Open Project and choose the appropriate chemistry set/mechanism and run the Pre-Processor. After this is complete, the model should be ready for receiving input of initial test conditions.

[4] Further details/references for the exact CHEMKIN software and flame speed models are provided in Appendix C

3. Open the C1_Inlet1 window and select the Species-specific Properties tab. Under the Fuel Mixture sub-section, input the Species of the fuel to be tested along with the Fuel Fraction of each species with respect to the Total Fuel Species.
4. Under the Oxidizer Mixture sub-section, confirm that air is auto-populated (O_2 and N_2) or select the Auto-populate Air option to do so.
5. In the same C1-Inlet1 window under the Species-specific Properties tab, select the [+/-] button next to the Equivalence Ratio text box in order to set up a Parameter Study.
6. In the Parameter Study window, various combinations of parameters can be specified; for the current study, the first parameter that was varied was the Equivalence Ratio and the second parameter was the initial pressure. After specifying the details in the Parameter Study window, the C1-Inlet1 window may be closed.
7. Open the C1_Flame Speed window. Under the Reactor Physical Properties tab, confirm that the Unburnt Gas temperature and Ambient Temperature both correspond to the desired initial test temperature, and that the Pressure value is set to the first pressure value specified in the Parameter Study window.
8. Under the Grid Properties tab, and under the Basic sub-section, confirm that the desired values for grid points, adaptive grid control, starting axial position and ending axial position match the values as shown in Appendix C. These values correspond to the Automatic Estimated Temperature Profile calculated by the flame speed model, and overall the Grid Properties are important during the Continuations process as the domain and grid of the solution are refined with each continuation until a desired accuracy and grid-independence is achieved. After confirming the details in the Grid Properties window are correct, the C1-Flame Speed window may be closed.

9. Select the Continuations option under the Flame_Speed (C1) reactor and confirm that the desired values match those found in Appendix C. Overall, each set of parameter combinations will run three times – an initial test, followed by Continuation #1 and finally Continuation #2. The final flame speed results are determined by analyzing the results following the last continuation. After confirming the details in the Continuations window are correct, the window may be closed.
10. Under the Open Project, select the Run Calculations option and begin the Parameter Study.
11. Following the Run Calculations step, the Analyze Results option will be available; you may choose to analyze the results through post-processing using the built in Post-processor or output as a comma separated value document.
12. Repeat the procedure from Step 6 for a given test mixture, reducing the range of Equivalence Ratio values, until the lower flammability limit is determined. It will be important to refine the interval between each successive value for Equivalence Ratio in order to find the most exact value for the lower flammability limit.
13. If subsequent tests involve the use of a different fuel, be sure to repeat the procedure from Step 3 and confirm the correct Fuel Species and Fuel Fraction is specified; if a different mechanism is required, the procedure should be repeated from Step 2 which prompts the user to run the Pre-Processor after changing the respective chemistry set/mechanism.

5 RESULTS AND DISCUSSION

5.1 EXPERIMENTAL RESULTS

5.1.1 Choosing an Ignition Criterion

In order to determine the lower flammability limit experimentally at elevated temperature and pressure conditions, it is necessary to decide on an ignition criterion appropriate for the given experimental setup. As previously mentioned, an ignition criterion based on the amount of pressure rise after the test mixture has been ignited is preferred for these conditions as visual flame propagation is not typically possible due to the design of the test vessel at elevated pressures. The criterion suggested by the ASTM E918 standard that this experimental setup was first modeled after is a 7 percent pressure rise, however, it is widely accepted that a lower percent pressure rise is more suitable as it would result in a more conservative flammable range (ASTM E918 1983). The bomb method discussed in the European Standard EN 1839 includes a pressure rise criterion of 5% which is widely used in the literature (EN 1839 2003). A criterion of 2% pressure rise reportedly agrees consistently with visual flame propagation data according to De Smedt et al. (1999). The experimental results presented in this chapter are determined based on only one ignition criterion and the following example is presented to support the choice of ignition criterion.

Following the experimental test procedure proposed in Section 4.1.4, a pure mixture of hydrogen in air is prepared at room temperature ($T = 25°C$) and at an elevated pressure of $P = 5\ bar$. As is shown in Figure 14, the option for Fuel #1 is chosen to be H_2 at 100% while Fuel #2 is left blank with a value of 0%. The target test pressure is set to 5 bar and the target concentration of fuel for this particular test is 4.90%. These options combined with the fuel split details provide a calculation for the amount of fuel to add during each partial pressure fuel addition step.

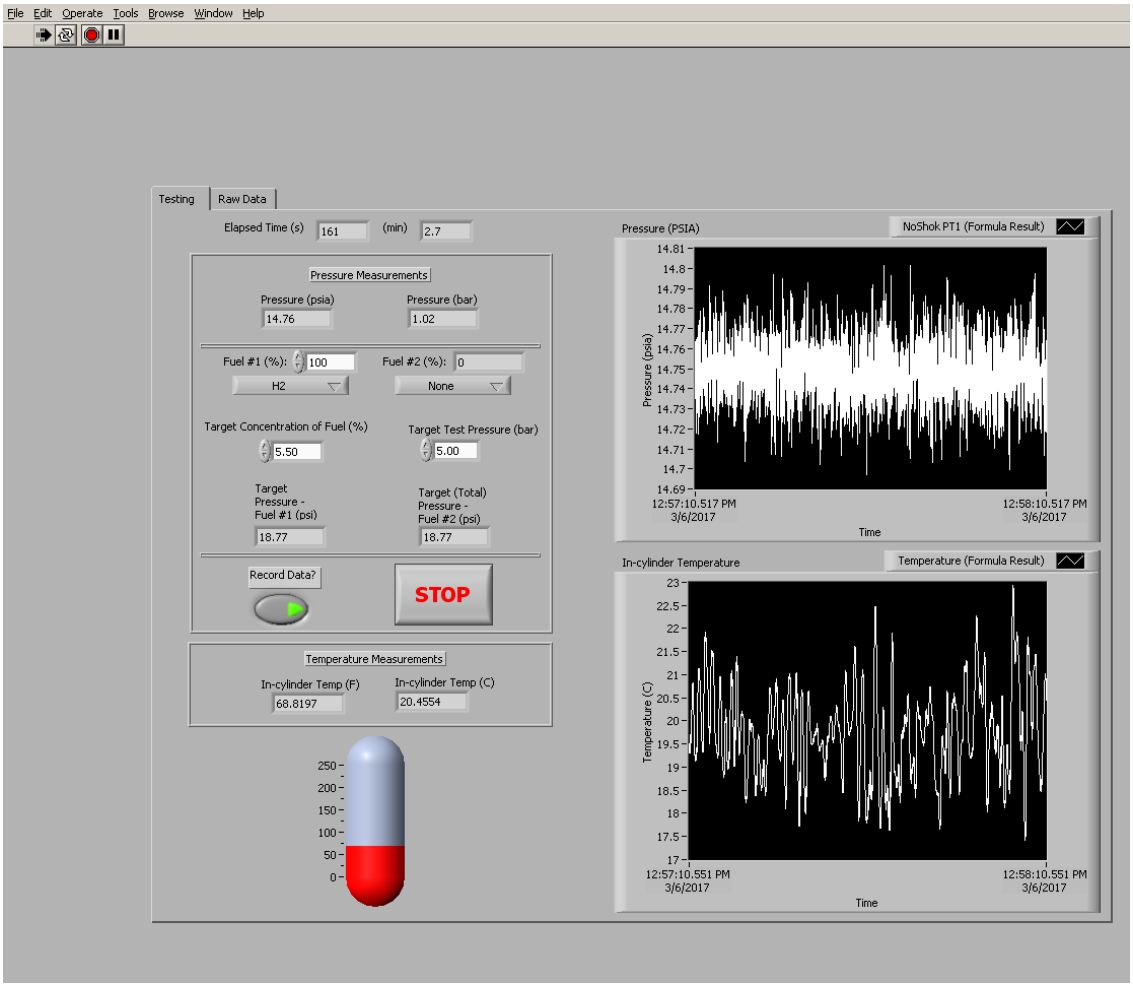

Figure 14: LabVIEW user interface for example 5.1.1; 100% H_2, P = 5 bar, T = 25°C

The experimental setup is prepared per the test procedure, the "Record Data?" button is selected and the LabVIEW program is initiated. After the test mixture is prepared, the ignition transformer is energized and the operator determines if ignition has occurred by noting a pressure spike in the real-time pressure plot displayed in the LabVIEW VI interface (Figure 14). At this point, a quick calculation can be performed in order to determine the actual pressure rise, however, a more accurate approach for the determination of the amount of pressure rise as well as the verification of the mixture composition is in the post-processing of the pressure-time data. Post-processing of the data is accomplished using a Matlab code which is included in Appendix A: Sample MATLAB Codes.

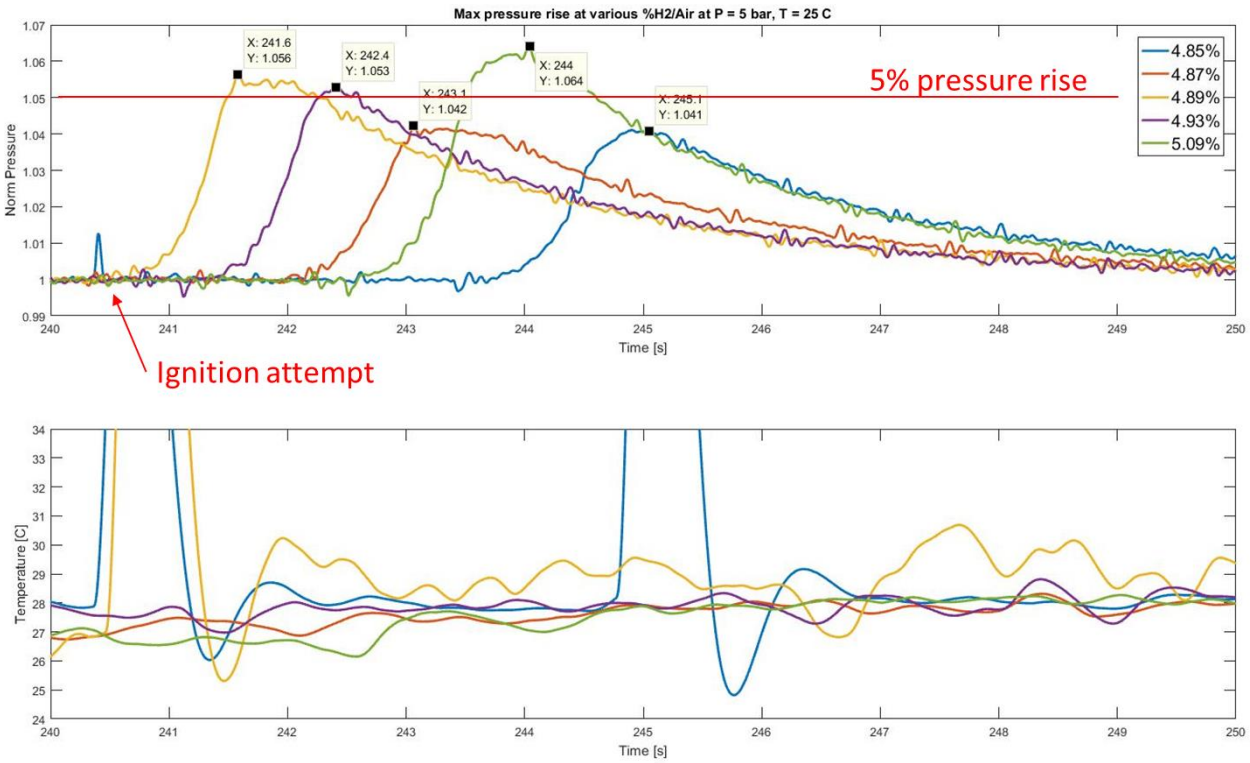

Figure 15: Post-processing procedure for example 5.1.1; 100% H_2, P = 5 bar, T = 25°C

In the figure above, one of the Matlab scripts is run to plot the pressure rise for various concentrations of hydrogen in air. It is clear that with an increasing amount of hydrogen in air, the normalized pressure rise (absolute pressure/initial pressure) increases. This example serves to show how different ignition criteria choices vary the apparent lower flammability limit (LFL). Beginning with the largest percent pressure rise considered, the threshold of 7% pressure rise as stated in ASTM E918 would suggest that all the mixtures plotted would be considered not flammable since they fall under a 7% pressure rise (1.07 normalized pressure), therefore the LFL would be a value larger than 5.09% H_2 in air. The limit for a 5% pressure rise is shown in red and indicates that three of the mixtures shown (4.89% H_2, 4.93% H_2, 5.09% H_2) are considered flammable (Figure 15). This choice of ignition criterion is more conservative and better represents the lean flammability limits by including mixtures that were determined non-flammable according to ASTM E918. The LFL for this case would be 4.88% H_2 in air. The option for a 2% pressure rise

ignition criterion would include the remaining two mixtures that are plotted, and a subsequent LFL value lower than 4.85% H_2 in air, however it should be noted that it can be too difficult to differentiate ignition with noise for too low of a pressure rise. Figure 15 is annotated with an ignition attempt that did not initially ignite the mixture but did cause a pressure rise of about 1.5% pressure rise. Some published studies discuss that a small pressure rise ignition criterion such as 2% is suitable at elevated pressures, but not as reliable at pressures near atmospheric. In order to avoid erroneous data due to noise from the pressure transmitter, or small pressure rises due to local heating rather than complete ignition of the fuel mixture, the conclusion is to use 5% pressure rise as the ignition criterion for determining the LFL at all test conditions.

The following sections present the results of the experimental determination of the lower flammability limits for all fuels and fuel mixtures at elevated conditions using the 5% pressure rise ignition criterion as per the preceding discussion. Literature data will be used to validate the results of this study, when possible, and the conditions for the LFL data found in the literature will be clarified with respect to ignition criterion, test vessel, conditions of use, etc.

5.1.2 LFL of Pure Fuels (Methane/Air, Hydrogen/Air)

The results for the dependence of temperature and pressure on the lower flammability limit (LFL) for pure methane (CH_4) in air are provided in Figure 16. The effect of temperature produces the most noticeable trend as the LFL decreases by approximately 0.8 vol %[5] across the entire range of test pressures. This decrease of the lower limit corresponds to a widening of the flammable range which is consistent with the conclusions of the theoretical background presented in Chapter 2. An increase in pressure, however, does not seem to be consistent with these same conclusions.

[5] % volume (% vol) of fuel in air; interchangeable with mol % (% mol)

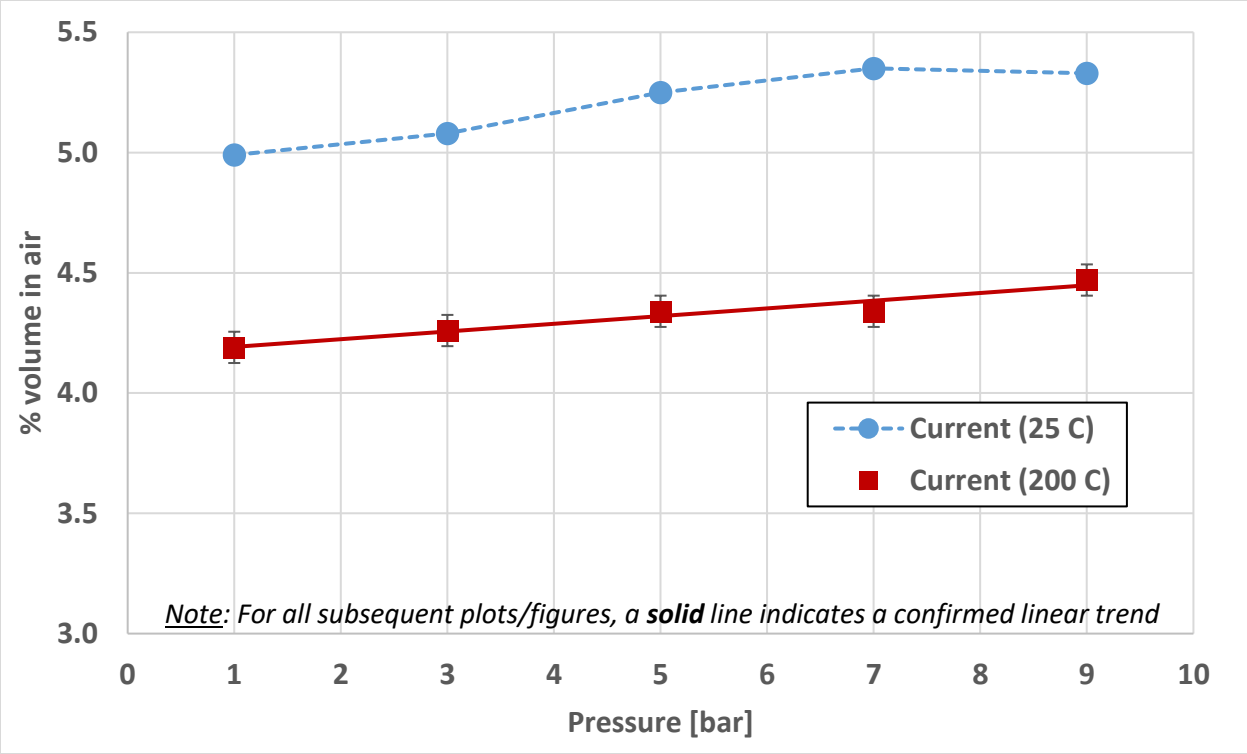

Figure 16: Dependence of temperature and pressure on the LFL of methane/air mixtures

The influence of pressure was expected to be similar to the influence of temperature, that is, a widening of the flammable range (decrease of the LFL) with an increase in either parameter. Rather, the results show a general increase of the LFL with increasing pressure; the increase is minimal but cannot be neglected. In Figure 16, the LFL data collected at ambient temperature ($T = 25°C$) is plotted in blue while the data collected at a higher temperature ($T = 200°C$) is plotted in red. The difference in the way each data set is plotted is due to whether a linear trend can be confirmed for either set. The solid red line that is fitted through the high temperature data is a confirmed linear trend between the LFL at $T = 200°C$ and the initial test pressure. This linear trend is confirmed because it does not deviate from the data points more than the experimental uncertainty, which for this data set is approximately ±0.065 vol %. This uncertainty is determined

based on the calculation of a 95% confidence interval[6] for all flammability tests conducted at or near the LFL for the conditions in question. The confidence interval for the ambient temperature data is less than the high temperature data set (±0.023 vol %) and therefore does not show a clear linear trend. Overall, for both data sets presented in Figure 16, the LFL increases slightly with pressure by approximately 0.30 vol % from $P = 1\ bar$ to $P = 9\ bar$.

The results for the dependence of temperature and pressure on the lower flammability limit (LFL) for pure hydrogen (H_2) in air are provided in Figure 17. Similar to the results for methane, the influence of temperature on the LFLs is well defined.

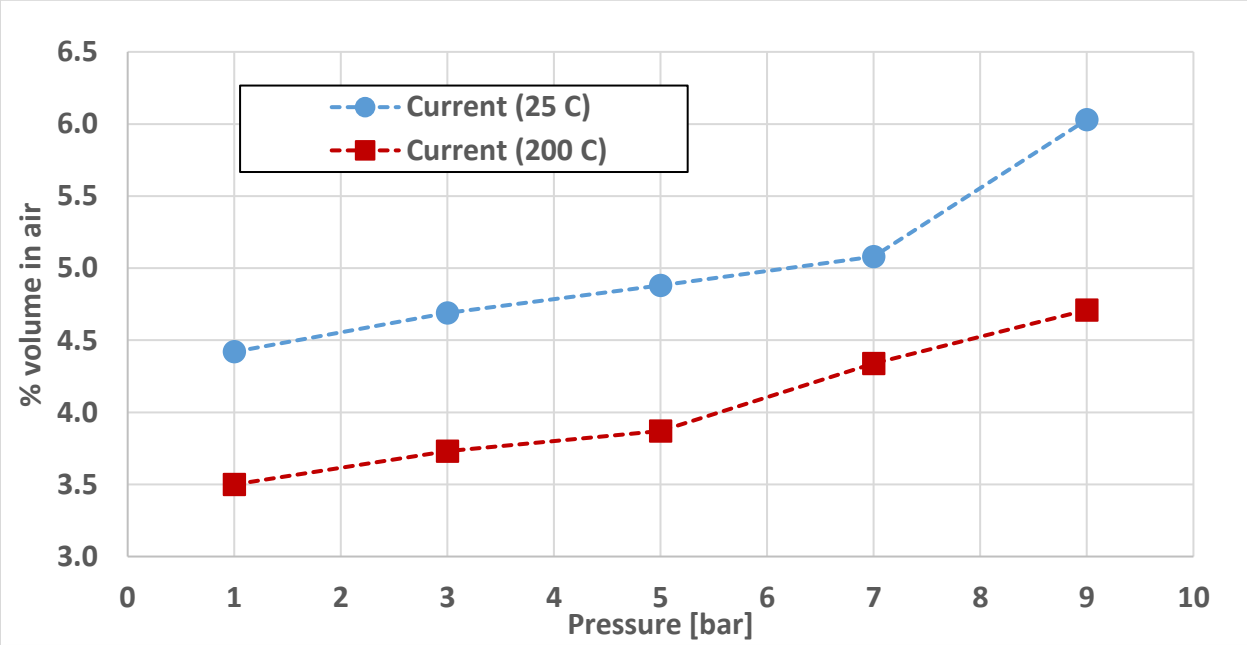

Figure 17: Dependence of temperature and pressure on the LFL of hydrogen/air mixtures

With an increase in temperature to $T = 200°C$, the LFL decreases by 0.91 vol % for $P = 1\ bar$ and by 1.32 vol % for $P = 9\ bar$. In addition to a larger difference in the LFL due to elevated temperatures, the results for hydrogen also show a larger difference in the LFL due to

[6] Refer to Appendix D for more details on the error analysis of the LFL data.

elevated pressures when compared to the results for methane. With an increase in pressure from $P = 1\ bar$ to $P = 9\ bar$, the LFL increases by 1.61 vol % for $T = 25°C$ and by 1.20 vol % for $T = 200°C$. In contrast to the results for methane, the 95% confidence interval for the ambient temperature data (±0.058 vol %) is larger than the interval for the elevated temperature data (±0.02 vol %). These uncertainty intervals are too small to guarantee the existence of a linear trend among the data; however, it should be noted that both the dependence of temperature and pressure on the LFL for H_2/air mixtures are well established.

Figure 18 shows the addition of elevated literature data for methane from Tschirschwitz et al. and Holtappels to the corresponding results of the current study first presented in Figure 16 (Tschirschwitz et al. 2015; Holtappels 2006). The LFL data provided by the latter study is for two test vessel volumes $V = 2.8\ L$ and $V = 6\ L$, select pressures up to 10 bar and for temperatures $T = 20°C$ and $T = 200°C$, while the LFL data provided by the former study is for select pressures up to 10 bar but only for $T = 20°C$. Both studies confirm the observed increase of the LFL with increasing pressure, and the results of the current study at ambient temperature fall within the uncertainty of the literature data (±0.2 vol %). The results for methane of the current study are in relatively good agreement with the elevated data provided by Holtappels, however there is a major deviation near ambient pressure tested (1 bar). As the test pressure approaches 9 bar, most if not all of the LFL data at both test temperatures were consistently comparable and fell within their respective uncertainty intervals. The main deviation from the literature occurred at 1 bar for the case of $V = 2.8\ L$ where the data point fell outside the average error of the other three data points at that pressure. Overall, the trend of increasing LFL with increasing pressure is confirmed for the current study and available literature data, contrary to the theoretical conclusions from Chapter 2.

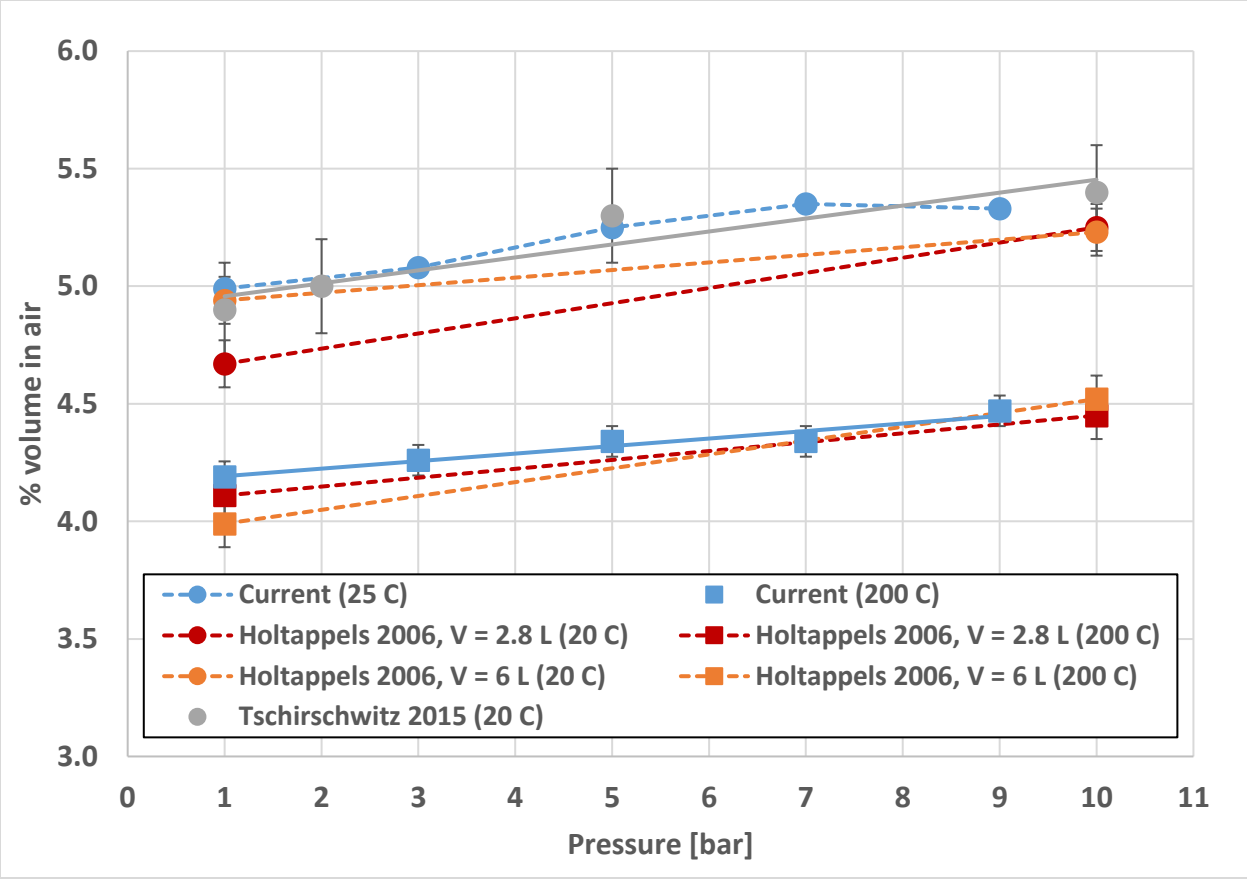

Figure 18: Comparison of methane/air LFL data with literature data (Tschirschwitz et al. 2015; Holtappels 2006)

The dependence of temperature and pressure on the LFL results of hydrogen/air mixtures of the current study are less in agreement with the results provided by Holtappels (2006) than for methane/air mixtures. From Figure 19, it can be seen that previous confirmed effects of pressure and temperature on the LFL are observed, with all data exhibiting an increase of the LFL with increasing pressure and a decrease of the LFL with increasing temperature. It should be noted that the literature data for a volume of $V = 6\ L$ exhibit a clear linear dependence, as the trend lines do not deviate more than the experimental uncertainty (±0.1 vol %) of the LFL data from the Holtappels study.

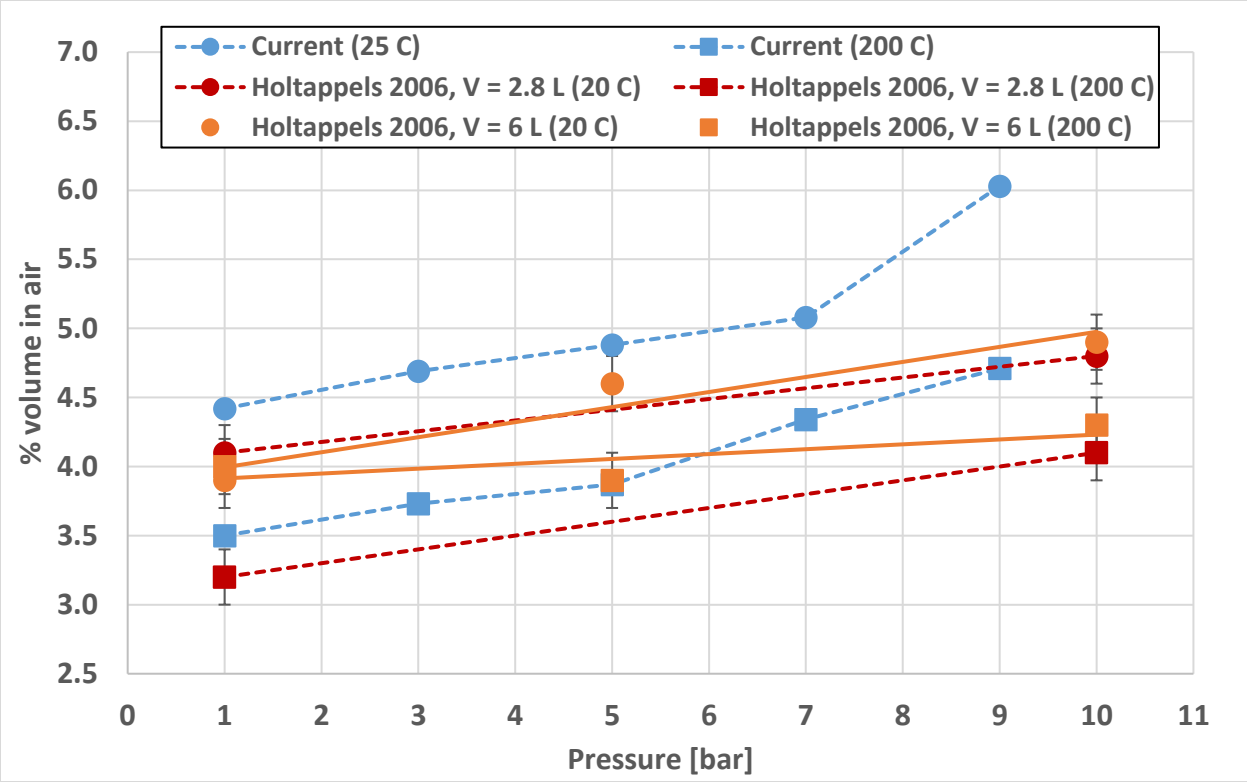

Figure 19: Comparison of hydrogen/air LFL data with past study (Holtappels 2006)

Comparing Figure 18 and Figure 19, it clear that the LFL data for methane/air are less dependent on the volume of the test vessel than the LFL data for hydrogen/air. As was mentioned in the experimental methods section, the current study utilizes a test vessel of volume $V = 1\ L$. The results for hydrogen/air mixtures shows a decrease of the LFL, or increase of the flammable range, with an increase in the test vessel size. Holtappels noted a slight decrease of the flammable range (decrease of UFL, increase of LFL) for methane/air mixtures with an increase in test vessel volume, but concluded that the LFL for hydrogen/air mixtures was independent of test vessel size; the results shown in Figure 18 and Figure 19 suggest the opposite is true. An argument for an intermediate test vessel size can be made from the results for hydrogen/air mixtures, where the results for test vessel volumes of $V = 1\ L$ and $V = 2.8\ L$ exhibit the expected dependence of temperature on the LFL, that is an increase in temperature results in a decrease in the LFL, however

the results for $V = 6\ L$ at 1 bar instead show a negligible dependence on temperature. For a test vessel volume of $V = 2.8\ L$, an increase in temperature to $T = 200°C$ results in a decrease of the LFL by 0.9 vol % for $P = 1\ bar$ and by 0.7 vol % for $P = 9\ bar$. With respect to an increase in pressure from $P = 1\ bar$ to $P = 9\ bar$, the LFL for this specific test vessel volume increases by 0.7 vol % for $T = 25°C$ and by 0.9 vol % for $T = 200°C$. These effects on the LFL due to elevated temperature and pressure are comparable to the results of the current study, but result in a wider, more conservative flammable range. Overall, the LFL results for methane/air and hydrogen/air mixtures are consistent with flammability literature data at elevated conditions, and also suggest considering an optimal test vessel size in the range of $V = 2.8\ L$ and $V = 6\ L$.

The key conclusions for pure fuel (methane/air, hydrogen/air) mixtures include:

- For methane/air mixtures, the LFL decreases with increasing temperature by approximately 0.8 vol % from $T = 25°C$ to $T = 200°C$; also, the LFL increases slightly with pressure by approximately 0.3 vol % from $P = 1\ bar$ to $P = 9\ bar$.
- For hydrogen/air mixtures, the LFL decreases with increasing temperature by approximately 1.0 vol % from $T = 25°C$ to $T = 200°C$; also, the LFL increases with pressure by approximately 1.4 vol % from $P = 1\ bar$ to $P = 9\ bar$.
- LFL results for methane/air mixtures are consistent with available flammability data at similar elevated conditions, and exhibit a negligible dependence due to test vessel size.
- LFL results for hydrogen/air mixtures are dependent on the volume of the test vessel, especially at lower test pressures; an ideal test vessel size between $V = 2.8\ L$ and $V = 6\ L$ is suggested to promote consistent flammability data for hydrogen/air test mixtures.

5.1.3 LFL of Methane/Hydrogen/Air Mixtures

The results for the dependence of pressure on the lower flammability limit (LFL) for methane/hydrogen (CH4/H2) mixtures in air at $T = 25°C$ are provided in Figure 20. These results show that the fuel composition has a minor effect on the LFL of methane/hydrogen/air mixtures; however, it should be noted that the main reason for this is that pure methane and pure hydrogen have a similar LFL range (4.5 - 6.0 vol %) for the pressure range of the current study.

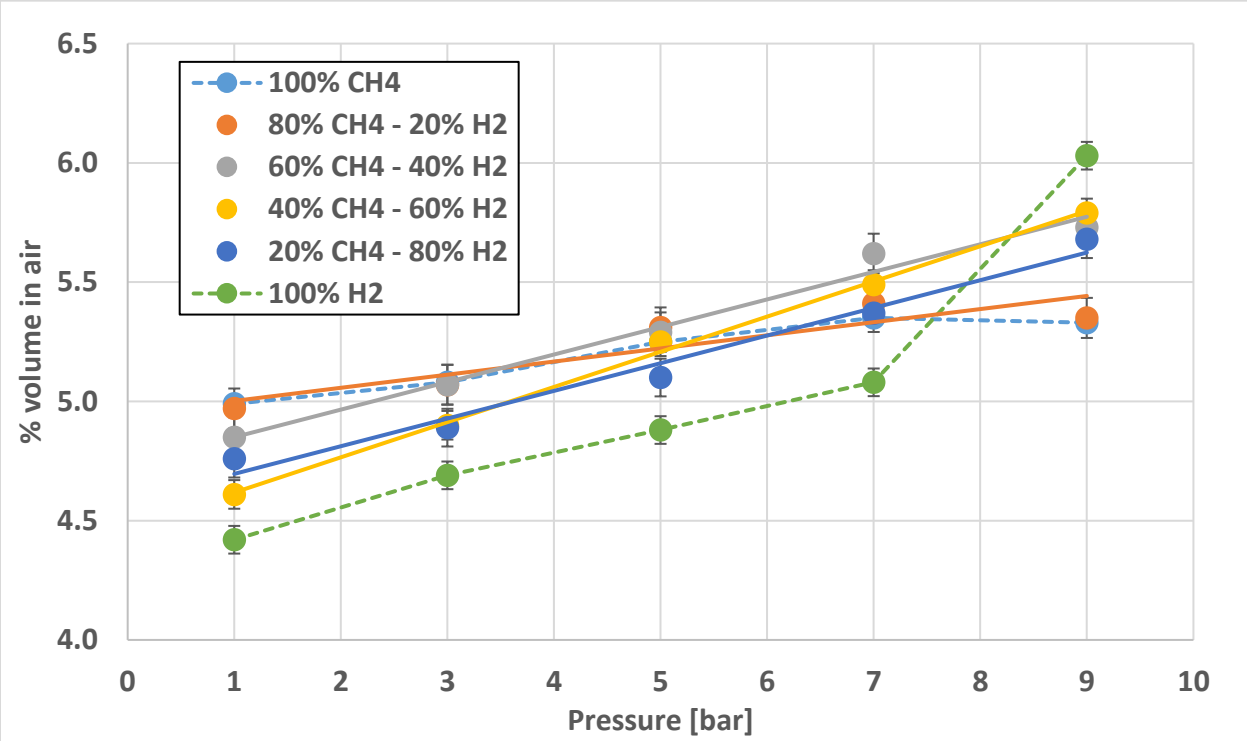

Figure 20: Dependence of pressure on the LFL of methane/hydrogen/air mixtures at $T = 25°C$

All mixtures of methane/hydrogen/air exhibited an increase in the LFL with an increase in pressure; in fact, besides the results for pure methane and pure hydrogen, a linear trend of the LFL with respect to initial test pressure was able to be confirmed for each methane/hydrogen/air mixture investigated. It is also evident that the influence of pressure increases as the amount of hydrogen in the fuel/air mixture increases. From $P = 1\ bar$ to $P = 9\ bar$, the LFL increases by 0.34 vol % for the 100/0 (% CH_4/% H_2) fuel blend, 0.38 vol % for the 80/20 fuel blend, 0.88 vol % for the

60/40 fuel blend, 1.18 vol % for the 40/60 fuel blend, 0.92 vol % for the 20/80 fuel blend, and 1.61 vol % for the 0/100 fuel blend. Another significant result shown in Figure 20 is the opposite dependence of hydrogen fuel addition on the LFL when data from the current study at $P = 1\ bar$ are compared to the results at $P = 9\ bar$. At $P = 1\ bar$, the mixtures containing increasing amounts of hydrogen are characterized by a wider flammable range; however, the opposite is true at $P = 9\ bar$ with increasing amounts of hydrogen resulting in a narrower flammable range. The LFL results in question are plotted as a function of hydrogen fraction by volume in Figure 21, in order to further investigate the effect of fuel composition on the lean flammability limit.

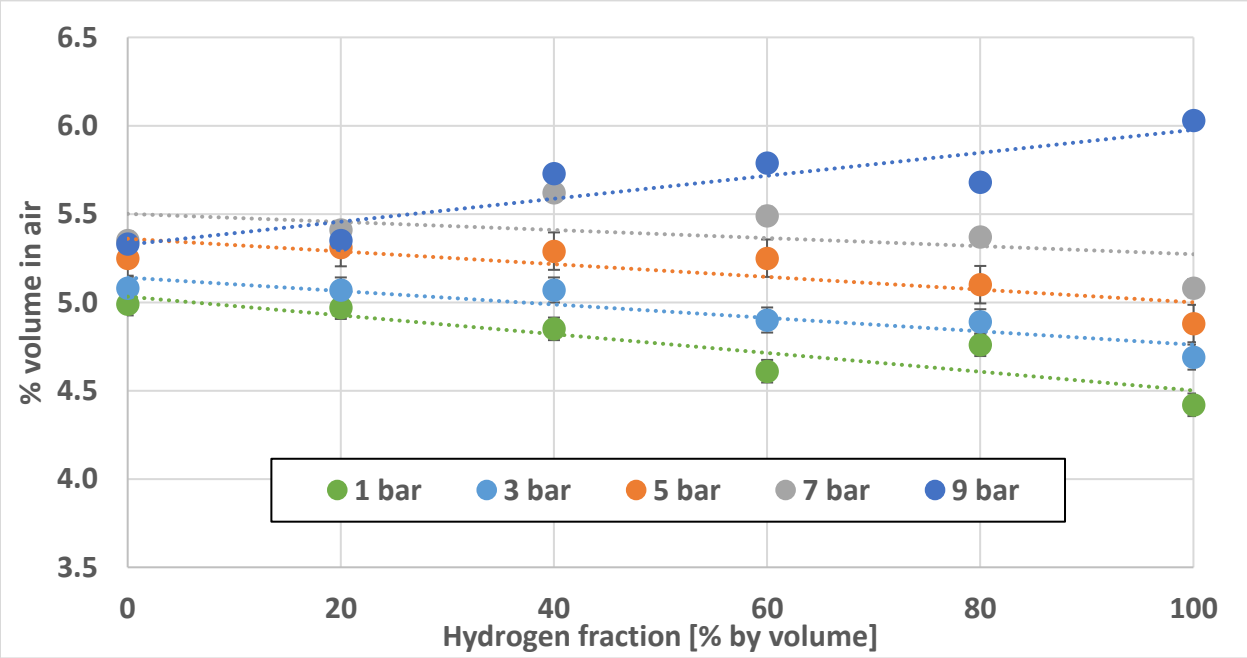

Figure 21: Influence of hydrogen addition on a volume basis on the LFL of methane/hydrogen/air mixtures at $T = 25°C$ and for various pressures

The above figure confirms both of the first key results, namely an increase of the LFL with increasing pressure as well as the widening of the range of LFL values with increasing amounts of hydrogen in the fuel mixture. The effect of initial pressure on the behavior of the LFL for fuel blends with increasing amounts of hydrogen is also clearly shown. For lower pressures, an increase in the hydrogen component of the fuel results in a decrease of the LFL. At higher pressures, the

LFL tends to increase with increasing hydrogen fraction up to 40%. For $P = 5\ bar$ and $P = 7\ bar$, the LFL decreases after 40% H_2 by volume, however the LFL for $P = 9\ bar$ continues to increase. An important consideration involves the difference between identifying the fraction of hydrogen in the fuel on a volume basis versus on a mass basis. Since the molecular weight of methane is 8 times greater than that of hydrogen gas, the hydrogen fraction for mixtures containing methane are greater on a volume basis than when calculated on a mass basis. Figure 22 plots the LFL data for methane/hydrogen/air mixtures at $T = 25°C$ against hydrogen fraction, this time calculated on a mass basis. As can be seen, the general trend of decreasing LFL with increasing hydrogen concentration is confirmed for the majority of the data excluding data for $P = 9\ bar$. At a given pressure, the largest difference in the LFL is shown to be more distinct between the 20/80 (CH_4/H_2) fuel blend and pure hydrogen as the fuel; the reason for this distinction is that the effect of hydrogen addition is not truly dominant for any of the fuel blend splits since the hydrogen fraction on a mass basis is always less than half.

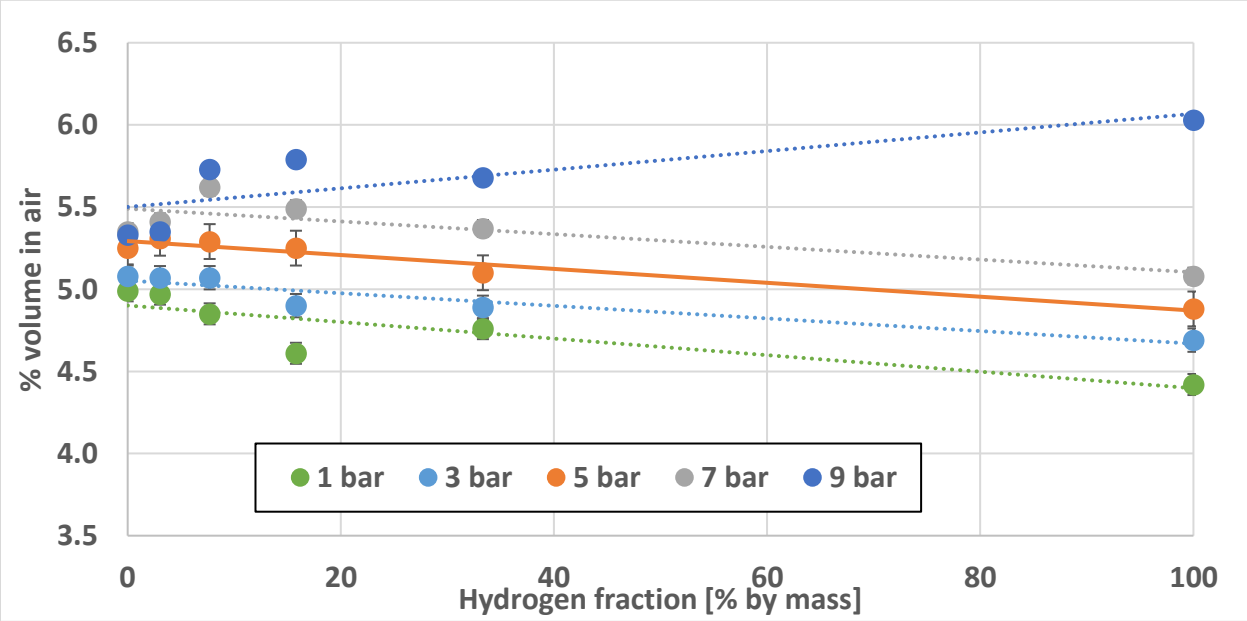

Figure 22: Influence of hydrogen addition on a mass basis on the LFL of methane/hydrogen/air mixtures at $T = 25°C$ and for various pressures

The results for the dependence of pressure on the lower flammability limit (LFL) for methane/hydrogen (CH_4/H_2) mixtures in air at $T = 200°C$ are provided in Figure 23. These results are similar to the results of pure methane and pure hydrogen as the fuel, as all LFL data points consistently decrease with an increase in temperature. As discussed previously, for an increase in temperature from $T = 25°C$ to $T = 200°C$, the average decrease of the LFL for methane is approximately 0.8 vol % and the average decrease of the LFL for hydrogen is approximately 1.0 vol %. The average decrease of the LFL values due to this same increase in temperature, for all other fuel blends, are 0.67 vol % for the 80/20 (% CH_4/% H_2) fuel blend, 0.76 vol % for the 60/40 fuel blend, 0.56 vol % for the 40/60 fuel blend, and 0.66 vol % for the 20/80 fuel blend.

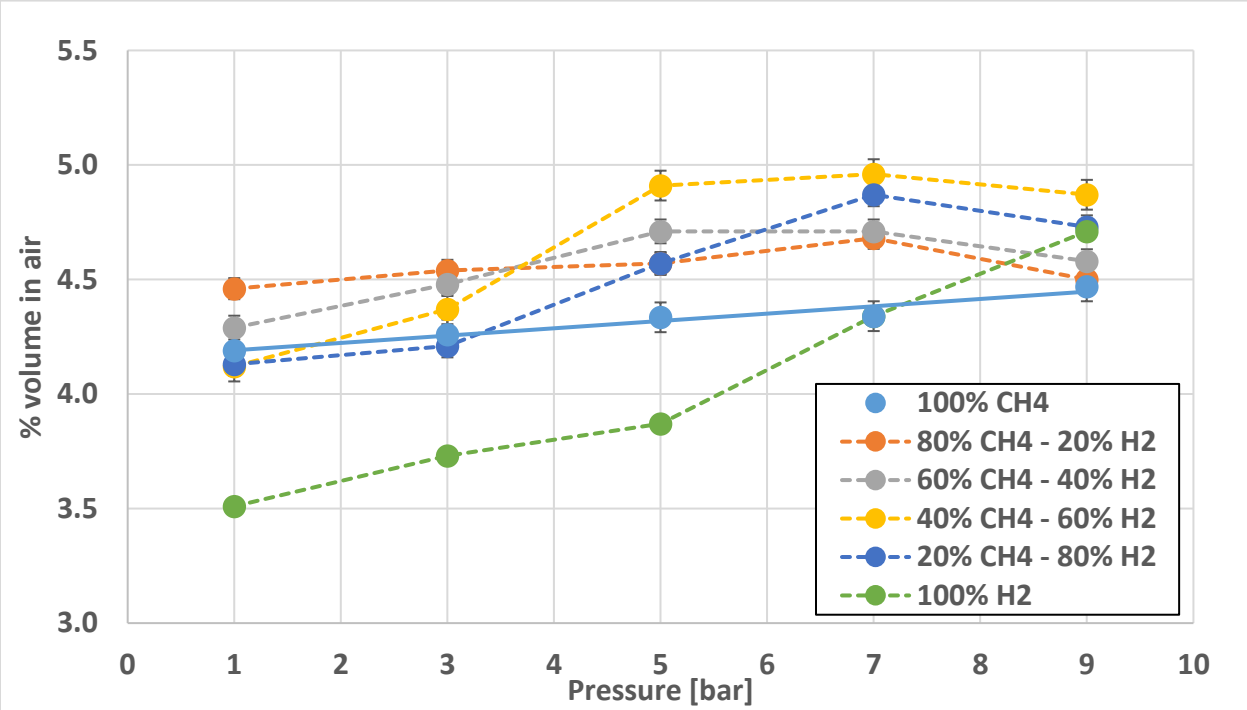

Figure 23: Dependence of pressure on the LFL of methane/hydrogen/air mixtures $T = 200°C$

As we previously mentioned, plotting the LFL results against hydrogen fraction helps to understand the effect due to different fuel composition. Figure 24 plots the LFL data for methane/hydrogen/air mixtures at $T = 200°C$ against hydrogen fraction on a mass basis. Whereas

the general trend of decreasing LFL with increasing hydrogen concentration is confirmed for only lower pressures at $T = 25°C$, increasing the temperature to $T = 200°C$ results in all methane/hydrogen mixtures exhibiting an eventual decrease of the LFL with increasing hydrogen concentration. In contrast to the monotonic behavior of the LFL data at $T = 25°C$, the LFL at $T = 200°C$ demonstrates a notable increase with an initial increase in the hydrogen fraction, followed by a certain decrease of the LFL with the addition of more hydrogen in the fuel. For $P = 1\ bar$ and $P = 3\ bar$, the LFL increases slightly due to hydrogen addition but only up to 20% H_2 by volume; further hydrogen addition results in a strict decrease of the LFL. For higher pressures greater than or equal to $P = 5\ bar$, the LFL increases up to a hydrogen fuel fraction of 60% by volume, followed by a sudden decrease in the LFL. Overall, this non-monotonic behavior was observed only at the elevated temperature condition of $T = 200°C$.

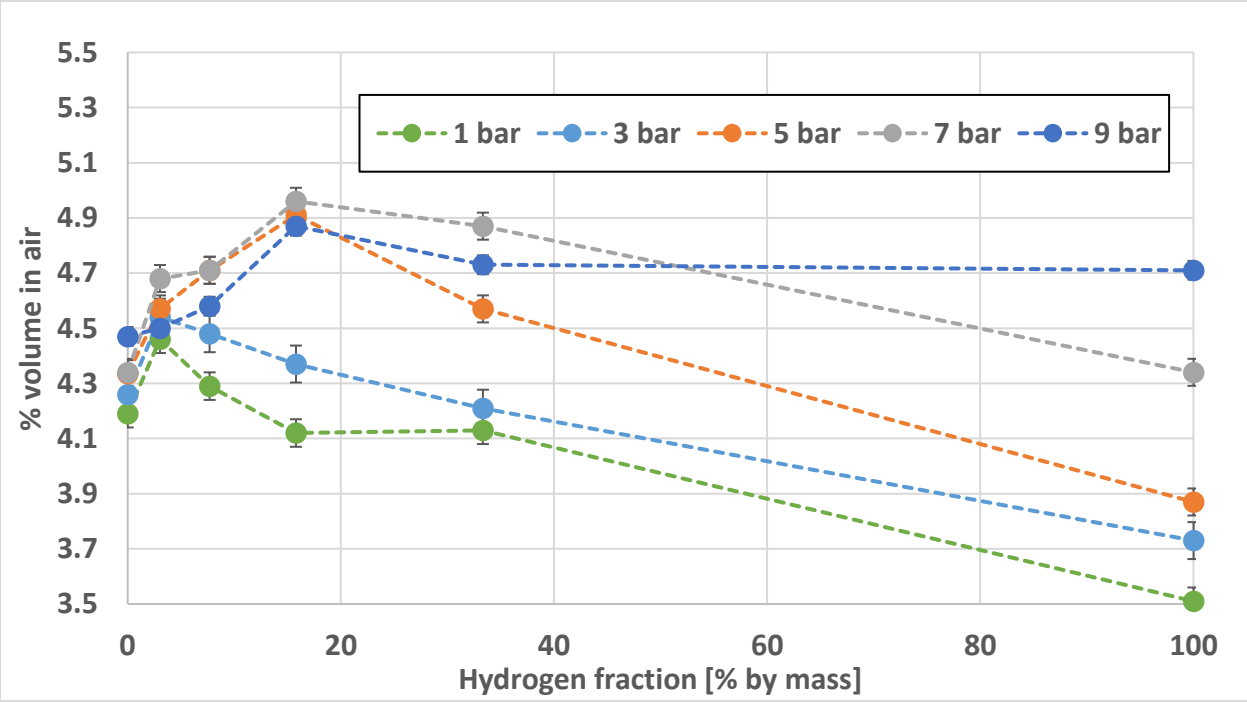

Figure 24: Influence of hydrogen addition on a mass basis on the LFL of methane/hydrogen/air mixtures at $T = 200°C$ and for various pressures

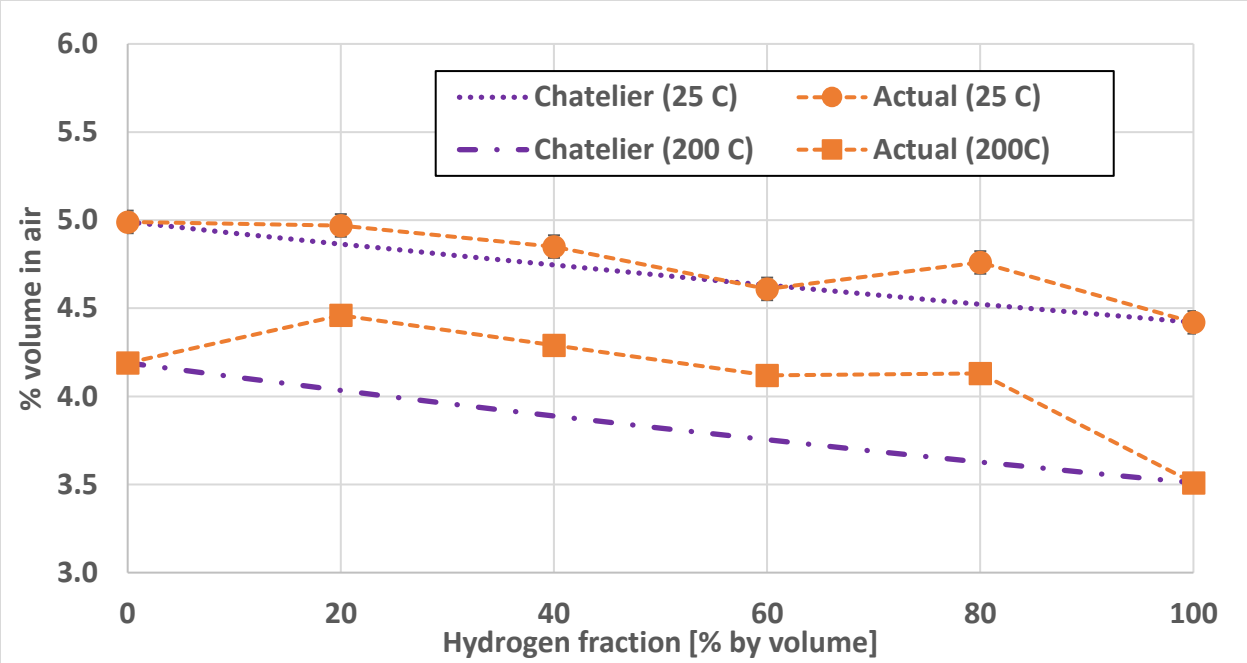

Figure 25: Comparison of methane/hydrogen/air LFL data with Le Chatelier estimates for P = 1 bar

Methane/hydrogen/air LFL data at $P = 1\ bar$ and related Le Chatelier estimates are plotted versus hydrogen fraction in Figure 25. The calculations using Le Chatelier's law are performed following the methods found in Section 4.1.5, and employ the LFL results of each individual energetic component (e.g. CH_4, H_2) found at the corresponding temperature and pressure condition. Due to the nature of Le Chatelier's law, the resulting behavior of the estimated LFL as a function of the concentration of hydrogen is almost linear as the law acts as a "weighted average". At $T = 25°C$, the experimental results follow the predicted LFL values closely, however, the uncertainty intervals for three of the data points do not coincide with the estimated values. The experimental results at $T = 200°C$ agree even less with the estimates provided by Le Chatelier's law. For all methane/hydrogen/air mixtures at this temperature, the predicted LFL values are approximately 0.42 vol % less than experimentally determined LFLs. Therefore, Le Chatelier's law predicts a wider flammable range for the fuel mixtures in question, more so at elevated temperatures. This result is contrary to a study by Wierzba & Ale, who investigated the

flammability limits of fuel (methane, ethylene, propane) mixtures involving hydrogen at elevated temperatures up to 350 °C (Wierzba & Ale 2000). In this study, Le Chatelier's Rule for estimating the flammability limits of multi-component gases agreed well at elevated temperatures, however, it was not clear whether the hydrogen concentration exceeded 70%. The estimated LFLs shown in Figure 25 do not exhibit this validity limit at a specific concentration of hydrogen since they do not agree well enough with the majority of the actual results found experimentally. Overall, at $P = 1\ bar$ and for all tested methane/hydrogen/air mixtures, Le Chatelier's law underestimates the LFL by approximately 0.11 vol % for $T = 25°C$, and by approximately 0.42 vol % for $T = 200°C$.

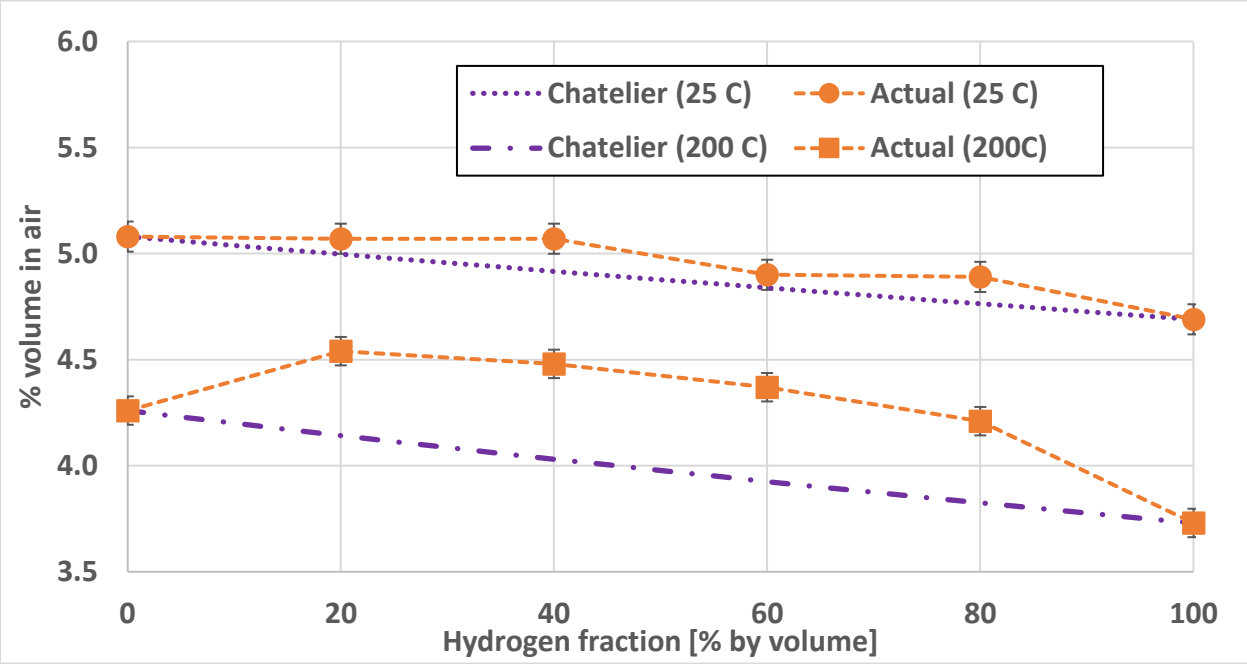

Figure 26: Comparison of methane/hydrogen/air LFL data with Le Chatelier estimates for P = 3 bar

To investigate the effect of pressure on Le Chatelier estimates, the previous comparison is repeated and presented for $P = 3\ bar$ (Figure 26), $P = 5\ bar$ (Figure 27), $P = 7\ bar$ (Figure 28) and for $P = 9\ bar$ (Figure 29). The results for $P = 3\ bar$ are almost identical to the results for $P = 1\ bar$, as Le Chatelier's law underestimates the average LFL by approximately 0.10 vol %

for $T = 25°C$, and by approximately 0.42 vol % for $T = 200°C$. An increase in pressure to 5 bar and 7 bar results in less accurate estimates and larger underestimation, especially at $T = 25°C$. For an initial pressure of $P = 5\ bar$, Le Chatelier's law underestimates the average LFL by approximately 0.18 vol % for $T = 25°C$, and by approximately 0.60 vol % for $T = 200°C$; while for $P = 7\ bar$, Le Chatelier's law underestimates the average LFL by approximately 0.26 vol % for $T = 25°C$, and by approximately 0.47 vol % for $T = 200°C$. Up to this point, it is shown that Le Chatelier's law provides increasingly inaccurate estimates for the LFL of methane/hydrogen/air mixtures as the initial pressure and temperature increase. However, the predicted LFL values also do not deviate from experimental values by more than 0.30 vol % for $T = 25°C$, therefore Le Chatelier's method would be possible to use as a rough predictive tool with these limitations in mind. In addition to being used as a predictive tool, the results for $P = 1\ bar$ to $P = 7\ bar$ for both test temperatures also suggest that Le Chatelier's law provides a consistent underestimation and could be suitable for determining a safe flammable range rather than estimating exact LFL values. Since the predicted values are less than the experimentally determined LFL values, the prediction results in a wider flammable range than actual, and so for methane/hydrogen/air mixtures under these conditions, it would be possible to propose the overestimate flammable range as a safe "rule of thumb" when flammability data for mixtures may not be readily available. Further analysis of the results at the final test pressure ($P = 9\ bar$) is required to finalize this claim for the data set of the current study and the also conclude the overall validity of Le Chatelier's law.

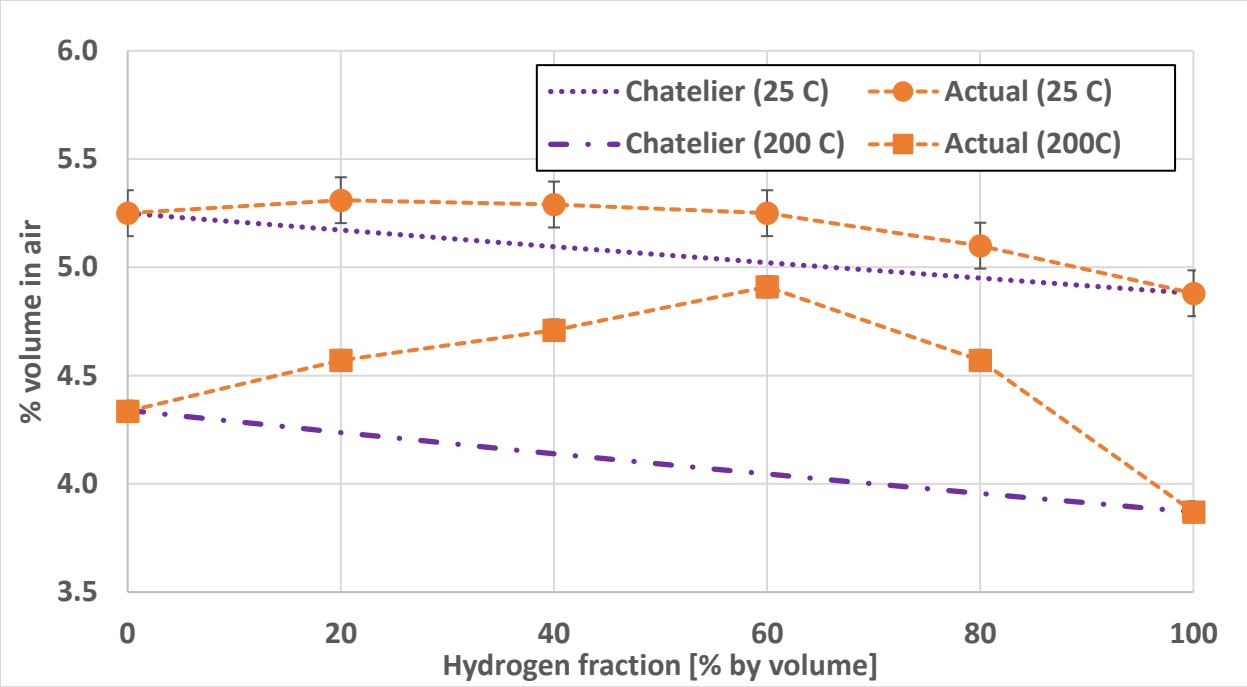

Figure 27: Comparison of methane/hydrogen/air LFL data with Le Chatelier estimates for P = 5 bar

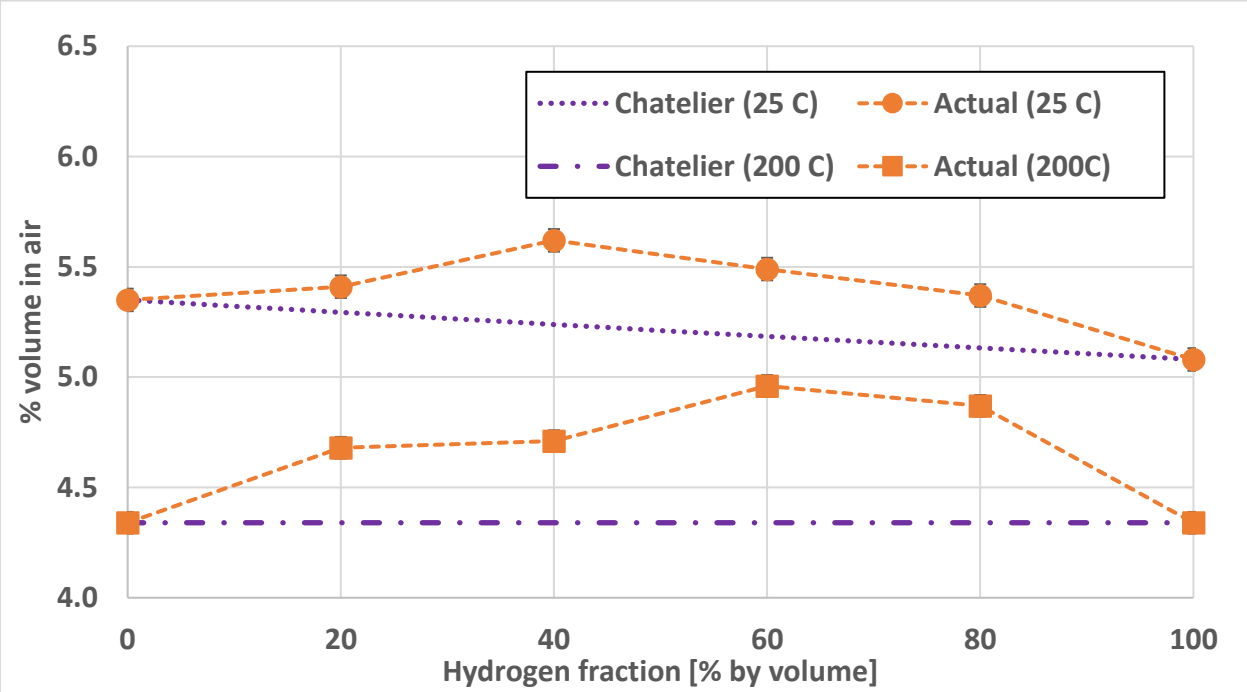

Figure 28: Comparison of methane/hydrogen/air LFL data with Le Chatelier estimates for P = 7 bar

The results for $P = 9\ bar$ differ from the results at other test pressures as Le Chatelier's law overestimates the LFL for certain concentrations of hydrogen when compared to the experimentally derived values (Figure 29). The predicted LFL values are in agreement with actual LFL data at $T = 25°C$, however, these values fall outside the calculated intervals of uncertainty. Despite this, the maximum deviation of the predicted values from the experimentally derived LFL values does not exceed 0.20 vol % and therefore Le Chatelier's law is as consistently accurate as with all other test pressures. For $P = 9\ bar$, Le Chatelier's law slightly overestimates the average LFL by approximately 0.03 vol % for $T = 25°C$, and slightly underestimates the average LFL by approximately 0.08 vol % for $T = 200°C$. At this latter temperature, the estimates provided by Le Chatelier's law are much closer than at lower pressure and thus this result is inconsistent with the previous analysis. Regardless of this result, Le Chatelier's law is not fully recommended for use at conditions of elevated temperature and pressure for methane/hydrogen/air mixtures.

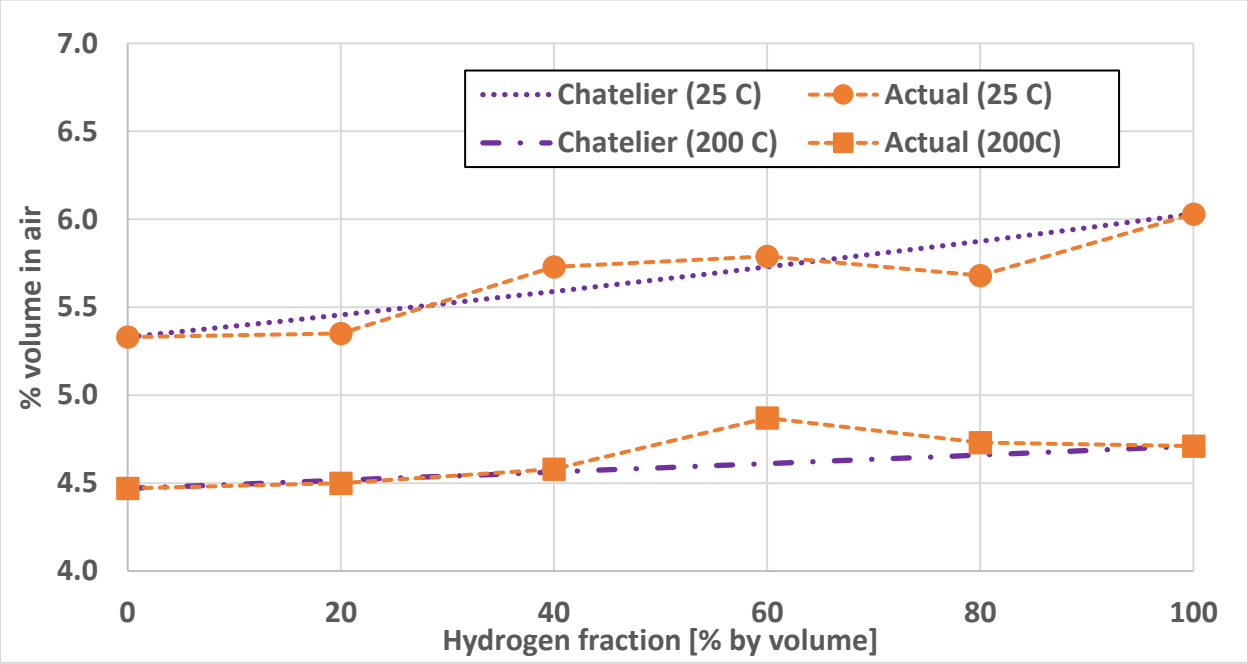

Figure 29: Comparison of methane/hydrogen/air LFL data with Le Chatelier estimates for P = 9 bar

To summarize, Le Chatelier's law is not a precise predictive method for determining the LFL of methane/hydrogen/air mixtures, although at low pressures and temperatures it provides close estimates approximately 0.1 vol % less than the experimentally derived values. For all test pressures $P = 1\ bar$ to $P = 9\ bar$ and for $T = 200°C$, Le Chatelier's law consistently underestimates the LFL on average 0.41 vol %. For $T = 25°C$, the effectiveness of Le Chatelier's law for predicting the LFL decreases with increasing pressure. The majority of the predicted LFL values were underestimations (wider flammable range than actual), which would be appealing as a safe, simple "rule of thumb" calculation; however, an overestimation occurs at to $P = 9\ bar$ and $T = 25°C$ and therefore application of Le Chatelier's law is not recommended at elevated conditions. It has been suggested by many authors that the presence of hydrogen in a gaseous mixture causes deviation in the effectiveness of Le Chatelier's law, and this consensus has been somewhat confirmed in the foregoing discussion, however similar investigations into different fuel blends (CH_4/CO_2 and H_2/CO) are necessary to come to a definitive conclusion (Ale et al. 1981; Wierzba & Kilchyk 2001; Law 2006).

The key conclusions for methane/hydrogen (CH_4/H_2) mixtures in air include:

- Similar to methane/air and hydrogen/air mixtures, all CH_4/H_2 mixtures exhibit an increase in the LFL with increasing pressure, and a decrease of the LFL with increasing temperature.
- An increase in the concentration of hydrogen in the fuel mixture results in a widening of the range of LFL values: From $P = 1\ bar$ to $P = 9\ bar$ and for $T = 25°C$, the LFL increases by 0.34 vol % for the 100/0 (% CH_4/% H_2) fuel blend, 0.38 vol % for the 80/20 fuel blend, 0.88 vol % for the 60/40 fuel blend, 1.18 vol % for the 40/60 fuel blend, 0.92 vol % for the 20/80 fuel blend, and 1.61 vol % for the 0/100 fuel blend.

- For $P = 1\ bar$, $P = 3\ bar$ and $P = 5\ bar$, and for $T = 25°C$, an increase in the hydrogen component of the fuel results in a decrease of the LFL; for $P = 7\ bar$ and for $T = 25°C$, the LFL tends to increase with increasing hydrogen fraction up to 40%, then decreases for larger concentrations of hydrogen; for $P = 9\ bar$ and for $T = 25°C$, an increase in the hydrogen component of the fuel results in an increase of the LFL.
- From $P = 1\ bar$ to $P = 9\ bar$ and for $T = 200°C$, the LFL increases by 0.28 vol % for the 100/0 (% CH_4/% H_2) fuel blend, 0.04 vol % for the 80/20 fuel blend, 0.29 vol % for the 60/40 fuel blend, 0.75 vol % for the 40/60 fuel blend, 0.60 vol % for the 20/80 fuel blend, and 1.20 vol % for the 0/100 fuel blend.
- For $P = 1\ bar$ and $P = 3\ bar$, and for $T = 200°C$, an increase in the hydrogen component up to 20% of the fuel results in an increase of the LFL, followed be a decrease in the LFL for larger concentrations of hydrogen thereafter; for $P = 5\ bar$, $P = 7\ bar$ and $P = 9\ bar$, and for $T = 200°C$, the LFL tends to increase with increasing hydrogen fraction up to 60%, then decreases for larger concentrations of hydrogen.
- Le Chatelier's law provides close estimates approximately 0.1 vol % less than the experimentally derived values for near atmospheric conditions.
- Le Chatelier's law underestimates the LFL for all test mixtures and for all pressure and temperature conditions, except for $P = 9\ bar$ and $T = 25°C$; it is not recommended for use as a prediction tool to determine the LFL of methane/hydrogen/air mixtures at elevated temperature and/or pressure conditions.

5.1.4 LFL of Hydrogen/Carbon Monoxide/Air Mixtures

The results for the dependence of pressure and temperature on the lower flammability limit (LFL) for hydrogen/carbon monoxide (H_2/CO) mixtures in air are provided in Figure 30.

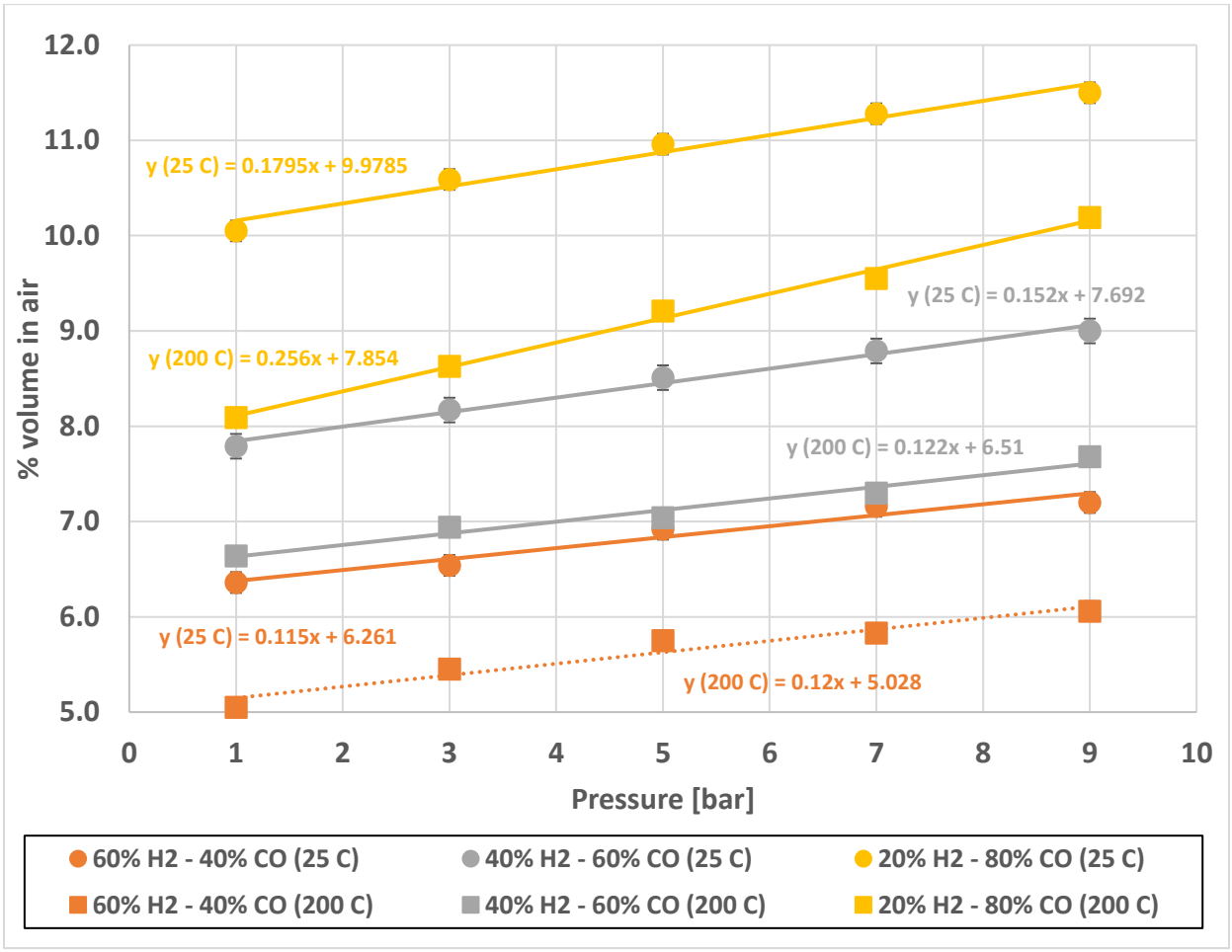

Figure 30: Dependence of temperature and pressure on the LFL of hydrogen/carbon monoxide/air mixtures

In contrast to the results for methane/hydrogen/air mixtures, the effect of fuel composition on the LFL of hydrogen/carbon monoxide mixtures is clear and distinct. The reason for this is due to the widely different combustion characteristics of hydrogen and carbon monoxide as individual gaseous fuels. At atmospheric conditions, the reported LFL value for hydrogen is approximately 4.0 vol % while the reported LFL value for carbon monoxide is about 12.5 vol %. The results

clearly show that the addition of hydrogen results in a much lower LFL value, and consequently a wider flammable range; this is true at all experimental values for a given initial test pressure.

Regarding the effect of pressure on the LFL of H_2/CO fuel mixtures in air, all three fuel splits (60/40, 40/60 and 20/80) exhibited a linear increase of the LFL with pressure at both initial test temperatures. Each linear trend is confirmed because it does not deviate from the data points more than the respective experimental uncertainty of each data set (with the slight exception of the trend line for the 60/40 blend at $T = 200°C$, which deviates by only 0.018 vol% or 0.3% of the LFL value at $P = 5\ bar$): for $T = 25°C$, the interval of uncertainty is approximately ±0.109 vol % for the 60/40 (% H_2/% CO) blend, approximately ±0.129 vol % for the 40/60 blend, and approximately ±0.108 vol % for the 20/80 blend; for $T = 200°C$, the interval of uncertainty is approximately ±0.104 vol % for the 60/40 (% H_2/% CO) blend, approximately ±0.081 vol % for the 40/60 blend, and approximately ±0.093 vol % for the 20/80 blend. The specific amount of increase of the LFL per increase of pressure is determined from the slope of the linear trend lines: for $T = 25°C$, the increase of the LFL per 1 bar of pressure is +0.115 vol % for the 60/40 blend, +0.152 vol % for the 40/60 blend, and +0.180 vol % for the 20/80 blend; for $T = 200°C$, the increase of the LFL per 1 bar of pressure is +0.120 vol % for the 60/40 blend, +0.122 vol % for the 40/60 blend, and +0.256 vol % for the 20/80 blend. It is evident that an increase in the amount of hydrogen in the fuel results in a decrease of the "slope" or unit change/increase of the LFL as a function of pressure.

Overall, the complete LFL data set for syngas (H_2/CO) as the fuel for the current study as shown in Figure 30 can be condensed to an empirical formula provided in Table 7. The formula was derived from the specific trend line equations previously determined and displayed in Figure 30, assuming also a linear relationship with respect to temperature to help determine the $f(T)$ and

$g(T)$ functions. The derived formula can be used to calculate the experimentally determined LFL values of the current study but can also extend to intermediate temperatures and pressures within the scope of this study ($25°C < T < 200°C$, $1\ bar < P < 9\ bar$). Further flammability tests for the syngas/air mixtures and blends in question are required to fully validate this formula, and to also confirm its validity outside of the scope of this study.

$\boldsymbol{LFL_{syngas} = f(T) \cdot P + g(T) = [a \cdot T + b] \cdot P + c \cdot T + d;\ T = [C];\ P = [bar]}$				
% H_2 / % CO	$\boldsymbol{a}$	$\boldsymbol{b}$	$\boldsymbol{c}$	$\boldsymbol{d}$
20/80	4.3714×10^{-4}	1.6857×10^{-1}	-1.214×10^{-2}	$1.0282 \times 10^{+1}$
40/60	-1.7143×10^{-4}	1.5629×10^{-1}	-6.7543×10^{-3}	7.8609×10^{0}
60/40	2.8571×10^{-5}	1.1429×10^{-1}	-7.0457×10^{-3}	6.4371×10^{0}

Table 7: Empirical relationship for the LFL of syngas/air mixtures as a function of temperature and pressure

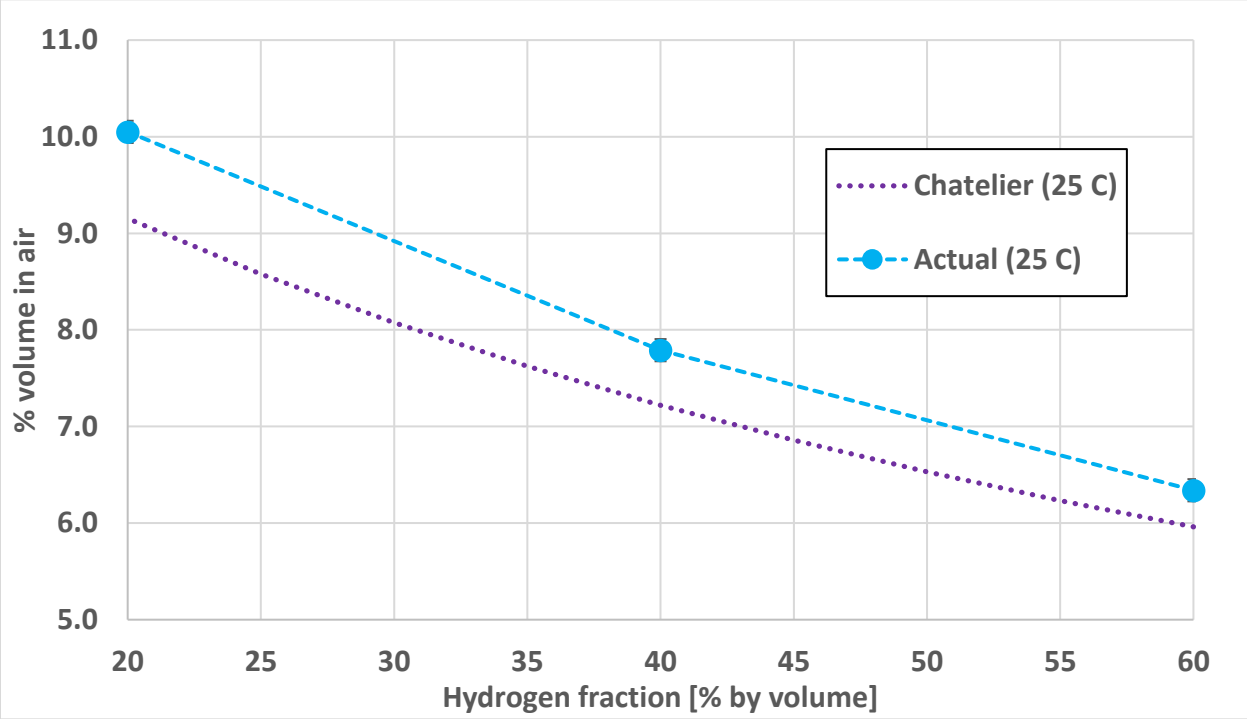

Figure 31: Comparison of hydrogen/carbon monoxide/air LFL data with Le Chatelier estimates; P = 1 bar, T = 25°C

Hydrogen/carbon monoxide/air LFL data and Le Chatelier estimates at $P = 1\ bar$ and $T = 25°C$ are plotted versus hydrogen fraction in Figure 31. It should be noted that the LFL of pure carbon monoxide (CO) is needed to calculate estimated LFL values using Le Chatelier's law, however, these values are outside of the scope of the current study. The predicted values plotted in Figure 31 use the literature LFL value for carbon monoxide of 12.5 vol %, which is only applicable at ambient conditions of temperature and pressure.

For the three fuel blends tested, the estimated LFLs calculated using Le Chatelier's law closely follow the general trend of the actual, experimentally-derived values, which is a decrease of the LFL with increasing amounts of hydrogen in the fuel mixture. The predicted values are on average 0.62 vol % less than the actual LFL values, which is a deviation slightly larger than that of methane/hydrogen/air mixtures at the same test temperature and pressure. Taking this underestimation into consideration, it is determined that the estimates found using Le Chatelier's law are sufficiently accurate as a predictive tool. As previously mentioned for methane/hydrogen/air mixtures, this underestimation can be appealing if Le Chatelier's law is to be used as a quick and simple calculation when data are not available, as it provides a wider (safer) flammable range than actual. However, the above results for hydrogen/carbon monoxide/air mixtures are presented for atmospheric conditions only, and are only applicable at these conditions if a predictive method for determining the lean flammability limit is desired. To reiterate, the claim that many authors make regarding the presence of hydrogen in a gaseous mixture as the cause of deviation in the effectiveness of Le Chatelier's law is further supported by the results of both CH_4/H_2 and H_2/CO mixtures (Ale et al. 1981; Wierzba & Kilchyk 2001; Law 2006). The results for methane/carbon dioxide/air mixtures in the following section will be necessary to come to a conclusion regarding these claims.

The key conclusions for hydrogen/carbon monoxide (H_2/CO) mixtures in air include:

- From $P = 1\ bar$ to $P = 9\ bar$: for $T = 25°C$, the LFL increased by 0.84 vol % for the 60/40 (H_2/CO) fuel blend, 1.21 vol % for the 40/60 fuel blend, and 1.45 vol % for the 20/80 fuel blend; for $T = 200°C$, the LFL increased by 1.01 vol % for the 60/40 (H_2/CO) fuel blend, 1.04 vol % for the 40/60 fuel blend, and 2.10 vol % for the 20/80 fuel blend.
- For test mixtures at $T = 25°C$, the LFL increased linearly with pressure +0.115 vol % per increase of 1 bar of pressure for the 60/40 blend, +0.152 vol % per increase of 1 bar of pressure for the 40/60 blend, and +0.180 vol % per increase of 1 bar of pressure for the 20/80 blend; at $T = 200°C$, the LFL increased linearly with pressure +0.120 vol % per increase of 1 bar of pressure for the 60/40 blend, +0.122 vol % per increase of 1 bar of pressure for the 40/60 blend, and +0.256 vol % per increase of 1 bar of pressure for the 20/80 blend.
- An empirical formula was derived for calculating the LFL of all syngas/air test mixtures at the specific test pressure and temperature conditions investigated in the current study.
- Le Chatelier's law provided a relatively close estimate, approximately 0.62 vol % less than the experimentally derived values at atmospheric temperature and pressure.
- Le Chatelier's law underestimates the LFL for all test mixtures at ambient temperature and pressure, however it is not recommended for use as a prediction tool to determine the LFL of hydrogen/carbon monoxide/air mixtures at elevated temperature and/or pressure conditions.

5.1.5 LFL of Methane/Carbon Dioxide/Air Mixtures

The results for the dependence of pressure and temperature on the lower flammability limit (LFL) for methane/carbon dioxide (CH_4/CO_2) mixtures in air are provided in Figure 32.

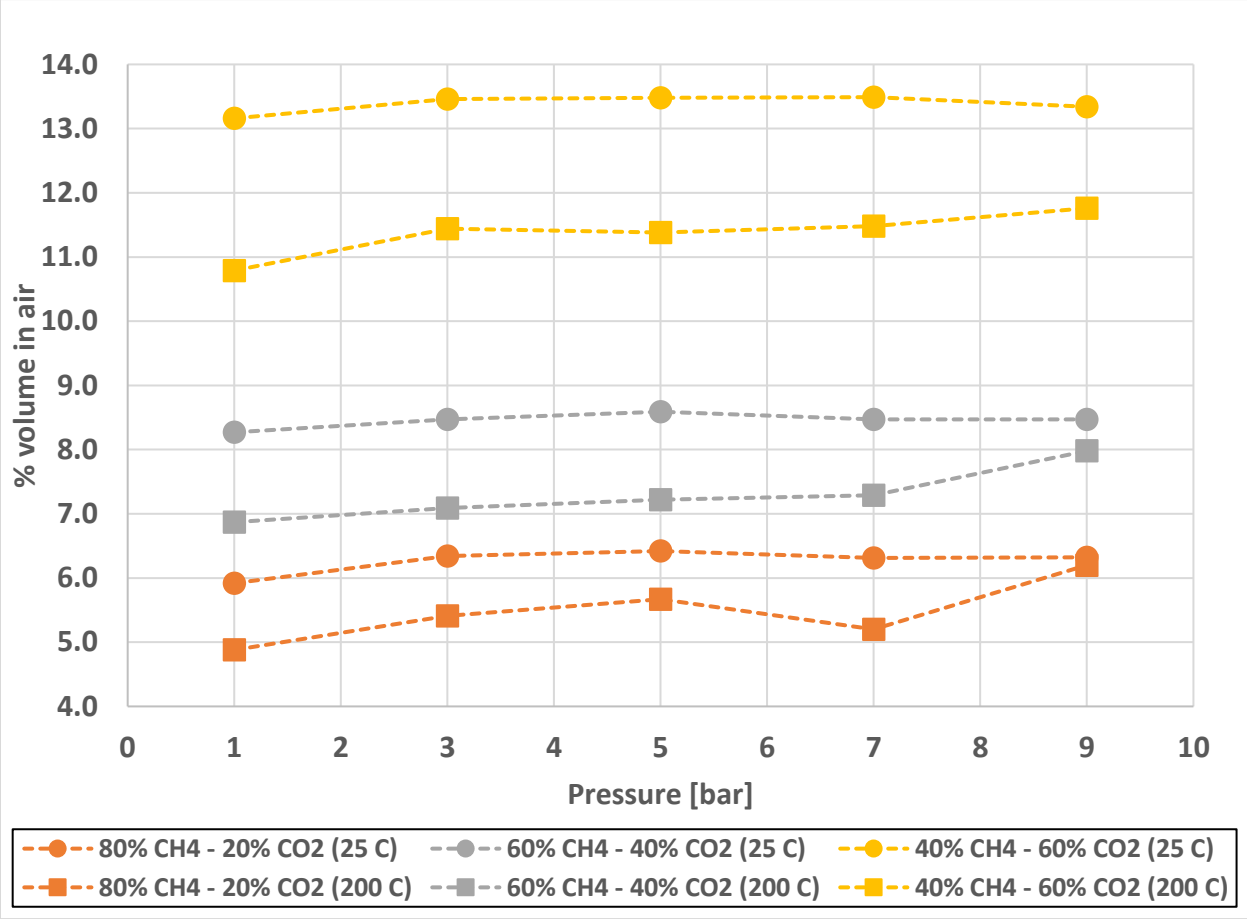

Figure 32: Dependence of temperature and pressure on the LFL of methane/carbon dioxide/air mixtures

The methane/carbon dioxide set of fuel mixtures is unique in the current study as it is the only fuel combination that contains a diluent (CO_2) component. An expected result that can be seen in the figure above is the decrease of the flammable range (increase in the LFL) with an increase in the diluent component. The dependence of pressure on the LFL for these mixtures differs from the dependence observed for the previously tested mixtures containing hydrogen. The aforementioned results for methane/hydrogen/air and hydrogen/carbon monoxide/air mixtures

both exhibited an increase in the LFL with increasing initial pressure; however, this was not as evident in the results for methane/carbon dioxide/air mixtures. Figure 32 shows a weak dependence of pressure on the LFL of CH_4/CO_2 fuel mixtures at $T = 25°C$. From $P = 1\ bar$ to $P = 9\ bar$ at $T = 25°C$, the LFL increases by approximately 0.40 vol % for the 80/20 (% H_2/ % CO) fuel blend, 0.20 vol % for the 60/40 fuel blend, and 0.18 vol % for the 40/60 fuel blend. The dependence of pressure on the LFL of CH_4/CO_2 fuel mixtures at $T = 200°C$ is slightly larger. From $P = 1\ bar$ to $P = 9\ bar$ at $T = 200°C$, the LFL increases by approximately 1.32 vol % for the 80/20 fuel blend, 1.11 vol % for the 60/40 fuel blend, and 0.97 vol % for the 40/60 fuel blend. The influence of temperature on the LFL of CH_4/CO_2 fuel mixtures increases as the concentration of methane in the fuel decreases (carbon dioxide increases). The average decrease of the LFL for CH_4/CO_2 mixtures due to a change of temperature from $T = 25°C$ to $T = 200°C$ is approximately 0.79 vol % for the 80/20 fuel blend, 1.16 vol % for the 60/40 fuel blend, and 2.02 vol % for the 40/60 fuel blend.

Methane/carbon dioxide/air LFL data and Le Chatelier estimates for both $T = 25°C$ and $T = 200°C$ are plotted versus methane fraction in Figure 33 for $P = 1\ bar$, Figure 34 for $P = 3\ bar$, Figure 35 for $P = 5\ bar$, Figure 36 for $P = 7\ bar$, and Figure 37 for $P = 9\ bar$. Previous comparisons using Le Chatelier's law used hydrogen as a reference for plotting the estimates. For CH_4/CO_2 fuel mixtures, methane will be used as the reference since it is the only energetic in the fuel. For $P = 1\ bar$, Le Chatelier's law approximates the LFL well for all CH_4/CO_2 tested mixtures at both $T = 25°C$ and $T = 200°C$. The largest deviation, approximately 0.68 vol %, occurs for the 40/60 fuel blend, while the LFL values for the 80/20 fuel blend are slightly overestimated by approximately 0.32 vol %. Overall, the predicted LFL provides close approximations for the mixtures in questions at $P = 1\ bar$ and at both $T = 25°C$ and $T = 200°C$,

however further testing is needed to validate the agreement of the predicted values with all mixtures in the range of 40% CH_4/ 60% CO_2 and 80% CH_4/ 20% CO_2.

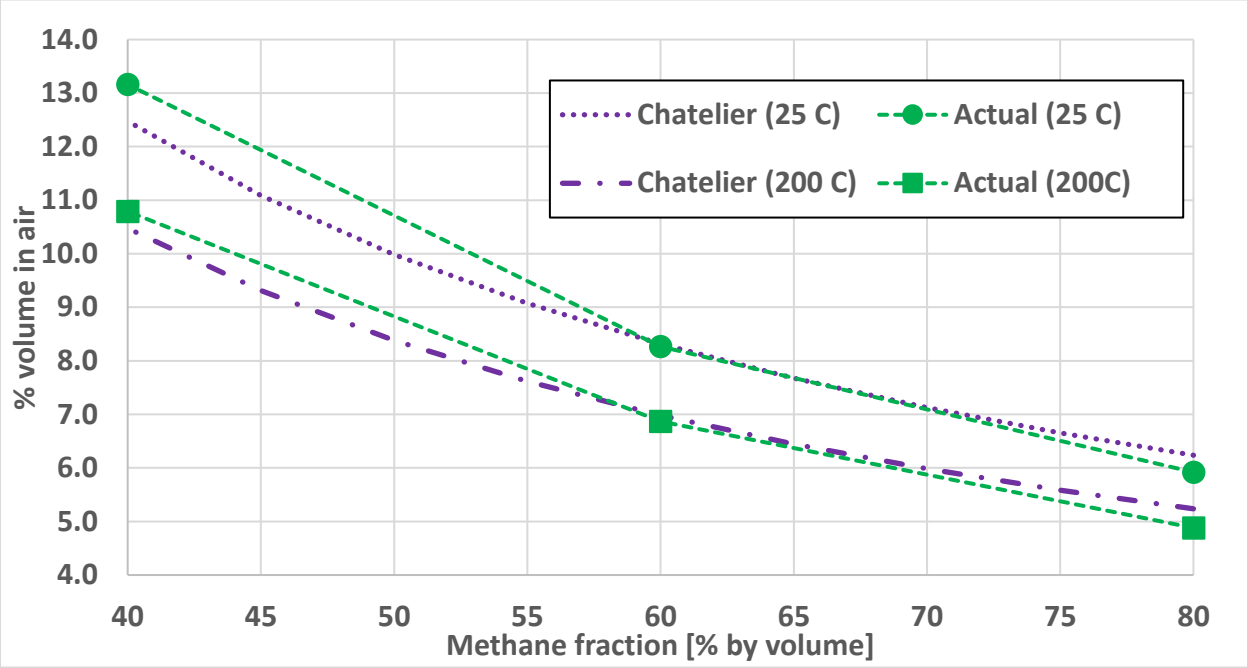

Figure 33: Comparison of methane/carbon dioxide/air LFL data with Le Chatelier estimates for P = 1 bar

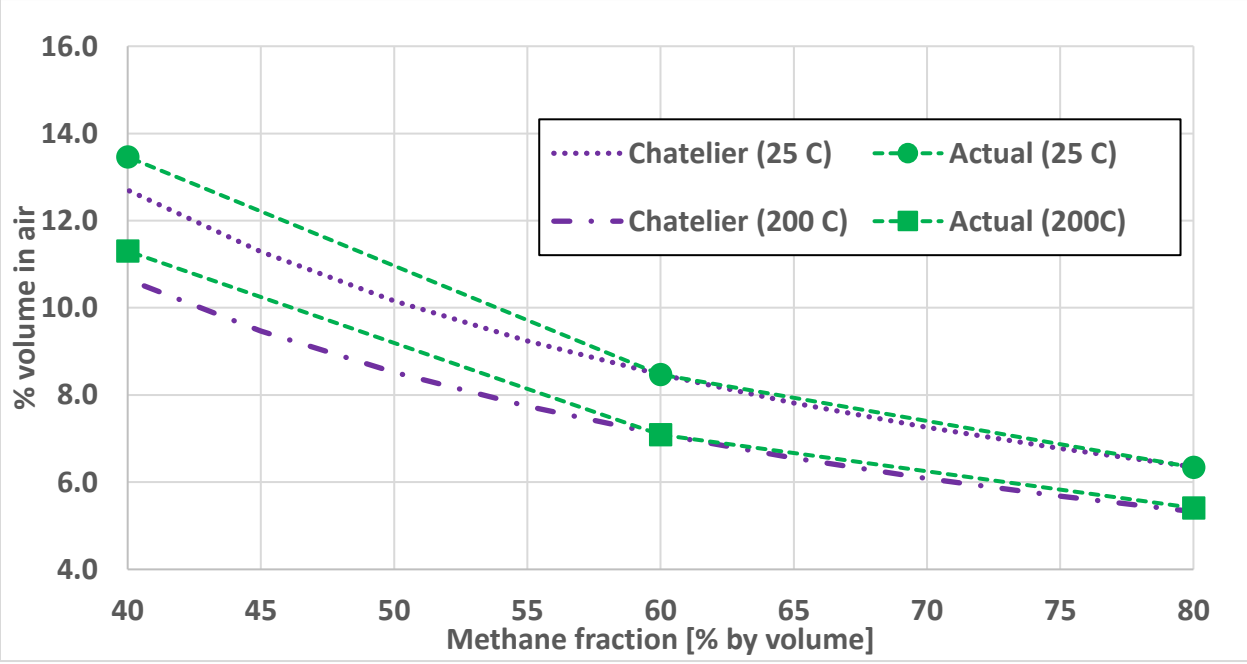

Figure 34: Comparison of methane/carbon dioxide/air LFL data with Le Chatelier estimates for P = 3 bar

The results for $P = 3\ bar$ at both $T = 25°C$ and $T = 200°C$ in the figure above agree more with the predicted values using Le Chatelier's law than for the previous results at $P = 1\ bar$. The LFL values predicted for the 80/20 (CH_4/CO_2) fuel blend are no longer overestimated, however the results for the 40/60 fuel blend differ by a slightly larger amount. At $P = 5\ bar$ (Figure 35), the difference between the estimated LFL values and the experimentally-derived values at $T = 25°C$ is the smallest compared to the results at other test pressures, and therefore the most accurate prediction, with an average difference of 0.02 vol %.

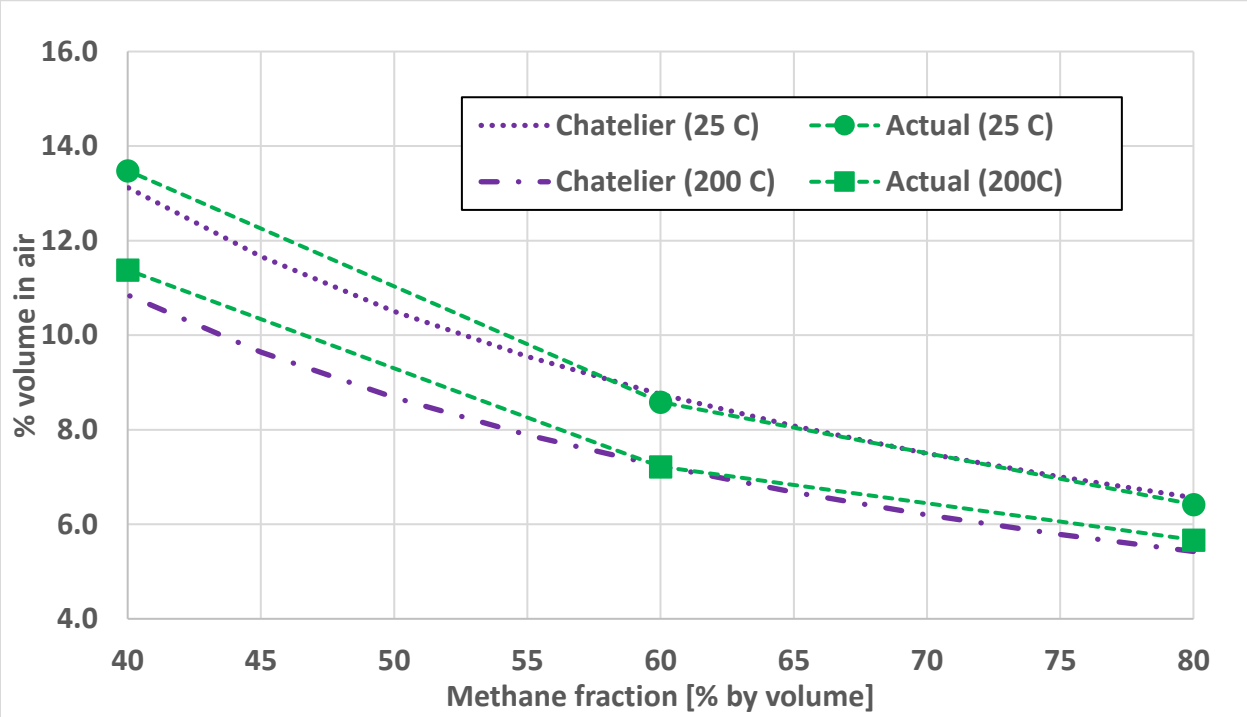

Figure 35: Comparison of methane/carbon dioxide/air LFL data with Le Chatelier estimates for P = 5 bar

The results for $P = 7\ bar$ (Figure 36) and for $P = 9\ bar$ (Figure 37) show that Le Chatelier estimates now overestimate the LFL value for both the 60/40 and 80/20 fuel blends at $T = 25°C$. This result is similar to the result for CH_4/H_2 fuel mixtures where an overestimation occurred at an elevated pressure of $P = 9\ bar$. Although Le Chatelier provides accurate LFL values for all test pressures at $T = 200°C$, a relatively large deviation of approximately 0.58 vol

% occurs at $P = 9\ bar$. Overall, Le Chatelier's law performed better at predicting LFL values for CH_4/CO_2 fuel mixtures than the other fuel blends tested, however, concerns for its use arose at elevated pressure and temperature conditions as was also the case for CH_4/H_2 and H_2/CO mixtures.

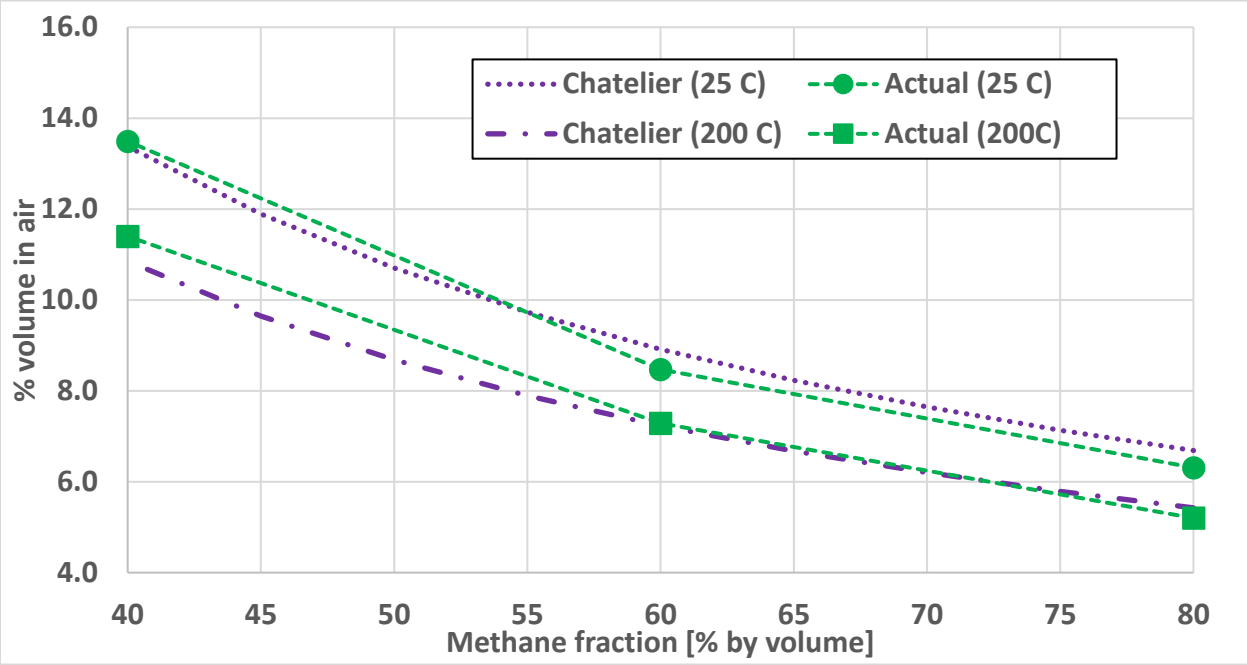

Figure 36: Comparison of methane/carbon dioxide/air LFL data with Le Chatelier estimates for P = 7 bar

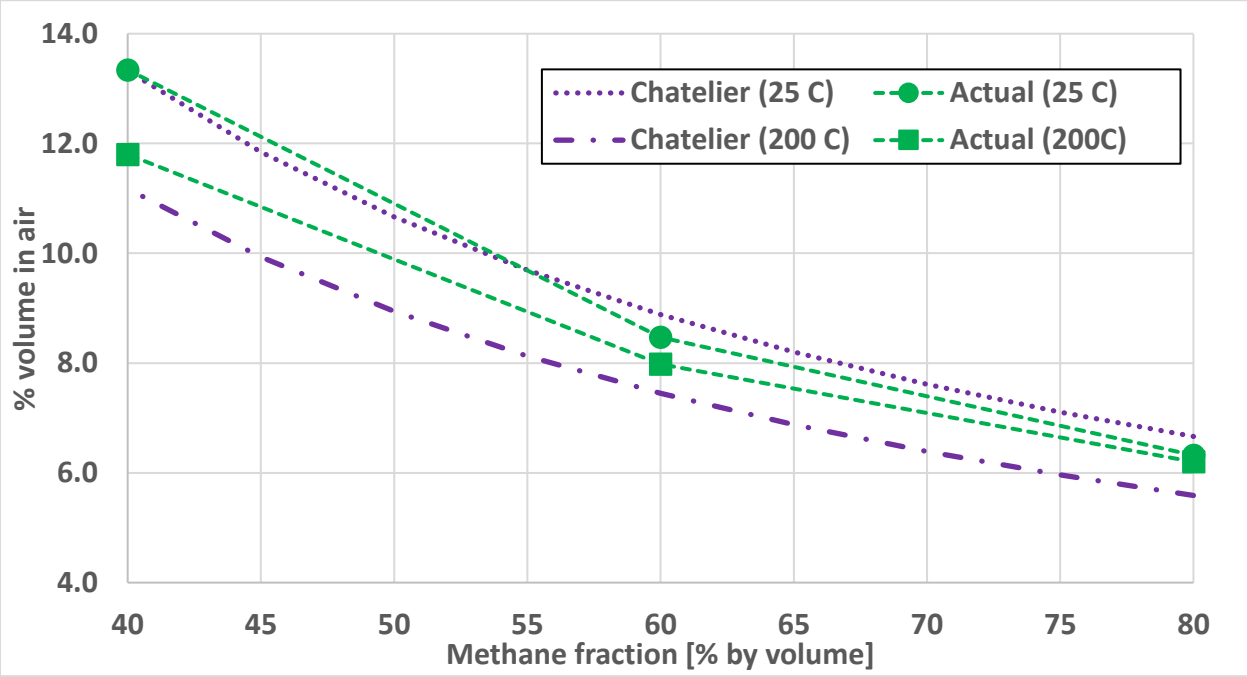

Figure 37: Comparison of methane/carbon dioxide/air LFL data with Le Chatelier estimates for P = 9 bar

The key conclusions for methane/carbon dioxide (CH_4/CO_2) mixtures in air include:

- From $P = 1\ bar$ to $P = 9\ bar$ and for $T = 25°C$, the LFL increased by 0.40 vol % for the 80/20 (CH_4/CO_2) fuel blend, 0.20 vol % for the 60/40 fuel blend, and 0.18 vol % for the 40/60 fuel blend.
- From $P = 1\ bar$ to $P = 9\ bar$ and for $T = 200°C$, the LFL increased by 1.32 vol % for the 80/20 fuel blend, 1.11 vol % for the 60/40 fuel blend, and 0.97 vol % for the 40/60 fuel blend.
- Across all test pressures, the average decrease due to a change of temperature from $T = 25°C$ to $T = 200°C$ is approximately 0.79 vol % for the 80/20 fuel blend, 1.16 vol % for the 60/40 fuel blend, and 2.02 vol % for the 40/60 fuel blend.
- Le Chatelier's law provides a relatively close estimate for both $T = 25°C$ and $T = 200°C$ at low initial test pressures.
- Le Chatelier's law provides sufficiently accurate LFL values for all test mixtures, except at $P = 7\ bar$ and $P = 9\ bar$ for $T = 25°C$, and at $P = 9\ bar$ for $T = 200°C$; it is not recommended for use as a prediction tool to determine the LFL of methane/carbon dioxide/air mixtures at elevated temperature and/or pressure conditions.

5.2 NUMERICAL RESULTS

5.2.1 LFL of Methane/Air

The numerical results for the dependence of temperature and pressure on the lower flammability limit (LFL) for pure methane (CH_4) in air are provided in Figure 38. The experimentally determined LFL values of the current study are also plotted for comparison.

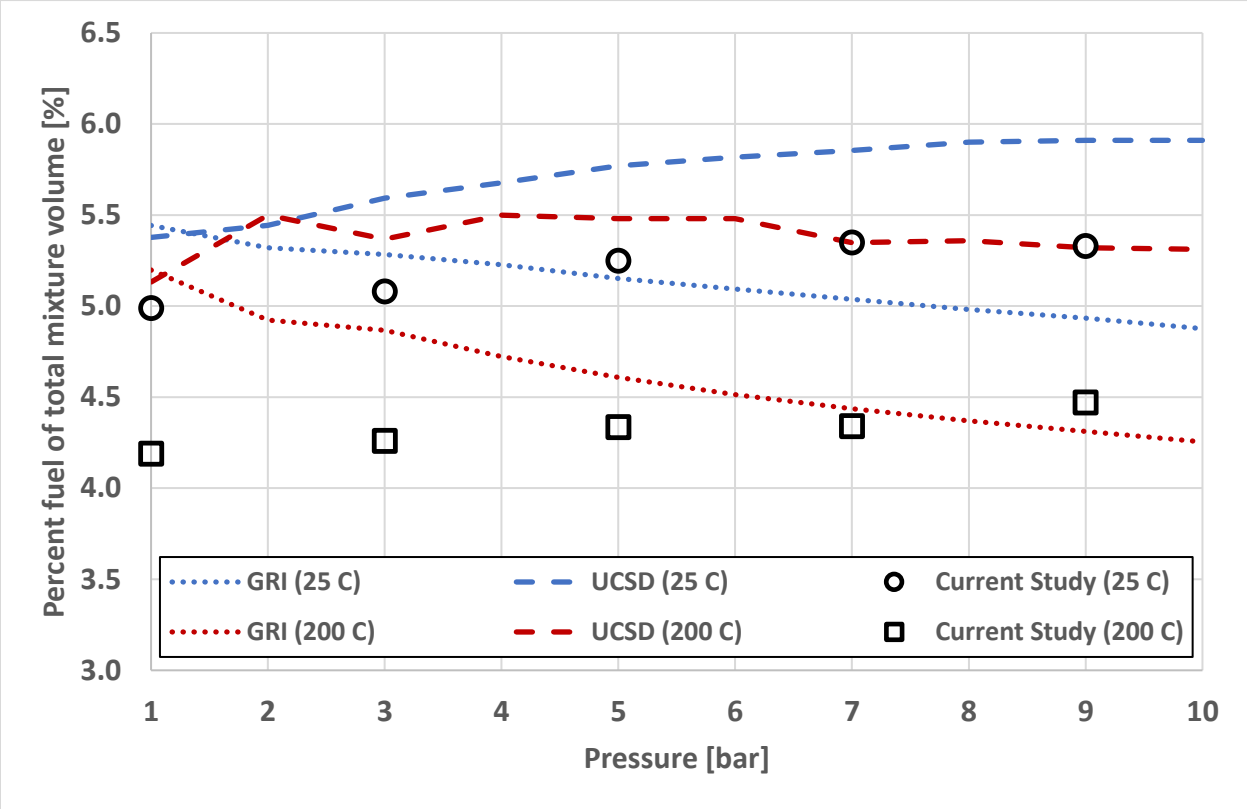

Figure 38: Comparison of methane/air LFL data with numerical calculations using GRI and UCSD mechanisms

For the LFL results at $T = 25°C$, the numerically determined values using the CECR-UCSD mechanism agreed best with capturing the influence of pressure on the LFL when compared to the experimentally determined values. The CHEMKIN flame speed model was able to predict the behavior of the LFL for methane for all test pressures and for $T = 25°C$, but on average the model overestimated the actual LFL value by approximately 0.50 vol %. Across the test pressure

range from $P = 1$ bar to $P = 9$ bar, and for $T = 25°C$, the average LFL value using the GRI-Mech 3.0 mechanism was nearly identical to the actual value (5.17 vol % versus 5.20 vol %). However, the differences in the methane oxidation chemistry of the GRI mechanism when compared to the UCSD mechanism results in an inversely proportional relationship of the LFL with respect to initial pressure, which is contrary to the previously discussed experimental results.

The LFL results for $T = 200°C$ are similar in that the GRI mechanism best simulates the magnitude of the LFL when compared to the current study, while the UCSD mechanism is able to capture the increase in the LFL due to an increase in pressure that was observed in the experiments. It should be noted however that the accuracy of the flame speed model decreases with this increase in initial temperature. The average overestimation of the LFL value using the UCSD mechanism increases to approximately 1.01 vol %, while the LFL is overestimated by approximately 0.37 vol % when the GRI mechanism is used. An argument against use of the UCSD mechanism can be made relative to its resultant behavior following an increase in the initial temperature. The experimental results consistently showed an overall decrease of the LFL for each fuel/air mixture tested, and at all pressure conditions; this is contrary to the result found using the UCSD mechanism at $P = 2$ bar where an increase in the LFL is observed with an increase in temperature from $T = 25°C$ to $T = 200°C$. Overall, the CHEMKIN flame speed model introduced in Section 4.2 was able to provide reasonable numerical LFL values for methane/air mixtures at elevated conditions with the use of two different reaction mechanisms. Further investigation into each mechanism is required in order to fully develop a reliable model that agrees with the experimentally derived LFL values with respect to magnitude of the values, as well as with accurately exhibiting the influence of elevated temperatures and pressures on the LFL.

5.2.2 UFL of Hydrogen/Air

The results presented in this section address only the influence of temperature and pressure on the upper flammability limit (UFL) rather than lower flammability limit (LFL) due to issues that were experienced with the CHEMKIN flame speed model that were related to lean hydrogen (H2) combustion. The physics of lean H2 combustion differ significantly with those of typical light hydrocarbons fuels, as interactions between thermo-diffusive effects attributed to the combined Lewis number (ratio of thermal and mass diffusivity) and preferential diffusion and stretch of laminar-premixed flames strongly affect the properties of premixed flames. Brower et al. experienced difficulty calculating laminar flame speed for natural gas/hydrogen blends at elevated pressures when the equivalence ratio was less than 0.5, while Natarajan et al. reported the largest discrepancies in laminar flame speed at fairly lean equivalence ratios of 0.6-0.8 while investigating the pressure and preheat dependence of laminar flame speeds of syngas/diluent mixtures (Brower et al. 2012; Natarajan et al. 2007; Natarajan et al. 2009). For syngas combustion, Natarajan et al. (2007) observed underestimations as large as 10% to 15% for lean equivalence ratios less than 0.6 when comparing measurements with GRI model results. In comparison, an expected LFL value of 4.0 vol % corresponds to an equivalence ratio of approximately 0.1 which would be considered extremely lean. Use of the CHEMKIN laminar flame speed model developed for the current study to determine the LFL was only able to achieve an equivalence ratio of 0.33 (approximately 12 vol %) as the leanest condition with a convergent flame speed calculation; this result was 3 times larger than the experimental value and so the model was deemed unsuitable for predictive use at this stage. In order to still investigate use of the CHEMKIN flame speed model for use in the determination of flammability limits, numerical calculations were performed for the appropriate test parameters for temperature and pressure of the current study with the goal of

characterizing the upper flammability limit for hydrogen/air mixtures. It was appropriate to adopt a mechanism tailored for hydrogen and syngas (hydrogen/carbon monoxide) combustion in air, and so the Hydrogen/Syngas mechanism developed by NUI Galway was used for the determination of the UFL for pure hydrogen/air mixtures at elevated initial conditions.

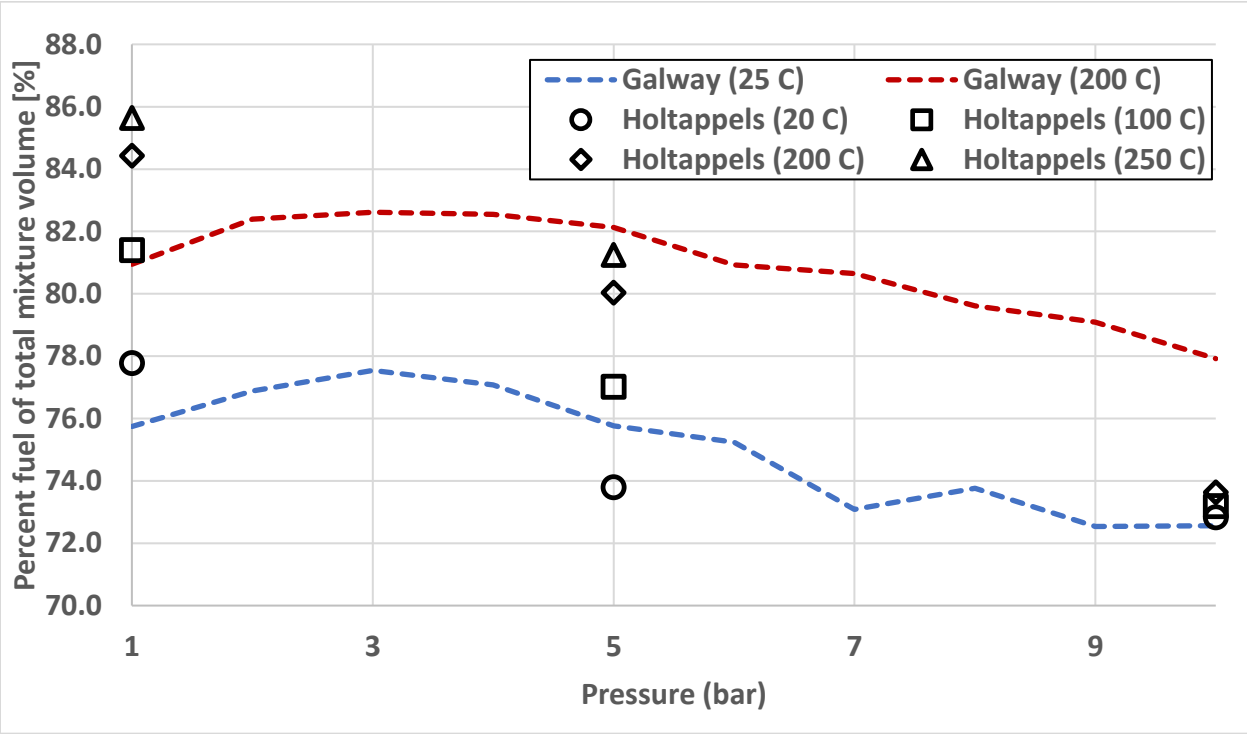

Figure 39: Comparison of hydrogen/air UFL data with numerical calculations using NUI Galway mechanism

The numerical results for the dependence of temperature and pressure on the upper flammability limit (UFL) for pure hydrogen (H_2) in air are provided in Figure 39. All experimental tests conducted for the current study only focused on determination of the LFL; therefore, in order to validate the CHEMKIN flame speed model for accuracy, UFL data provided by Holtappels (2006) are also plotted for comparison in Figure 39. In general, the influence of temperature and pressure on the UFL for hydrogen/air mixtures is consistent for both the literature UFL data as

well as the numerical model results. An increase in temperature results in an increase of the UFL or equivalently an increase in the flammable range, while an increase in pressure results in a decrease of the UFL or equivalently a decrease of the flammable range. The numerical model is most accurate at room temperature ($T = 25°C$), at most deviating from the literature data by 2.04 vol %, while at a temperature of $T = 200°C$ the numerical model differs at most by 4.19 vol %. Although these values may seem large, relative to the average UFL values for the hydrogen/air mixtures in question these discrepancy values correspond to small differences of 2.72% and 5.41%, respectively. Overall, the CHEMKIN flame speed model was validated alongside literature data for use in the determination of the UFL for hydrogen/air mixtures at elevated temperatures and pressures, confirming the accuracy of the NUI Galway mechanism for hydrogen combustion. As was the case for the flame speed results for methane/air, further investigation is necessary for improving the model to minimize the difference between the numerically derived results and the experimental/literature flammability limit data.

5.2.3 LFL of Methane/Carbon Dioxide/Air Mixtures

The numerical results for the dependence of pressure on the lower flammability limit (LFL) for 80/20 (% CH_4/% CO_2) biogas fuel blend in air are provided in Figure 40. Due to the similarity between this 80/20 biogas fuel blend and pure methane, the results shown in the figure below closely resemble the results shown in Figure 38. The influence of pressure on the LFL for this biogas mixture is captured only by the UCSD reaction mechanism, however this mechanism results in the largest discrepancy with the experimental values. Using the UCSD mechanism, the average difference between the LFL results of the numerical model and the experimentally derived values is approximately 0.58 vol %; the GRI mechanism however provides LFL values much closer to the experimental values on average, only differing by approximately 0.01 vol %.

Comparing the results of Figure 38 and Figure 40 directly confirms that the addition of carbon dioxide had a larger negative impact on the accuracy of the CHEMKIN flame speed model using the UCSD mechanism versus the GRI mechanism. With this insight, it is recommended to investigate a reduced mechanism primarily based on GRI-Mech 3.0 but incorporating the specific reactions/species from the UCSD mechanism that correctly result in capturing the effect of pressure at the lean flammability limit. The CHEMKIN flame speed model developed in the current study is altogether preliminary, but the results discussed in the foregoing results/discussion section provide significant understanding that can serve as a basis for completely developing a numerical tool for the precise determination of the flammability limits and the influence of elevated temperature and pressure on these limits.

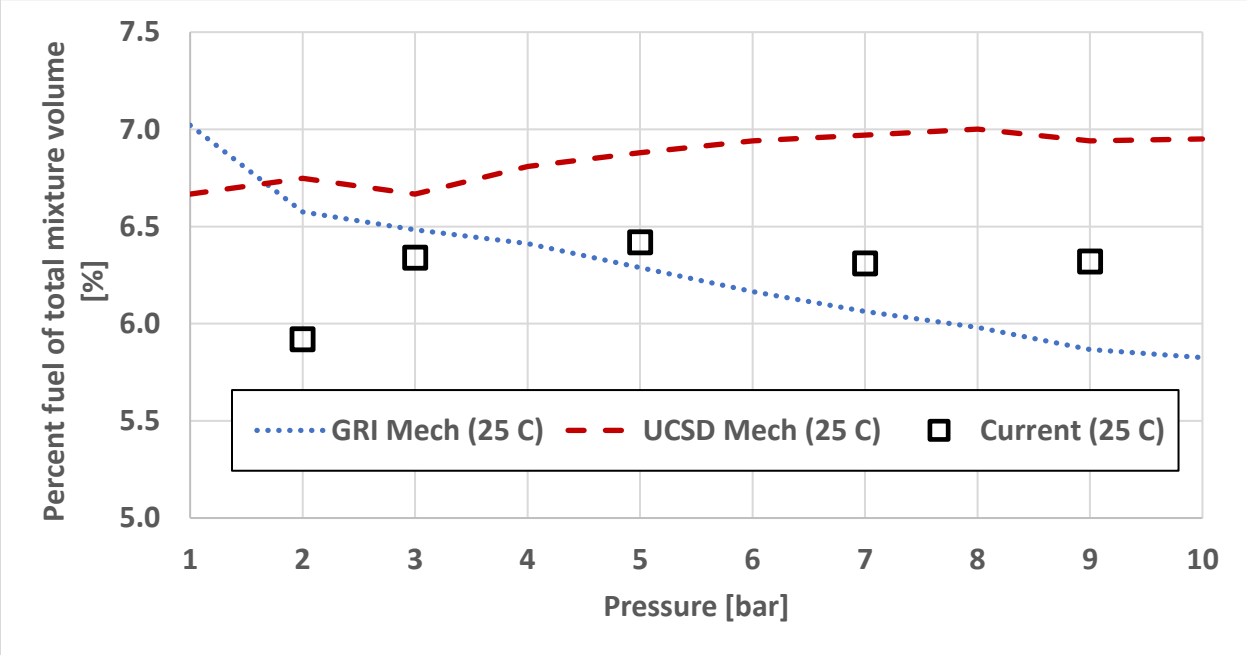

Figure 40: Comparison of biogas/air (80% CH_4/20% CO_2) LFL data with numerical calculations using GRI and UCSD mechanisms

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 SUMMARY

Various methods were investigated throughout this work, and an experimental and numerical method were developed in an effort to characterize the lean flammability limits of methane, hydrogen, carbon monoxide, in addition to mixtures of these gases (i.e. CH_4/H_2, H_2/CO, and CH_4/CO_2). These methods were specifically designed to also determine the influence of initial temperature and pressure on these flammability limits, and the resultant flammability data was compared with available literature data for verification of the accuracy of the test methods.

The experimental test method involved developing a test setup that was similar to those found in pertinent standards and other flammability studies, especially if the intended scope included elevated initial conditions of temperature pressure. ASTM E918 was selected as the most appropriate standard for elevated flammability tests and an experimental setup was assembled and prepared according to this standard (ASTM E918 1983). A numerical test method for the determination of the lean flammability limits was also developed based on a laminar flame speed CHEMKIN model which closely matched the typical method for determining flammability limits, namely flame propagation. The results from the experimental tests and numerical simulations were compared with available flammability data for the previously mentioned pure fuels and renewable gaseous fuel mixtures at a given specified test temperature and pressure; studies conducted by Van den Schoor, Holtappels and Tschirschwitz et al. were among the most notables sources of flammability data pertinent to the current study (Van den Schoor 2007; Holtappels 2006; Tschirschwitz et al. 2015).

The following section summarizes the conclusions and main takeaways of this study in more detail.

6.2 CONCLUSIONS

Lean flammability limits (LFLs) were determined for three binary gaseous fuel mixtures (CH_4/H_2, H_2/CO, and CH_4/CO_2) at temperatures up to 200° C and pressures up to 9 bar. The key conclusions of this study include:

- **A suitable experimental setup was developed and verified for the determination of lower flammability limits for the test parameters of interest.**

  The experimental results discussed in Section 5.1 were consistent with available flammability data for the test mixtures at the specified initial temperature and pressure, and therefore the experimental setup developed in this study was validated for use in determining the flammability limits. The experimental setup was adapted from the ASTM E918 standard, with modifications made in order to improve the accuracy for the safe preparation of the fuel/air test mixtures while also simplifying the design/test procedure when possible. LFL results for methane/air mixtures were consistent with available flammability data at similar elevated conditions, and also exhibited a negligible dependence due to test vessel size. The LFL results for hydrogen/air mixtures were dependent on the volume of the test vessel, especially at lower test pressures; therefore, an ideal test vessel size between $V = 2.8\ L$ and $V = 6\ L$ is suggested to promote consistent flammability data for hydrogen/air test mixtures.

- **The most reliable ignition criterion was determined to be a 5% pressure rise.**

  ASTM E918 suggest the use of a 7% rise of the initial absolute pressure as indication that ignition has occurred, or as the ignition criterion. The use of a pressure rise criterion is widely used, and occasionally the only criterion possible, when determining ignition of a flammable mixture at conditions of elevated pressure. European Standard EN 1839

suggests use of a 5% pressure rise criterion and various studies use unique variations such as a study by De Smedt et al. where a 2% pressure rise is chosen (De Smedt et al. 1999). Ultimately, the choice of a 5% pressure rise criterion is decided upon as it is more conservative than the suggested 7% but is not too low to be susceptible to error due to noise/local heating.

- **Experimentally derived LFLs decrease with an increase in temperature for all gaseous fuel mixtures and at all test pressures.**

  This result was expected as it is widely agreed upon that an increase in temperature widens the flammable range (decreases LFL, increases UFL), regardless of other parameters. Also, this results agrees with the theoretical background discussed in Chapter 2 and the conclusions of Section 2.1.3. Due to the general agreement of the influence of temperature on the flammability limits, only one condition of elevated temperature was included as a parameter (200° C), results of which would be compared with ambient conditions (25° C). For this increase in temperature, pure methane and pure hydrogen as the fuel mixture exhibited an average decrease of the LFL of approximately 0.88 vol % and 0.99 vol %, respectively; all methane/hydrogen/air (CH_4/H_2) mixtures tested, however, experienced a lower average decrease of the LFL (approximately 0.66 vol %). Compared to the methane/hydrogen/air mixtures, syngas/air (H_2/CO) and biogas/air (CH_4/CO_2) mixtures exhibited larger absolute decreases in the average LFL for an increase in temperature to 200° C; however, the average LFL for syngas and biogas is larger, and so a comparison of the relative percent decrease would be more appropriate. In order from largest to smallest, the relative percent decrease in the average LFL due to an increase in temperature from

25° C to 200° C is: 19.7% for hydrogen/air, 16.9% for methane/air, 16.5% for syngas/air, 13.8% for biogas/air and 12.7% for methane/hydrogen/air.

- **Experimentally derived LFLs of all fuel mixtures tested in this study exhibited an increase with an increase in pressure, however, the LFLs for biogas (CH_4/CO_2) mixtures exhibited a negligible dependence on pressure with larger quantities of diluent (CO_2).**

  Unlike the case for temperature, the influence of pressure on the flammability limits has been studied less and the conclusions in the available literature is less consistent. While a theoretical approach (Chapter 2) results in the conclusion that an increase in pressure increases the flammable range (decrease in LFL, increase in UFL), various studies conclude the opposite (Van den Schoor 2007; Tschirschwitz et al. 2015; Holtappels 2006). Overall, the experimental results of the current study agree with the available literature and confirm that the LFL increases with increasing pressure; this increase however is dependent on the initial temperature and the type of fuel. For the test pressure range of $P = 1\ bar$ to $P = 9\ bar$, pure hydrogen/air mixtures experience the largest increase in LFL: 36.4% at 25° C and 34.2% at 200° C. In contrast, pure methane/air mixtures exhibits a relatively small increase in LFL: 6.8% at 25° C and 6.7% at 200° C. For methane/hydrogen/air mixtures, the percent increase in LFL due to pressure consistently increases with increasing hydrogen concentration at both test temperatures. Although the average percent increase of the LFL due to pressure is greater at ambient temperature (25° C) for methane/hydrogen as the fuel, the opposite is true for syngas and biogas results. The average increase of the LFL due to pressure for syngas is 14.4% at 25° C and 20.5% at 200° C. The results for biogas are more sensitive to the fuel composition and the influence

of pressure on the LFL becomes negligible at larger amounts of CO_2. At 25° C, the percent increase of the LFL due to pressure is 6.8% for the 80/20 (CH_4/CO_2) fuel blend, 2.4% for the 60/40 fuel blend, and 1.4% for the 40/60 fuel blend.

- **Le Chatelier's mixing rule was validated for predicting the LFLs of biogas (CH_4/CO_2) mixtures, and for providing fair estimates of syngas (H_2/CO) mixtures, however it is not recommended for use in predicting the LFLs at elevated initial conditions or for methane/hydrogen (CH_4/H_2) mixtures.**

  A common predictive tool that is discussed in several flammability studies concerning the determination of the flammability limits of gaseous fuel mixtures is Le Chatelier's law for mixtures or mixing rule. Many studies confirm the use of Le Chatelier's rule provides accurate estimates for the LFL when flammability data are not available, however, its use at elevated initial temperature and pressure is inconclusive. Overall, the results of the current study were presented in the preceding chapter and compared with Le Chatelier estimates, and the closest approximations were for biogas and syngas as the fuel. Specifically, estimates were within 1.2% for all tested biogas fuel blends at both conditions of initial temperature. An increase in pressure increased the deviation to at most 3.7%, although this is still considered an accurate estimate considering the lack of flammability data at elevated conditions. At $P = 9\ bar$ and $T = 200°C$, the variation for biogas was maximized at 6.7%; therefore, Le Chatelier's provided accurate estimates for the LFL of biogas mixtures, but the deviation increased with increasing pressure and temperature. For syngas mixtures, LFL data at elevated temperature and pressure were not available for carbon monoxide (CO) and so the only estimates that were compared with the experimental results were at ambient conditions for temperature and pressure. Similar to biogas mixtures,

Le Chatelier's rule was able to predict the experimental results fairly well for syngas mixtures (within 7.7%); however, these estimates are expected to worsen at elevated conditions similar to the results for biogas. Finally, the LFL results for methane/hydrogen mixtures did not behave like the syngas or biogas mixtures, monotonically decreasing with increase in most reactive fuel component; therefore, the estimates provided by Le Chatelier's law exhibited the largest deviations of all the fuel mixtures, such as the largest difference of 13.3% at $P = 5\ bar$ and $T = 200°C$.

- **LFLs derived numerically were highly dependent on the reaction mechanism chosen; however, preliminary results were shown to be consistent with available flammability data and the experimentally derived LFLs.**

  The numerical results in the current study were calculated with the use of a laminar flame speed CHEMKIN model. The two main reaction mechanisms used for methane combustion were the GRI Mech 3.0 mechanism and the UCSD CECR mechanism. Preliminary numerical results for methane/air and biogas/air agreed well when compared with the experimental results of the current study and available literature data, however each mechanism had its own unique advantages. The GRI mechanism deviated less from the experimental results and simulated the influence of temperature best, though it was not able to capture the observed increase in the LFL due to pressure which the UCSD mechanism was able to exhibit. For hydrogen combustion, the NUI Galway Hydrogen/Syngas reaction mechanism was chosen and provided satisfactory estimates for the UFL when compared to pertinent literature data (Holtappels 2006). Overall, future work includes improving the CHEMKIN flame speed model to more closely simulate the actual LFL values, developing a more detailed reaction mechanism that includes the

strength both the GRI and UCSD mechanism for methane combustion, and investigating further the difficulties of simulating lean hydrogen combustion for the numerical determination of the lower flammability limit of hydrogen fuel mixtures.

6.3 RECOMMENDATIONS

In an effort to improve upon the foregoing results and further optimize the methods for the determination of the lower flammability limits of renewable type gaseous fuel mixtures, a revised ASTM E918 standard is proposed based on the following recommendations and revisions (ASTM E918 1983) :

- Section 3.2.1: Suggest use of a 5% pressure rise instead of 7% rise, similar to European standard and other flammability studies (EN 1839 2003).
- Section 7.1: Although the lower flammability limit (LFL) is independent of the size of the test apparatus volume for most fuels, an increase of the volume to 5 L similar to other standards and studies is recommended to improve the consistency of flammability data.
- Figure 1, Item 1: The addition of check valves along the fuel and air lines/manifold improve the safety of the experimental setup as well as the accuracy of the partial pressure preparation of the fuel/air mixtures.
- Figure 1, Item 2: Replace high and low pressure transducer with single high pressure (HP) transducer (Omega HP transmitter, see below for specific model/details); use of single pressure transmitter is possible for both recording test pressures and for preparing fuel/air mixtures as demonstrated in the preceding experimental methods section (Section 4.1).
- Figure 1, Item 3: “Gas to analyzer” connection is unnecessary as either ½-in. NPT female pipe connection (top and bottom) can be used for sampling.

- Figure 1, Item 4: For the current study, an extension rod/fuse wire was unnecessary as the spark plug used (see below for specific model/details) was sufficiently long enough to set the spark gap at the centerline of the test vessel.
- Section 10.7: Recording of the temperature and pressure can be improved by use of a LabVIEW system similar to the setup used for the current study (refer to Section 4.1).
- Section 10.9: Ignition energy is not specified; to be consistent with other standards and notable flammability studies, include detail of 10-20 Joules as minimum energy for ignition attempts (EN 1839 2003).
- Section 10.13: Edit value of pressure ratio to "1.05 or more".
- Section A1.1: Revise test vessel volume to be "no less than 5 L" and revise minimum inside diameter to one corresponding to new volume; also, the recommendation to add a ¼-in. NPT female pipe connection for the sampling tube should be removed for the previously mentioned reason.
- Section A1.3: Although the spark plug was not modified for the current study, a larger test vessel would most likely require the extension rod suggested in this section; revise procedure for appropriate modification to provide necessary spark ignition to the centerline of the test vessel. Also, instead of the Champion N-12Y spark plug, a Champion 220 FI21501 was used in the current study.
- Section A1.6: Heating of the test vessel in the current study was achieved using heating tape; depending on the size of the test vessel a furnace or heating tape may be used.
- Section A1, Footnote 6: Schrader solenoid valves were used in the current study; 75 max psig, 22 Watts, 120/60 Volts, 3/32 orifice.

- Section A1, Footnote 10: Omega high pressure transmitter was used in the current study; Model number PX41T0-3.5KGI, 0 to 3500 psi, stainless steel, 4-20 mA, 0.25% accuracy.
- Section A1.7: This section need only specify one pressure transducer for the above mentioned reasons; also, edit pressure rise from 7% to 5%.

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APPENDIX

A. SAMPLE MATLAB CODES

LFL Data Processer:

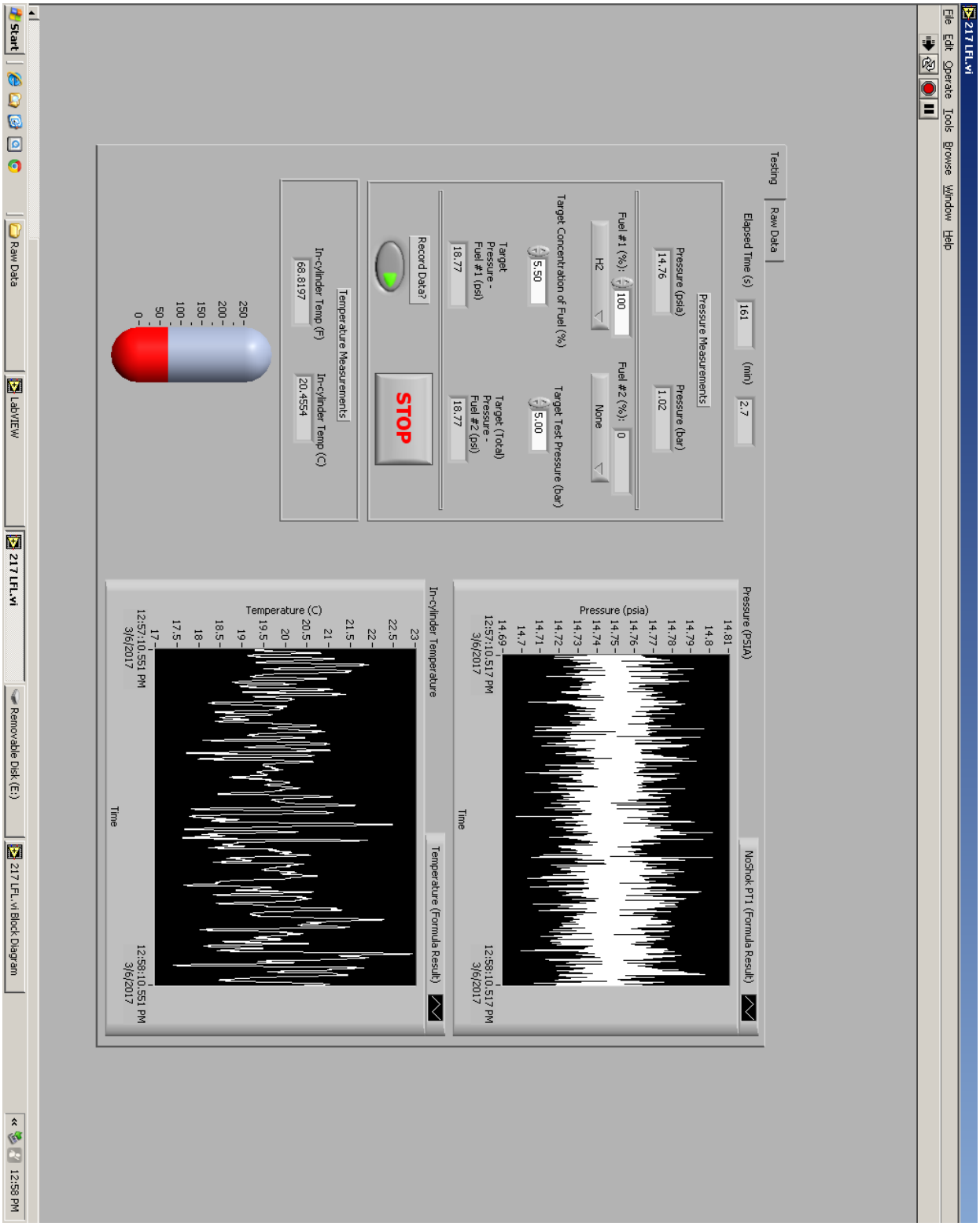
```
clear
clc

% Just change file name and run
% - djj

filename = '4.7 percent 9 bar 200 C H2 100616.xlsx';
[m,n] = size(xlsread(filename));

t = xlsread(filename,strcat('A22:A',num2str(m+1))); % read time data [sec]
P = xlsread(filename,strcat('B22:B',num2str(m+1))); % read pres data [psia]
T = xlsread(filename,strcat('C22:C',num2str(m+1))); % read temp data [F]

TC = (T-32)*5/9; % convert temp data [C]

avgTe = mean(T(22023:23022)); % test temp [F]
avgPe = mean(P(22023:23022)); % test pressure [psia]

avgT = (avgTe-32)*5/9; % test temp [C]
avgP = avgPe/14.5038; % test pressure [bar]

Pnorm = P/avgPe; % normalized pressure to test pressure

conc = 100*(mean(Pnorm(9023:10022))-mean(Pnorm(5023:6022))); % test conc of
CH4 in air
MaxP = (max(Pnorm)-1)*100; % maximum pressure rise

figure
subplot(2,1,1);
plot(t,Pnorm)
axis([300,400,.9,1.15])
xlabel(['Time [s]'])
ylabel(['Norm Pressure'])
title(['P = ' num2str(avgP) ' bar, T = ' num2str(avgT) ' C, ' num2str(conc)
'% H2, ' num2str(MaxP) '% max dP'])

subplot(2,1,2);
plot(t,TC)
axis([300,400,200,220])
xlabel(['Time [s]'])
ylabel(['Temperature [C]'])
```

LFL Pressure Rise Comparison:

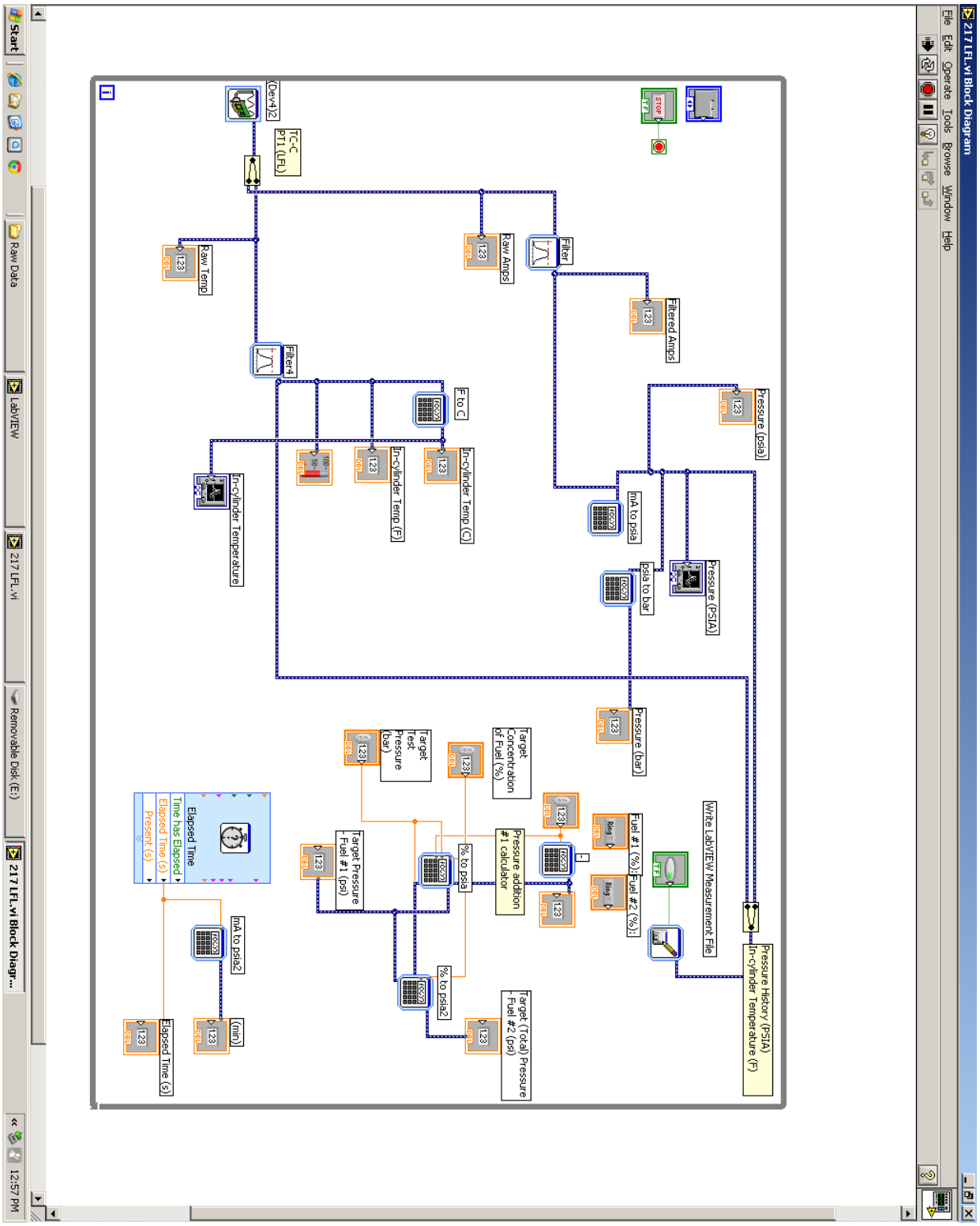
```
clear
clc

% Just change file names and run
% - djj

filename1 = '4.72 percent 9 bar 200 C H2 100616.xlsx';
filename2 = '5.13 percent 9 bar 200 C H2 100716.xlsx';
filename3 = '5.22 percent 9 bar 200 C H2 100716.xlsx';
filename4 = '4.58 percent 9 bar 200 C H2 100616.xlsx';
filename5 = '5.41 percent 9 bar H2 070516 (3).xlsx';
filename6 = '4.83 percent 9 bar H2 061616.xlsx';

for j = 1:3
functionName = eval(sprintf('filename%d', j));
[m,~] = size(xlsread(functionName));

t = xlsread(functionName,strcat('A22:A',num2str(m+1))); % read time data
[sec]
P = xlsread(functionName,strcat('B22:B',num2str(m+1))); % read pres data
[psia]
T = xlsread(functionName,strcat('C22:C',num2str(m+1))); % read temp data [F]

TC = (T-32)*5/9; % convert temp data [C]

avgPe = mean(P(22023:23022)); % test pressure [psia]

Pnorm = P/avgPe; % normalized pressure to test pressure

subplot(2,1,1);
plot(t,Pnorm)
axis([200,400,.99,1.2])
xlabel(['Time [s]'])
ylabel(['Norm Pressure'])
title(['Max pressure rise at various %H2/Air at P = 9 bar, T = 200 C'])
hold on

subplot(2,1,2);
plot(t,TC)
axis([200,400,200,220])
xlabel(['Time [s]'])
ylabel(['Temperature [C]'])
hold on

end
```

B. LABVIEW

Front Panel:

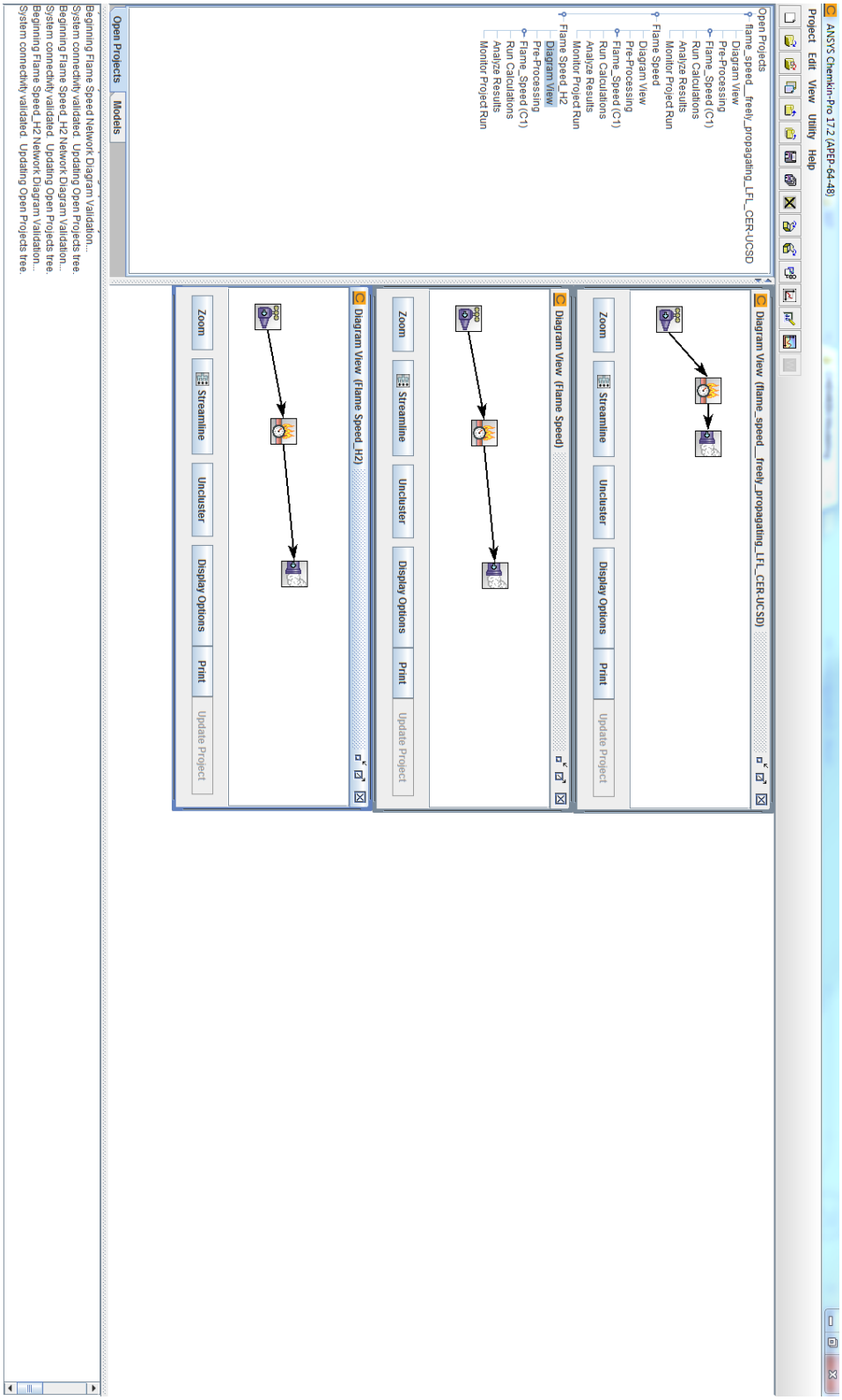


Block Diagram:

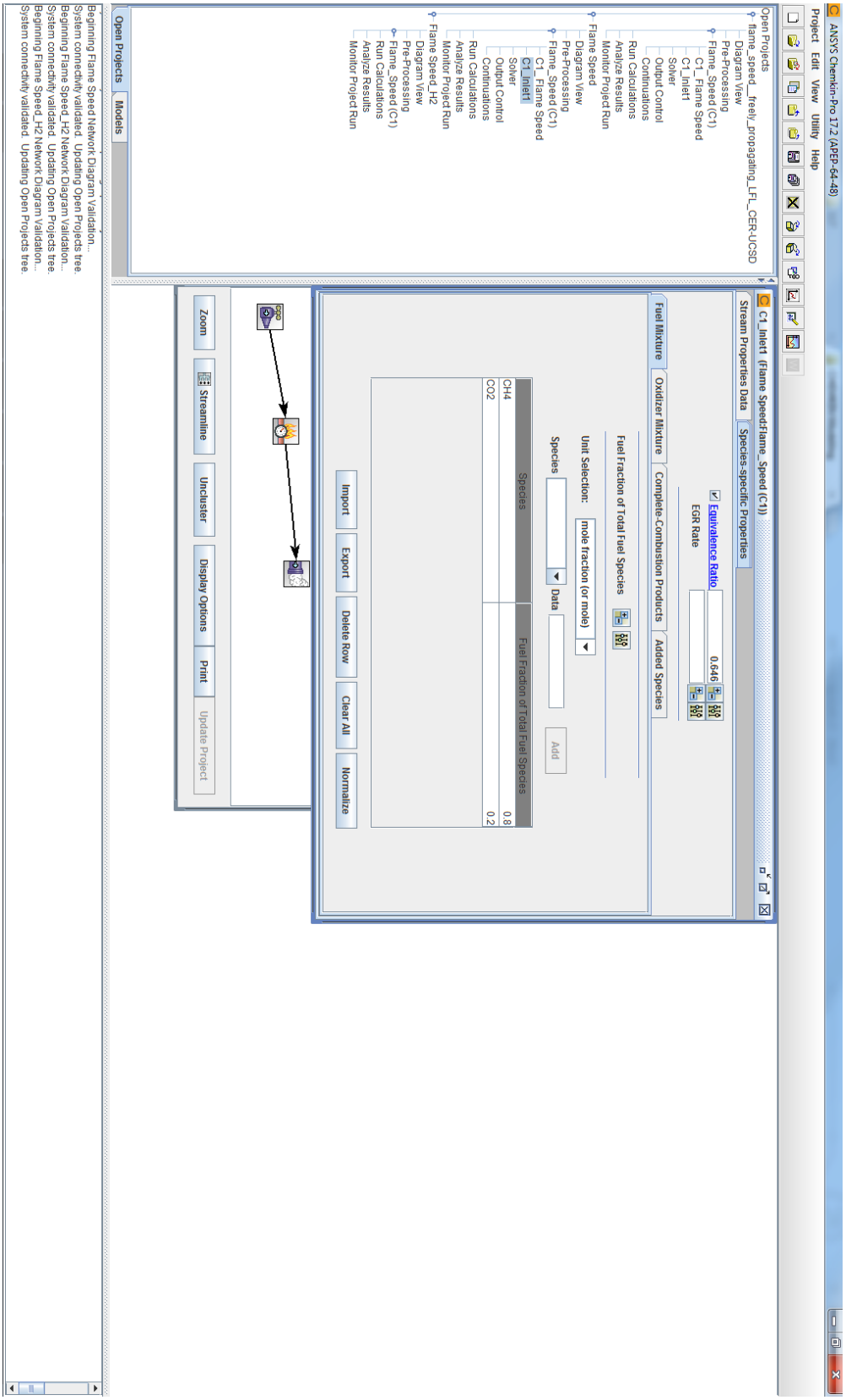


C. CHEMKIN

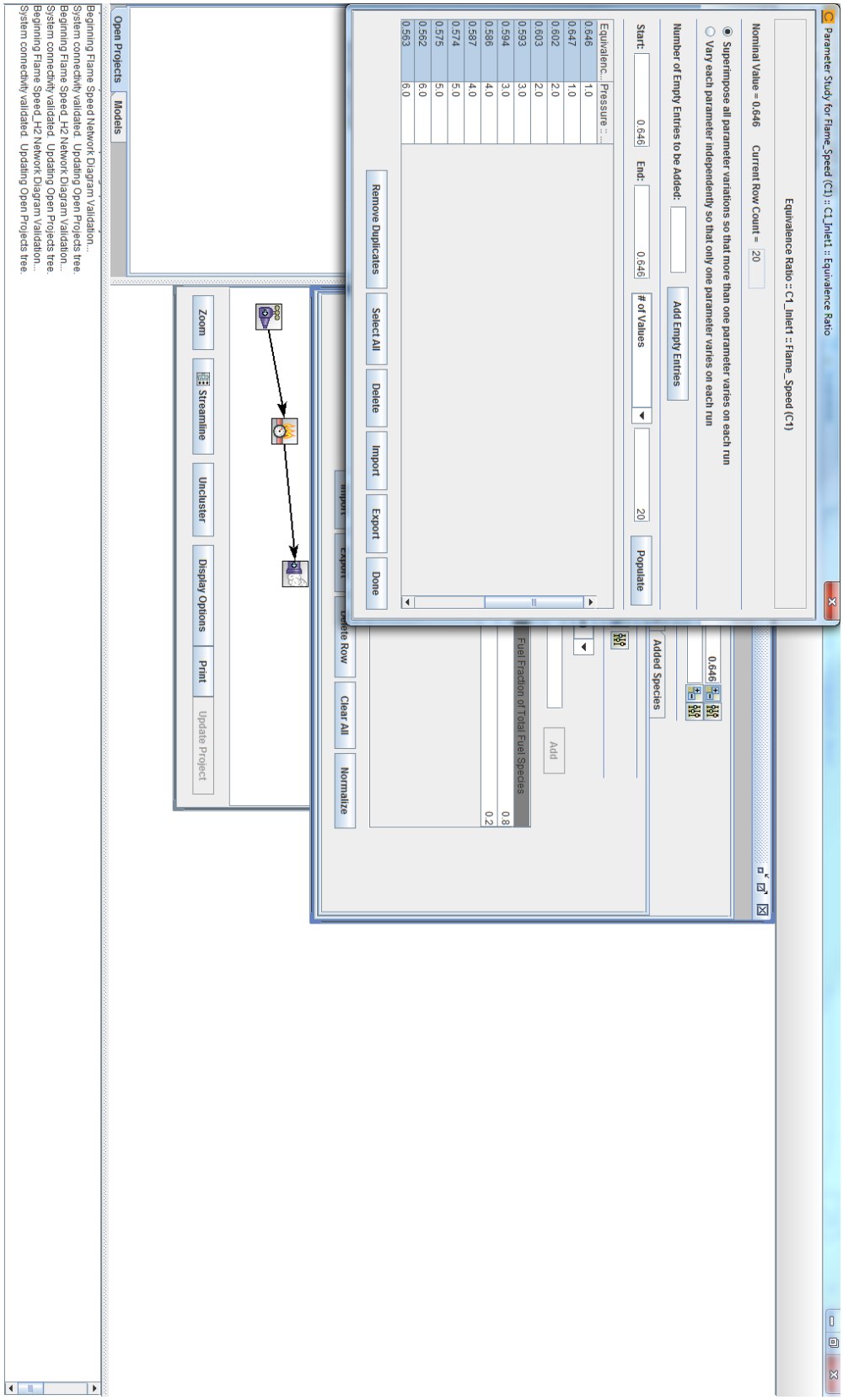
Freely-propagating Flame Speed Models – UCSD, GRI and Galway:



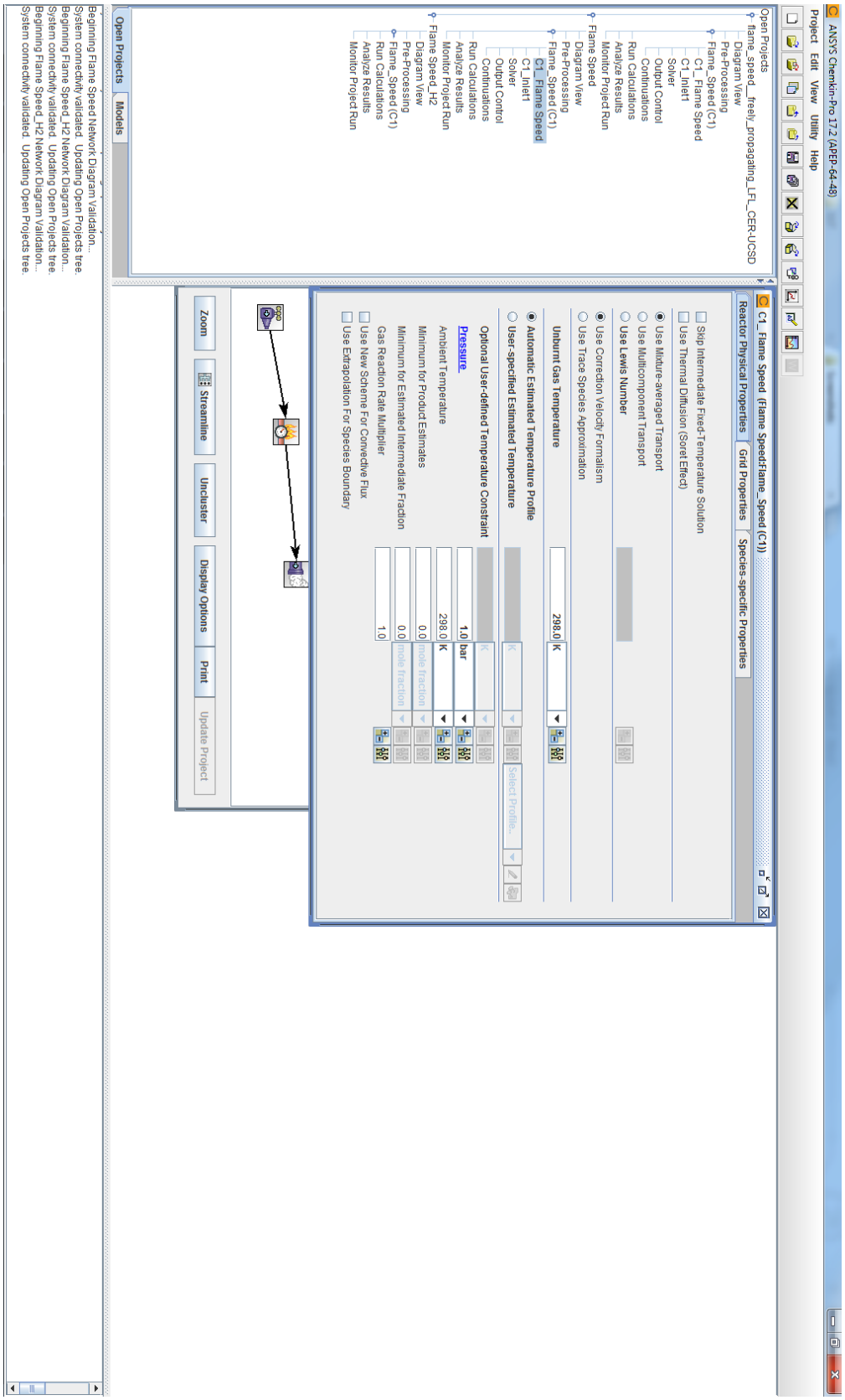
Flame Speed Model – Inlet/Species Specific Properties:



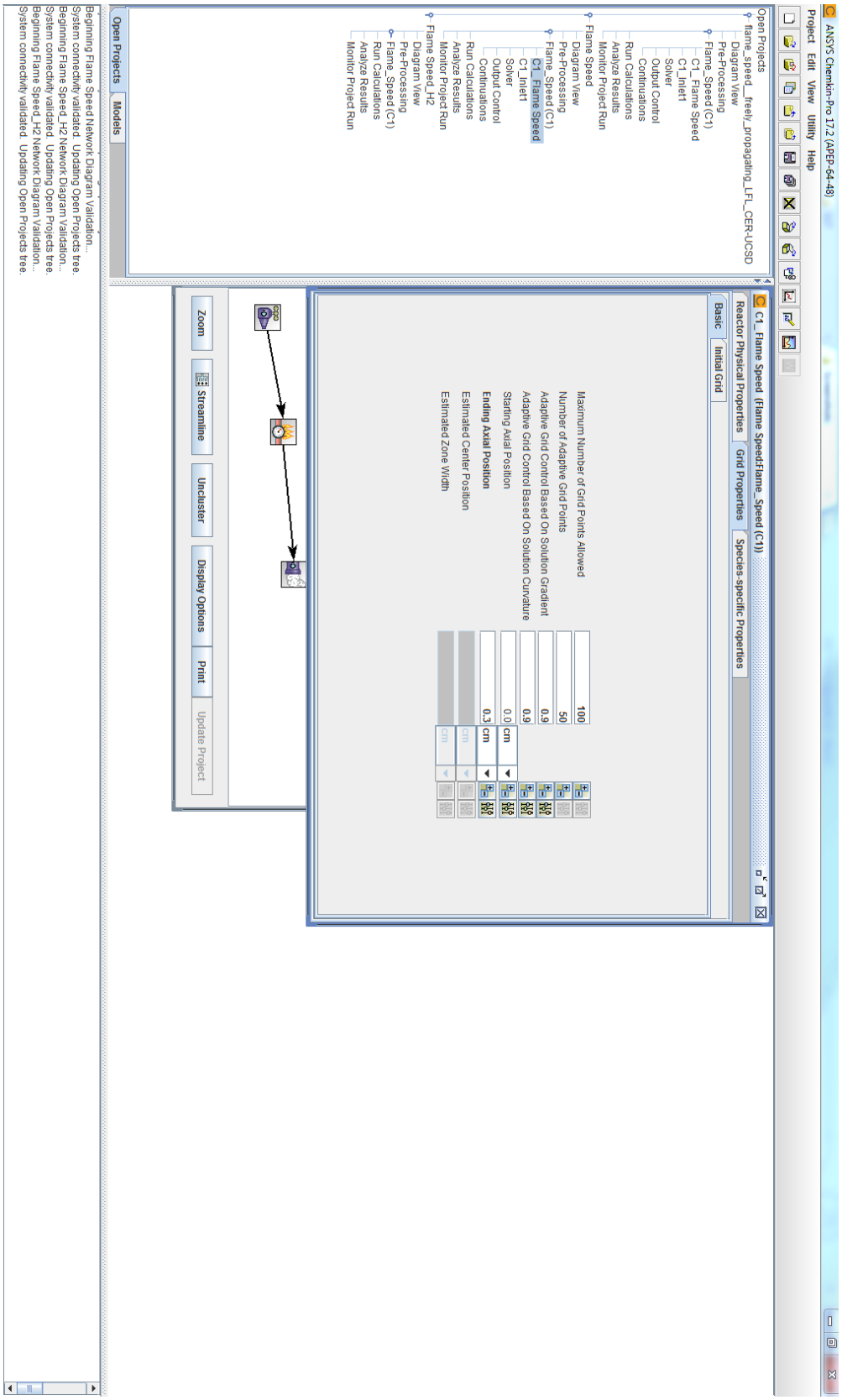
Flame Speed Model – Inlet/Parameter Study (EQR vs Pressure):



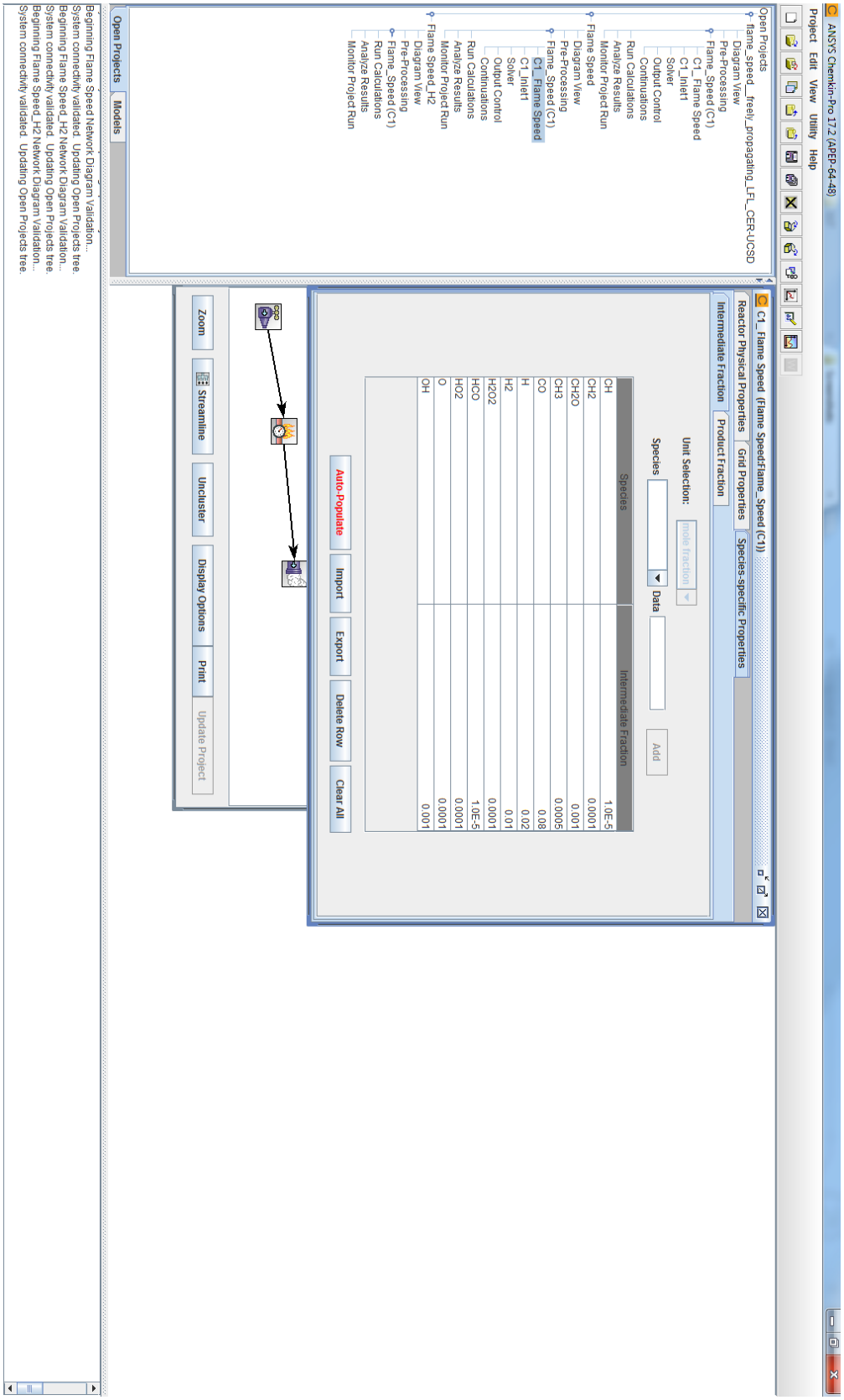
Flame Speed Model – Reactor/Reactor Physical Properties:



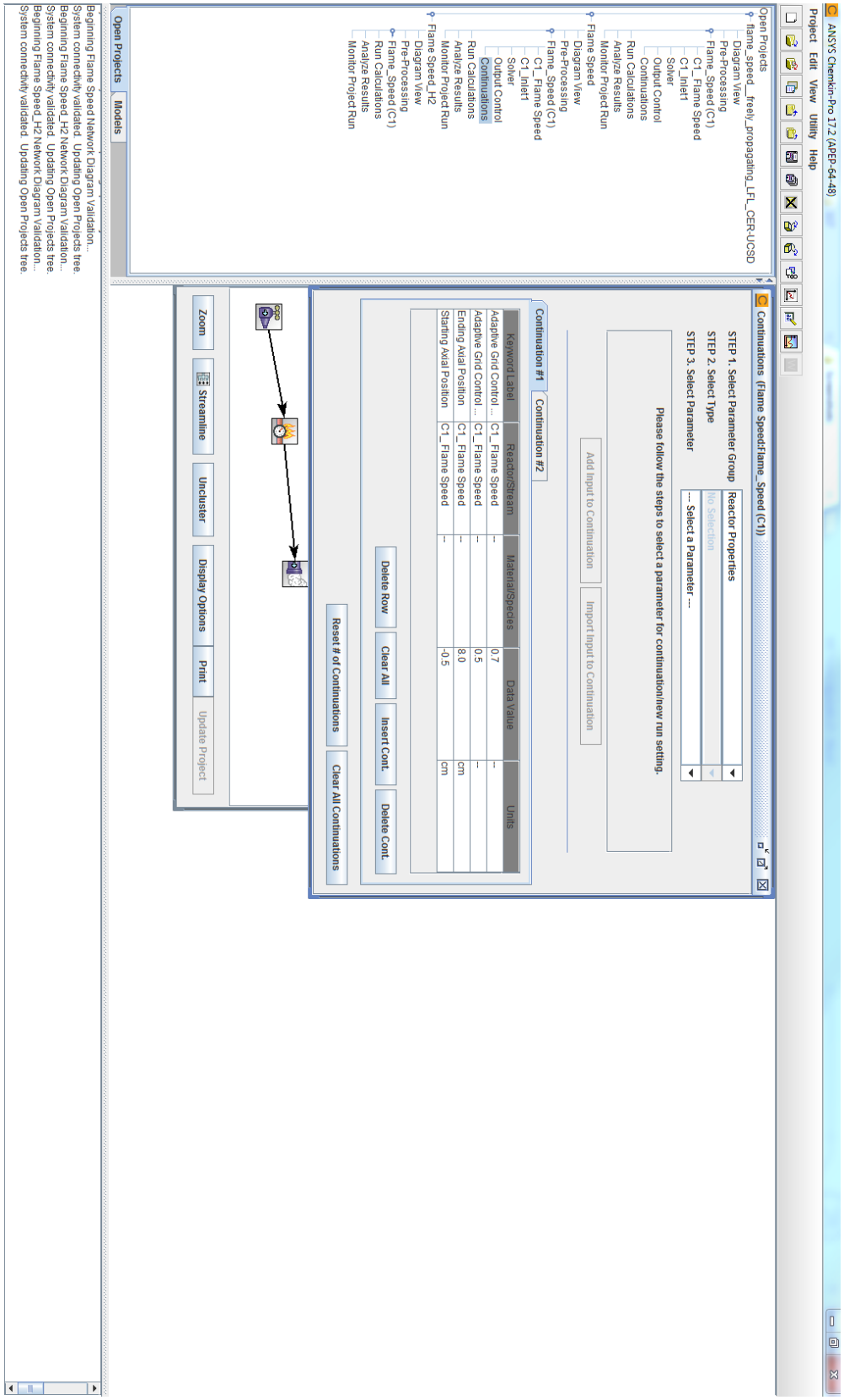
Flame Speed Model – Reactor/Grid Properties:



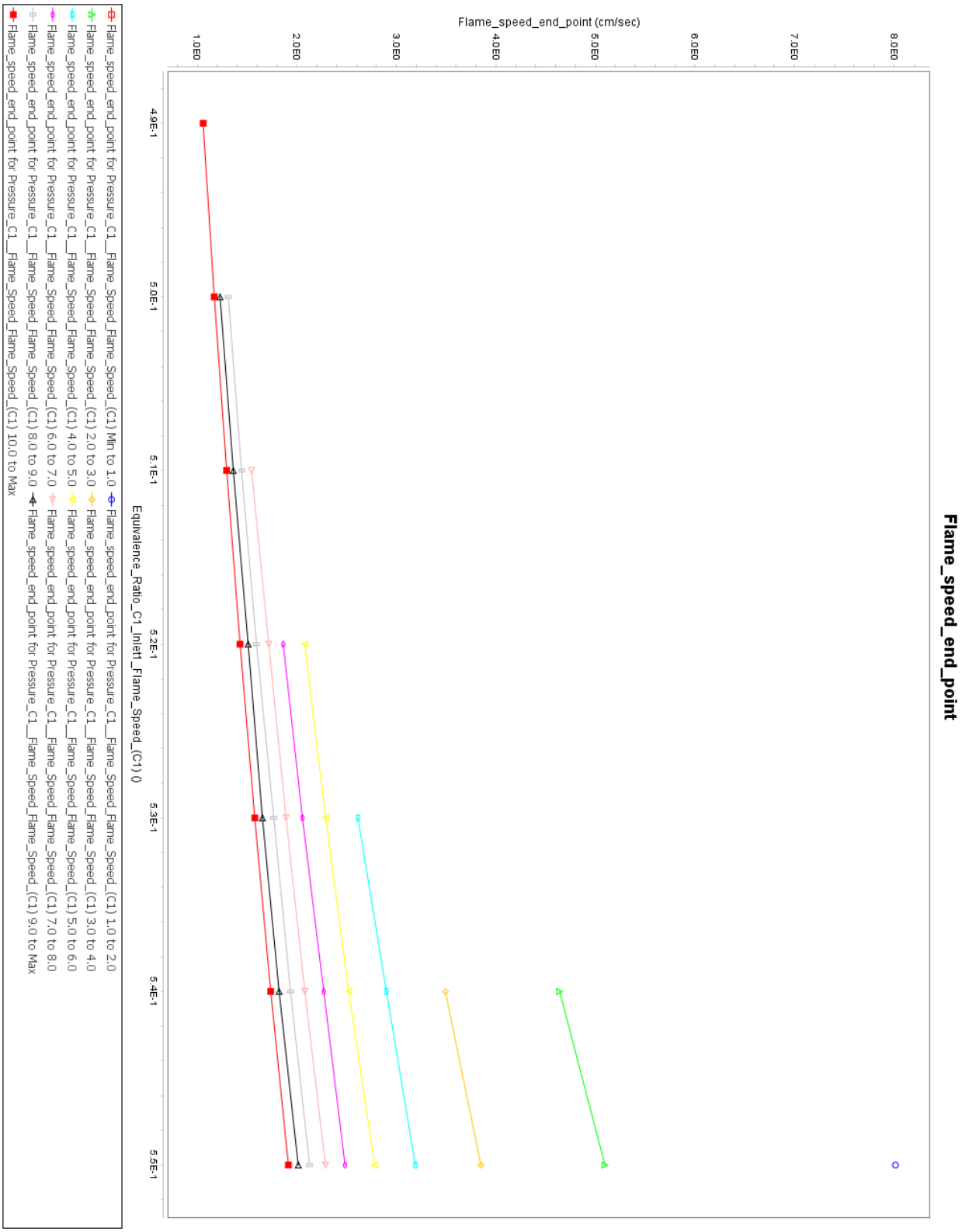
Flame Speed Model – Reactor/Species Specific Properties:



Flame Speed Model – Continuations:



Flame Speed Model – Sample Result:



Reaction Mechanisms:

GRI-Mech 3.0: http://combustion.berkeley.edu/gri-mech/version30/text30.html

CECR Research, UCSD: http://web.eng.ucsd.edu/mae/groups/combustion/Mechanisms/

NUI Galway, Hydrogen and Syngas (2013): http://c3.nuigalway.ie/syngas.html

D. EXPERIMENTAL ERROR ANALYSIS

The error for all test measurements, including experimentally derived LFL values, was determined based on a 95% confidence level and using the confidence interval to establish the error bars for the experimental data. A 95% confidence level corresponds to a probability of 0.95 that we will find a confidence interval in which the value of a given parameter will be between the stochastic endpoints, given by the following equations:

$$\text{Lower endpoint} = \bar{X} - 1.96\frac{\sigma}{\sqrt{n}}, \text{Upper endpoint} = \bar{X} + 1.96\frac{\sigma}{\sqrt{n}}$$

In the above equations, the sample mean is denoted by $\bar{X}$, the standard deviation of the population by σ and the size of the sample by n. A sample confidence interval calculation for a 40/60 (% CH4/% CO2) biogas/air mixture at $P = 9$ bar and $T = 200°C$ is provided below.

Parameter	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Fuel fraction (vol %)	11.85	11.77	11.85	11.80	11.91	11.89	11.85	11.75	11.69	11.75
Pressure (bar)	8.96	9.05	9.05	9.14	9.03	9.03	9.11	8.98	8.99	8.93
Temperature (C)	197	207	214	190	200	207	203	200	197	198

Parameter	Sample Size (n)	Sample mean ($\bar{X}$)	Standard Deviation (σ)
Fuel fraction (vol %)	10	11.811	0.07039
Pressure (bar)	10	9.027	0.065158
Temperature (C)	10	201.3	6.733828

$$95\%\ \text{Confidence Interval for Fuel Fraction} = \left(\bar{X} - 1.96\frac{\sigma}{\sqrt{n}}; \bar{X} + 1.96\frac{\sigma}{\sqrt{n}}\right)$$

$$= \left(11.811 - 1.96\frac{0.07039}{\sqrt{10}}; 11.811 + 1.96\frac{0.07039}{\sqrt{10}}\right) = \boxed{(11.77; 11.85)}$$

$$95\%\ \text{Confidence Interval for Test Pressure} = \left(\bar{X} - 1.96\frac{\sigma}{\sqrt{n}}; \bar{X} + 1.96\frac{\sigma}{\sqrt{n}}\right)$$

$$= \left(9.027 - 1.96\frac{0.065158}{\sqrt{10}}; 9.027 + 1.96\frac{0.065158}{\sqrt{10}}\right) = \boxed{(8.99; 9.07)}$$

$$95\%\ \text{Confidence Interval for Test Temperature} = \left(\bar{X} - 1.96\frac{\sigma}{\sqrt{n}}; \bar{X} + 1.96\frac{\sigma}{\sqrt{n}}\right)$$

$$= \left(201.3 - 1.96\frac{6.733828}{\sqrt{10}}; 201.3 + 1.96\frac{6.733828}{\sqrt{10}}\right) = \boxed{(197.13; 205.47)}$$

E. LE CHATELIER CALCULATIONS

Recall Le Chatelier's law/formula, equation (25):

$$LFL_{mix} = \frac{1}{\sum \frac{x_i}{LFL_i}}$$

Use of equation (25) requires knowledge of the lower flammability limit (LFL) value for each fuel component at a desired temperature and pressure. The intended use of Le Chatelier's law is to estimate the LFL value when mixture data are not readily available.

In the current study, the only fuel components that are considered are methane (CH_4), hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). At ambient conditions, the LFL values for all fuel components are widely reported (with the exception of carbon dioxide which is a diluent and therefore does not have defined flammability limits). A sample calculation for the LFL of a syngas/air mixture and a biogas/air mixture is shown below.

Fuel Component	LFL (% vol)
Methane	4.99
Hydrogen	4.42
Carbon Monoxide	12.50
Carbon Dioxide	-

Table 8: Ambient LFL values for fuel components of the current study

$$LFL_{syngas,20/80} = \frac{1}{\sum \frac{x_i}{LFL_i}} = \frac{100}{\frac{20}{4.42} + \frac{80}{12.50}} = 9.15\%$$

$$LFL_{biogas,40/60} = \frac{1}{\sum \frac{x_i}{LFL_i}} = \frac{100}{\frac{40}{4.99} + \frac{\mathbf{60}}{-}} = 12.48\%$$

The calculations are repeated for every combination of fuel split (%/%) pertinent to the study as well as intermediate fuel splits that may not have been explicitly tested during the experimental determination of the LFLs. It is important to note that for the LFL calculation of biogas/air mixtures using Le Chatelier's law, the term in red (contribution of carbon dioxide to the LFL) should be neglected as the LFL is not defined for the diluent; as was shown in Section 5.1.5, this approach leads to fairly accurate estimations in the range of parameters that were tested. Finally, estimation of the LFL using Le Chatelier's law has the capacity of being extended to multicomponent mixtures (not limited to just binary mixtures as was pertinent to the current study). If further investigation into the use of Le Chatelier's law at elevated temperature and pressure conditions is of interest, it is important to note that the LFL values at the elevated temperature and pressure conditions of interest are needed.

F. LFL DATA

Lean Flammability Limits for Methane/Hydrogen/Air Mixtures (% vol):

Fuel: 100% CH4

P vs. T	25 C	200 C
1 bar	4.99	4.19
3 bar	5.08	4.26
5 bar	5.25	4.34
7 bar	5.35	4.34
9 bar	5.33	4.47

Fuel: 40% CH4 - 60% H2

P vs. T	25 C	200 C
1 bar	4.61	4.12
3 bar	4.90	4.37
5 bar	5.25	4.91
7 bar	5.49	4.96
9 bar	5.79	4.87

Fuel: 80% CH4 - 20% H2

P vs. T	25 C	200 C
1 bar	4.97	4.46
3 bar	5.07	4.54
5 bar	5.31	4.57
7 bar	5.41	4.68
9 bar	5.35	4.50

Fuel: 20% CH4 - 80% H2

P vs. T	25 C	200 C
1 bar	4.76	4.13
3 bar	4.89	4.21
5 bar	5.10	4.57
7 bar	5.37	4.87
9 bar	5.68	4.73

Fuel: 60% CH4 - 40% H2

P vs. T	25 C	200 C
1 bar	4.85	4.29
3 bar	5.07	4.48
5 bar	5.29	4.71
7 bar	5.62	4.71
9 bar	5.73	4.58

Fuel: 100% H2

P vs. T	25 C	200 C
1 bar	4.42	3.51
3 bar	4.69	3.73
5 bar	4.88	3.87
7 bar	5.08	4.34
9 bar	6.03	4.71

Lean Flammability Limits for Hydrogen/Carbon Monoxide/Air Mixtures (% vol):

Fuel: 60% H2 - 40% CO

P vs. T	*25 C*	*200 C*
1 bar	6.36	5.05
3 bar	6.54	5.45
5 bar	6.92	5.75
7 bar	7.16	5.83
9 bar	7.20	6.06

Fuel: 40% H2 - 60% CO

P vs. T	*25 C*	*200 C*
1 bar	7.79	6.64
3 bar	8.17	6.94
5 bar	8.51	7.04
7 bar	8.79	7.30
9 bar	9.00	7.68

Fuel: 20% H2 - 80% CO

P vs. T	*25 C*	*200 C*
1 bar	10.05	8.09
3 bar	10.59	8.63
5 bar	10.96	9.21
7 bar	11.28	9.55
9 bar	11.50	10.19

Lean Flammability Limits for Methane/Carbon Dioxide/Air Mixtures (% vol):

Fuel:	80% CH4 - 20% CO2
P vs. T	***25 C***	***200 C***
1 bar	5.92	4.88
3 bar	6.34	5.41
5 bar	6.42	5.67
7 bar	6.31	5.20
9 bar	6.32	6.20

Fuel:	60% CH4 - 40% CO2
P vs. T	***25 C***	***200 C***
1 bar	8.27	6.87
3 bar	8.47	7.09
5 bar	8.59	7.22
7 bar	8.47	7.29
9 bar	8.47	7.98

Fuel:	40% CH4 - 60% CO2
P vs. T	***25 C***	***200 C***
1 bar	13.16	10.79
3 bar	13.46	11.44
5 bar	13.48	11.38
7 bar	13.49	11.48
9 bar	13.34	11.76