Using Numerical Reactors to Understand Autoignition

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Abstract

This thesis presents numerical results based on the experimental setup for a fuel jet issuing into a shrouding hot coflow. The numerical setup replicates these experimental conditions using a range of fuels and autoignition temperatures. The objective of this thesis is to gain a better understanding on the important species which influence the combustion of hydrogen, methane, and propane. Specifically, the aim is to analyse the coflow setup and identify the parameters that control ignition delay times. A zero-dimensional (0-D) reactor is first simulated to observe the contents of the autoignition kernels in the mixture. It is found that HO_2 and H_2O_2 peak relatively early compared to all other species, for all 3 fuels. CH₃O, however, is the prime indicator of autoignition for methane and propane as it peaks well before all other species in all the cases tested. Simulations of the coflow burner with additions of certain radicals to the coflow and dilution to the jet show that, from a vitiated H₂/air coflow, OH is the most influential on ignition delay time when added to the coflow, and hydrogen is the most sensitive additive for methane and propane to reduce the delay time. The 0-D simulations additionally identify that the autoignition is most sensitive to the chemical reactions involving OH, for the relevant concentrations obtained from a H_2/air coflow. Furthermore, for the addition of OH, the sensitivity analysis is completely different compared to a fuel issuing into a pure air coflow. Finally, it was uncovered that certain reactions have quite a large influence on the combustion process, that being chemical reactions which produce or consume oxygen (O) and hydrogen (H) atoms.

In conjunction, the counterflow configuration was employed by running one-dimensional (1-D) simulations to investigate the influence of strain rate on ignition delay time. Results show that increasing the strain rates increase the ignition delay times exponentially. The increased mixing transports valuable heat and species from possible locations where autoignition could occur. The mixture temperature evolves quite similarly to the 0-D reactor, however, the benefit of utilizing the 1-D reactor is that results are more relevant due to fluid mechanics effects being accounted for, at least for laminar flows. Conversely, the 0-D reactor, whilst not having any compositional gradients, can produce results with low computational cost. Regardless, each reactor has their own benefit and occasion where they are the preferable reactor to use.

Contribution of work

- I carried out the literature survey to understand where research is currently at regarding combustion.
- Andrew Macfarlane provided me with the base code for the 0D and 1D simulations.
- Andrew also helped advise what direction I should take my thesis, which helped me decide what code I should right.
- I used the open-source numerical solver Cantera and Ember to run my simulations and produce results.
- I plotted all my figures using original results and code.
- I carried out the analysis. The conclusions are my own, influenced by discussion with my supervisors.

The above points represent an accurate summary of the student's contribution.

11/11/2021 Student Date

Supervisor

Date

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Chapter 1.0 – Introduction

Global performance on energy consumption has improved in the year of 2020, with primary energy consumption falling by 4.5% last year [36]. 2020 also saw a decrease in carbon emissions from energy use by 6.3%, which is the lowest it has been since 2011 [36]. Regardless of this improvement, international efforts from all countries continue to be required to help decarbonize the economy and tackle the climate crisis. Especially because this improvement follows 10 consecutive years of the world setting new all-time high energy consumption levels [38]. To continue this decline in energy use, many member countries of the International Energy Agency (IEA) have pledged to reach net zero emissions by 2050 [37], with many more countries expected to follow.

To help achieve these goals, a great focus has been placed internationally on increasing renewable energy use. However, fossil fuel consumption remains high compared to renewable sources, with 2020 showing that oil, coal, and natural gas account for 33%, 27% and 24% respectively [38], which all require combustion to produce energy. It comes as no surprise that, although already contributing for much of the global energy consumption, natural gas is projected to increase by 70% from 2014 to 2050 [39]. Furthermore, the demand of fuel, in sectors such as transport, is so significant that combustion is and will be prevalent for many years to come [40]. For that reason, it is critical to continue to improve combustion processes even while the fuel sources are transitioning from fossil-based fuels to renewables. This thesis attempts to contribute to this space with a focus on autoignition.

Combustion processes can be nominally split into two main categories: premixed and nonpremixed (diffusion) combustion. The former involves the fuel and oxidizer being mixed at a molecular level prior to combustion or the occurrence of any chemical reactions. On the other hand, the non-premixed combustion separates the fuel and oxidant; the reaction only occurs at the interface between the fuel and oxidizer [41]. Premixing of the reactants does occur to some degree in practical applications that employ diffusion combustion. It is not uncommon for both types of flames, occurring from both types of combustion, to be seen in certain applications.

The benefit of premixing fuels is that the desired power output, flame velocity, and other parameter such as lift-off height can be achieved. Most beneficial, however, may be that premixed flames are not limited by mixing time scales [26]. Instead, they are influenced by

1

the chemical reactions which take between the fuel and oxidizer. The downside to premixing is that, at stoichiometry, there is a large amount of NO_x emissions [42, 43]. Moreover, premixed systems are at risk of explosive reactions if the temperature is raised substantially or a high concentration of radical's form [27]. It is not very safe to store premixed fuel and oxidant, so non-premixed fuels are most often used and will be the focus of this thesis.

Ignition of fuel and oxidant mixtures can occur via either spark ignition or autoignition. The former involves a spark which causes flame kernel development [44] leading to its self-sustainment and combustion. On the other hand, autoignition occurs when the mixture is heated such that the chemical reaction steps causing combustion and decomposition of the molecules overtake those that terminate the reactions [27]. These chemical reactions, also called chain reactions, can be split up into four categories, chain-initiation, -propagating, - branching, and -terminating reactions [41]. The temperature must be high enough that a chain-initiation reaction takes place, which forms a radical from a stable species. The chain-propagating and -branching reactions for thermal runaway and combustion to occur. These are the conditions of the chemical reactions for autoignition to take place.

Other important parameters for autoignition include the temperature, composition, and pressure of the fuel and oxidant, as well as mixing due to the flow for non-premixed turbulent systems. These parameters dictate the flame characteristics such as flame speed, lift-off height, ignition delay time and temperature.

Autoignition is prevalent in many physical applications, such as Rich-Burn, Quick-Mix, Lean-Burn (RQL) combustors, which utilizes the hot combustion products of the primary Rich-Burn stage to mix with additional air and autoignite in the second and third stages [42, 43]. Other applications include compression ignition (CI) engines [45] and exhaust gas recirculation (EGR) [46]. The phenomena of autoignition must therefore be controlled to achieve the desired effect. Controlling its occurrence allows for the minimisation of unwanted outcomes, such as 'knocking' in spark ignition engines [47] and damage caused to the engines through thermal fatigue from extended exposure to autoignition [48]. Controlling autoignition also allows for better overall performance of these physical applications, which requires a better understanding of the chemical kinetics which is investigated within this thesis.

Many research papers utilise the Jet in Hot Coflow setup (JHC) [3, 4-6] to analyse autoignition. This thesis was intended initially to utilise the JHC setup. Experimental work

was performed at the beginning of the year; however, no results were produced and work in the lab had to be stopped due to the COVID-19 pandemic. Instead, the open-source numerical solver Cantera [25] was used to numerically simulate the coflow setup in both zero and one dimensions, and the results presented in this thesis will be entirely from numerical simulations.

Regarding the JHC burner, a central jet is injected into a surrounding coflow. Commonly, this jet injects fuel while the coflow is the oxidant, usually air [3, 8, 9] but also possibly vitiated, referring to a coflow of the combustion products of hydrogen and air [4-6]. The hot coflow then heats up the fuel such that autoignition kernels will form and convect downstream, growing as they move until they merge with the formed flame base [9].

Within this thesis, the use of varied fuels in the jet will be investigated. Use of increasingly higher hydrocarbons or hydrogen, reduce the ignition delay time when compared to the relatively long ignition delay of methane [7]. Use of fuel additives may also increase the speed of the ignition time [20], which is in part due to the varied specific heats of the fuel, dilutants and oxidant. Choice of fuel is critical as hydrocarbons produce a large amount of NO_x emissions which is detrimental to the environment.

The aims of this thesis are summarised as follows:

- 1. Analyse the content of the ignition kernels forming from autoignition using 0-D numerical simulations of various fuels.
- 2. Measure the ignition delay times of these fuels issuing into various coflow setups and investigating the effects of dilution.
- 3. Conduct sensitivity analyses on the cases tested which showed to have the most influence on the delay times.
- 4. Perform 1-D numerical simulations using the counterflow configuration to investigate the influence of strain rate on ignition delay times.
- 5. Compare the results of both 0-D and 1-D simulations to investigate the influence strain rate and diffusion have on the ignition delay times.

The thesis chapter breakdown is as follows:

<u>Chapter 2</u> reviews previous experimental and numerical work done on the autoignition burners, while providing information on fundamental concepts which will be reference through this thesis. This chapter will also investigate literature regarding the sensitivity analysis employed in later chapters.

<u>Chapter 3</u> analyses the contents of the autoignition kernels of hydrogen, methane and propane using 0-D numerical simulations. The time at which autoignition occurs will then be defined, and species which indicate the onset of autoignition will be highlighted.

<u>Chapter 4</u> presents the ignition delay times of the three fuels tested in this thesis. An air and vitiated coflow will be tested, where the important changes of the vitiated coflow will be isolated and tested separately to see which has the greatest influence on delay time. Dilution of air, hydrogen and nitrogen will then be tested to each fuel, while also investigating the effect this has on the stoichiometric coefficient between the jet and coflow.

<u>Chapter 5</u> conducts sensitivity analyses on the key scenarios tested in chapter 4 and compares them. The chemical reactions which take place within the combustion of the fuels will be plotted with their sensitivity, which is a quantitative value of the reactions influence on combustion.

<u>Chapter 6</u> presents the results obtained from the 1-D simulations and analyses the influence of strain rate and dissipation of both streams on the delay times of each fuel.

<u>Chapter 7</u> provides a discussion of all the results obtained from the preceding chapter, providing an analysis on the difference between 0D and 1D simulations, and the effects of mixing/strain rates on ignition.

<u>Chapter 8</u> presents the conclusion of the thesis, summarizing the key findings of the thesis. Final recommendations for future work to be done with numerical simulations will be provided, with the aim to improve upon the work already done in this thesis.

Chapter 2.0 – Background

This chapter will review the current literature relevant to this thesis and provide an analysis on the background knowledge required to better understand the contents. This thesis investigates three different fuels, those being hydrogen, methane, and propane, in the coflow burner and counterflow burner setups. As such, a succinct review of the current literature for these burners will be provided, along with a review of some of the numerical simulation work that has already been performed.

Numerical simulations employed in this thesis involves the use of the Cantera and Ember open-source software. Zero-dimensional simulations will be run using Cantera's inbuilt 'Ideal Gas Constant Pressure Reactor' function, and unsteady 1D simulations using Ember's counter flow diffusion flame simulator. Therefore, a brief review of the background knowledge regarding the software and the mechanisms used within.

2.1 – Jet in Hot Coflow (JHC) Setup

In the coflow burner setup, a central jet is issued into a shrouding coflow. Cabra et al. [4] produced a diagram of the JHC setup which is seen in Fig. 2-1 The jet is placed at a height such that the fuel may exit into a coflow which is at the desired heat and uniform across all radial positions away from the jet. The equilibrium composition of the H₂ and air coflow provides the temperature/heat required to auto ignite the central fuel jet. Previous literature using this setup have investigated a coflow of pure air [3, 8, 9], and a vitiated coflow which is the hot combustion products of hydrogen and air [4-6]. This thesis reproduces some of this work by investigating both coflow types by simulating a homogeneous composition reactor with no flow characteristics through the 0-D numerical code. Investigating the effects of the vitiated coflow further, the amounts of each species which exist within the coflow are calculated and then tested by injecting them individually into an air coflow.

Another variation in the coflow setup that is tested in this thesis is adjusting the oxygen content in the air coflow. This has been studied before in literature, and so plots will be reproduced from Macfarlane [26]. Standard air consists of approximately 21% oxygen and 79% nitrogen. A decrease in the 21% of oxygen will be tested, where the amount removed will be added to the nitrogen.



Fig. 2-1 Jet in Hot Coflow burner schematic by Cabra et al. [4]

2.2 – Counterflow Setup

Another setup of importance is the counterflow setup, where laminar diffusion flames produced from these experiments are generally referred to as pure diffusion flames [68]. Diffusion flames refer to flames where the fuel and oxidizer are initially separated, such as in the coflow burner. Similarly, a counterflow burner separates the fuel and oxidizer into two separate inlets which are then placed opposite to each other so that both reactants flow into each other. Fig. 2-2 shows a schematic view of this setup.



Fig. 2-2 Schematic view of a counterflow diffusion flame by Ribert et al. [69]

In the diffusion flames, combustion occurs at the interface between the fuel and oxidizer and depends on the rate of mixing and diffusion compared to the chemical reaction between the reactants. Therefore, calculations of the properties of these flames must consider transport properties and the aerodynamics of the flow.

Chemical reaction rates of flames are generally much faster than the time it takes for the reactants to diffuse into each other. This means that the combustion rate of the fuel is greatly dependent on the flow rate of the fuel and oxidizer [68]. Experimentally, this can be adjusted by increasing the flow rate. Numerical simulations can also adjust the strain rate to increase the amount of diffusion which takes place. This thesis will explore the counter flow burner using 1D simulations to impose a strain rate on the flow of the two inlets.

2.3 – Flame Characteristics

Characteristics of flames in the JHC setup have been the focus of a significant amount of past research papers. Of all the characteristics, maybe the most relevant and extensively researched one is the lift-off height. The flame lift-off height is the distance measured between the exit of the jet and the base of the flame [49]. Measurements of the flame profile and other characteristics such as temperature can then be made at these axial locations. For example, Cabra et al. [4] investigated the radial profile of the temperature at the lift-off height and additional axial locations.



Fig. 2-3 Radial profile of temperature at various axial locations, including the lift-off height of the flame, reproduced from Cabra et al. [4].

Common amongst research involving lift-off height, is investigation on the influence of the coflow temperature. Macfarlane et al. [1] found that increasing the coflow temperature

decreases the lift-off height for all fuels and fuel to oxidant ratios tested. This is supported by further work [4, 19]. Therefore, it is common for fuels to have a flame base closer to the jet exit with increasing coflow temperatures.

Another characteristic which is directly correlated with the lift-off height, is the ignition delay time. Both work hand-in-hand, where smaller lift-off heights indicate quicker ignition. Ignition delay time is defined as the time it takes for a fuel and oxidizer mixture to react and ignite. Cabra et al. [19] found that the delay time depends strongly on the temperature, which correlates well with the research done on the lift-off height previously discussed [1]. It was found that the mass flux of the coflow must be larger than that of the jet, as the coflow does the heating. This leads to leaner equivalence ratios between the coflow and the jet. Equivalence ratios will be explained in more detail in a later section.

Research has been done to investigate the delay times of certain fuels. Methane, for example, has a relatively high ignition temperature compared to other fuels, but the ignition temperature can be reduced by mixing the fuel with different hydrocarbons or hydrogen [20, 50, 51] and increased by introducing water vapor [52]. This thesis will investigate the ignition delay times of the chosen fuels, examining the influence that additions of certain radicals and dilution of certain fuels/reactants to the jet has on the ignition.

Finally, many other characteristics of the flame, such as the main stabilization mechanism, has been investigated, with more and more literature stating that autoignition, in fact, stabilizes the flame [3, 4, 6]. Flame velocity [18], acoustic emissions [1] and hydroxyl concentration [53] are other important characteristics of the flame which have been studied in previous literature, however, are not the topic of this thesis.

2.4 – Chemical Equation and Calculations

Chemical equation balance is an important part of this thesis, which must be discussed in some depth in this section. To begin, the concept of equivalence ratio, φ , is seen frequently. It is defined as the ratio of stoichiometric air to fuel ratio over the actual air to fuel ratio [41] and is given in Eq. (2.1):

$$\varphi = \frac{(A/F)_{stoich}}{(A/F)_{actual}}$$
(2.1)

The equivalence ratio is used to indicate whether a mixture of fuel and oxidant is rich, lean, or stoichiometric. Mixtures at lean equivalence ratios have been found to be most reactive [21], so although stoichiometric mixtures theoretically completely burn all the fuel and oxidant, if increased reactivity is desirable, leaner equivalence ratios should be used.

To find the equivalence ratio, the stoichiometric and actual air to fuel ratios must be determined. These ratios can either be calculated on a mass or molar basis, where this thesis will use the latter. Actual ratios are known from the amounts of fuel and oxidant used in the physical experiments or numerical simulations. The stoichiometric ratios can be found by balancing the chemical equation of the fuel and oxidant and can be expressed by the global reaction mechanism [41]:

$$F + aOx \to bPr \tag{2.2}$$

Where a single mole of fuel reacts with a moles of oxidant to produce b moles of products. Knowing the composition of the fuel and any possible diluents, then allows for the calculation of the stoichiometric coefficient, a, which is as follows:

$$a = \frac{4x + y - 2z}{0.84} \tag{2.3}$$

Where x, y, and z, are the number of carbon, hydrogen and oxygen atoms in the fuel. Additions of diluents to the fuel adjust Eq. (2.3) and are shown in Eq. (2.4-2.6). Depending on the constituent species of the diluent, the stoichiometric coefficient can vary. This thesis investigates the dilution of the fuels using nitrogen, hydrogen, and air where the new definitions for the stoichiometric coefficient are shown in equations (2.4) – (2.6) respectively:

$$a = \frac{(1-k)[4x+y-2z]}{0.84} \tag{2.4}$$

$$a = \frac{(1-k)[4x+y-2z]+2k}{0.84}$$
(2.5)

$$a = \frac{(1-k)[4x+y-2z] - 0.84k}{0.84}$$
(2.6)

Where k is the mole fraction of nitrogen, hydrogen, and air in equations (2.4), (2.5) and (2.6) respectively.

Finally, adjustments to the concentration of oxygen in the air coflow will cause the stoichiometric coefficient to change and can be calculated as follows:

$$a = \frac{4x + y - 2z}{4X_{O_2}} \tag{2.7}$$

Where X_{O_2} is the mole fraction of oxygen in the coflow or air stream.

Proof of these definitions for Equations (2.4) - (2.7) will be provided within appendix A1.

To conclude concepts relevant to the chemical equation, the mixture fraction, a conserved scalar, is used to quantitatively describe the extent of mixing that has occurred at a specific point. A mixture fraction of 0 indicates an area of the system which is purely oxidant and 1 indicates an area that is purely fuel. Depending on the composition of the fuel and oxidant, the stoichiometric mixture fraction, where no fuel and oxidant exist, only products, can vary.

2.5 – Autoignition Kinetics

Autoignition of a mixture comes about when the chain reactions which initiate combustion exceed those which terminate combustion. Firstly, the temperature must be great enough for a molecule to dissociate and form radicals. Formation of at least one radical from stable species is considered a chain-initiation step. Once the combustion has initiated, chain-propagating and -branching steps then form or maintain the number of radicals [27]. This leads to ignition of the mixture and thermal runaway, a process which describes the continual release of heat from combustion processes which causes more reactions to take place repeatedly until there is not enough fuel or oxidant. The minimum temperature required for ignition to occur, referred to as the minimum autoignition temperature (AIT), has been researched extensively [54, 55].

Westbrook et al. [56] discovered that the chain branching steps involved in the autoignition of n-pentane, that the consumption of one radical, usually hydroxyl (OH) or hydroperoxyl (HO₂). In fact, research has shown that the consumption of either of these radicals results in a high rate of chain branching [57-59]. Further work by Westbrook [60] found that for

hydrocarbons in the range of 1000 K, the decomposition of hydrogen peroxide (H_2O_2) is as rapid as it is formed, however, the accumulation of H_2O_2 until the mixture reaches a temperature where it can decompose the radical, is the dominant feature of ignition.

Regarding the evolution of autoignition kernels, research has been done to investigate the radical species which precede ignition. Gordon et al. [5] found that formaldehyde (CH_2O) peaks prior to autoignition then decays shortly after, while OH peaks at autoignition and maintains this peak well into the steady flame. Fig. 2-4 shows the evolution of the mole fractions of these radicals.

Further work by Gordon et al. [7] found that a radical pool of precursors containing many minor species, builds up prior to autoignition. Among this pool, were the CH₂O, HO₂ and H₂O₂ radical. Overall, HO₂ and H₂O₂ were present in the smallest mass fractions, however, still played an important role in autoignition for methane. This finding validates Westbrook's [60] research stated earlier which found H₂O₂ is the dominant feature of ignition.

Hydrogen has been found to utilise similar chain branching and initiation steps where ignition is caused by the HO₂ and OH radical [61].



Fig. 2-4 Evolution of mole fractions of CH₂O and OH, reproduced from Gordon et al. [5]

This thesis will investigate these chemical reactions to see which has the most influence on the combustion of the tested fuels. The mole fractions of radicals will also be found within the autoignition kernels to identify which are important and observe their effect on the ignition delay times.

2.6 – Physical Experimentation

Physical experimentation has been utilised throughout most literature as ways to examine flames and combustion. These experiments can be broadly separated into two categories: intrusive and non-intrusive. Intrusive experiments involve the use of a probe which perturbs the flow in any way. Non-intrusive experiments, which are more commonly used, usually involve laser imaging techniques to observe the flames without disturbing the flame or inlets. One method which has been used in many research papers is the use of planar laser induced fluorescence (PLIF) imaging techniques [4-6].

In fact, the combustion laboratory within The University of Sydney has its own PLIF experimental setup. It was planned to utilise this setup to produce results for this thesis, however, due to the Covid-19 crisis, the lab had to be closed making it impossible to run experiments. Fig. 2-5 shows an image of the coflow burner and the PLIF experimental setup within the lab.



Fig. 2-5 Photo of the experimental setups of the (Left) Actively cooled coflow burner and (Right) PLIF imaging setup at the University of Sydney, 2021.

2.7 – Effect of Flame Type, Strain Rate and Diffusion on Ignition

Experiments involving the coflow burner may involve a laminar or turbulent flame. Spalding [62] and Libby et al. [63] developed a conceptual point of view of turbulent combustion, describing the flames as a collection of laminar reactive surfaces, commonly referred to as laminar flamelets. Common to these studies is the idea that the strain rates play an important role on the flamelets, where higher strain rates can be imposed by forcing turbulence to occur. Further work by Libby et al. [64] indicated that the flame surface of a laminar flame wrinkles in the presence of weak turbulence. As the turbulence grows, the reactive surface of the flame begins to tear, where the products and reactants then diffuse further into each other, without

definitive boundaries splitting the two. Pockets of reactants can then exist in a background of products and vice versa.

Further work in this field has been done by Carrier et al. [65] and Marble et al. [66] who discovered that, in addition to diminishing the flame surface, increased strain rates lead to increased fuel consumption per unit flame area. More importantly however, is the idea that the high strain rates can extinguish the flame due to rapid cooling at the flame surface and more simply if the fuel and oxidant are forced together too 'quickly' reaction rates cannot 'keep up'. Turbulence can cause entrainment of the cooler surrounding air or convects fresh reactants towards the flame surface at a faster rate which causes the cooling.

Turbulence, as in the cases as above, is usually brought about by increasing the Reynold's number of the flow by increasing the velocities, densities, or characteristic length. Experiments can also be utilized to cause turbulence and high strain rates, such as use of the counterflow which establishes a reacting zone between two opposing streams of fuel and oxidizer, as done by Papas et al. [67] and Tsuji [68]. Physical experiments were done to determine the strain rates near extinction for methane and propane with increasing amounts of other species premixed with the fuel.

Ignition depends on the temperature of the mixture; however, strain rate and diffusion of the species plays an important part too. This thesis will explore the influence of strain rate and diffusion by running numerical simulations to compare a coflow and counter-flow setup.

2.8 – Numerical Simulations

Numerical simulations are of great importance for understanding combustion. Developments in numerical combustion have made it possible to consider the full complexity of combustion phenomena and calculations of the flame structure including its complex kinetics [70].

Simulations can be performed in 0 to 3 dimensions using a variety of mechanisms. Each dimension increases in complexity. 3-D simulations can be used to calculate all features of the flame structure in three dimensions. 0-D simulations only consider the chemical kinetics of combustion which includes the chemical reactions which take place, the importance of each and the ignition delay times. 1-D simulations then include the effects of transport and diffusion, where now the reactants must travel a distance along one dimension where they then meet and react with each other, and the time taken to mix is taken into consideration. 0-D and 1-D simulations will be performed and compared within this thesis, by simulating a

coflow and counter flow burner setup respectively. To compute these simulations, this Thesis will utilise the Cantera [25] and Ember [72] solvers for the 0- and 1-D simulations respectively.

Finally, chemical mechanisms must be considered when conducting computational simulations. Each mechanism varies in the number of species and elementary reactions involved. Hydrogen combustion was one of the first chemical kinetics system to be modelled and has no more than 10 species and 20 elementary reactions [71]. Choice of mechanisms is important and depends on the choice of fuel and computational power and time available. Some mechanisms involve a larger number of reactions to calculate features of the flame more accurately, however, this has the downside of costing more computational power.

Literature has shown that currently available mechanisms lead to significant variations in the predicted ignition delay times [22-24], sometimes larger than an order of magnitude. Therefore, caution must be taken when reviewing results from computational simulations as the chemical mechanism considered can produce variations. In this thesis, the SanDiego mechanism will be used as it is an 'all-rounded' mechanism which the number of species and reactions are kept to the minimum required [72].

2.9 – Background Summary

In summary, the literature regarding autoignition utilises physical experiments involving the coflow and counterflow burners. The use of these two have allowed for the calculation of certain flame characteristics. Coflow burner experiments have been conducted to observe the lift off heights of flames, along with the occurrence of autoignition kernels, their concentration, and their impact on the stability of the flames. Various coflow setups have been tested in the past. This thesis will continue this work by running numerical simulation to investigate more variations in the coflow. The influence of the radicals that exist within a vitiated coflow will also be explored by isolating them and injecting them into a pure air coflow to observe the change in the ignition delay times of the fuels.

Research has also been done using the counterflow burners which have been referred to as pure diffusion flames. This setup will also be simulated numerically within this thesis, to observe the influence strain rate and diffusion has on the delay times. Numerical simulations can be done in many dimensions, but for this thesis, 0D and 1D simulations of the coflow and counterflow burners will be used. The literature has been quite limited when it comes to comparing 0D and 1D numerical simulations, so this thesis will emphasise on reproducing similar conditions tested using the coflow burner in the counterflow burner.

Chapter 3.0 – Composition of Autoignition Kernels

In this chapter, the aim is to identify and observe the species that dominate the ignition kernels which develop prior to heat release and to compute the ignition delay times for a range of mixtures. The 0-D homogenous reactor is employed to singularly simulate the chemical reactions which take place in the fuel and oxidant mixtures. Past studies have focused quite heavily on the peaks in hydroxyl (OH) content as being the principal indicator of autoignition [6, 8, 9]. However, it has been found that peaks in the levels of formaldehyde (CH₂O) precede that of hydroxyl and so may be a more defining feature of the onset of autoignition [5, 7]. This chapter will conduct tests to see which radical will be used to define the start of autoignition for the rest of the thesis.

Gordon et al. [5] studied the build-up of radicals for a methane jet issuing into a vitiated coflow of hot combustion products of hydrogen and air. He found that the evolution and onset of autoignition is confirmed by the build-up of a precursor pool which leads to reaction of these radicals and then a formation of a steady flame. Ignition is preceded by the formation of formaldehyde, hydroperoxyl (HO₂), and hydrogen peroxide (H₂O₂) among other less prevalent ones. As mentioned above, formaldehyde was the most distinct of the species in indicating the onset of autoignition as planar laser induced fluorescence (PLIF) imaging techniques show pockets of high formaldehyde content which grow and convect into the main flame base. These results were in line with the computational laminar transient calculations performed in parallel.

Another study of a methane flame by Gordon et. al. [7] found that a radical pool of precursors builds up prior to autoignition, with these species being a methyl group (CH₃), formaldehyde, acetylene (C₂H₂), ethylene (C₂H₄), ethane (C₂H₆), hydroperoxyl and hydrogen peroxide. Reproducing this work, the amounts of each species that exists within the reactor as a function of time will be calculated to find the times at which the peaks occur. The species which peak first will then take precedence in signifying when autoignition has started to occur. To validate these findings, temperature and heat release will be plotted and tracked to ensure that the peaks of the species content line up and match with the peaks in heat release and temperature. This is because the peak of heat release and rapid increase in temperature are indicators that reaction and ignition have taken place [27]. The fuels studied in this chapter, which will also be the fuels observed throughout the entirety of this thesis, will be hydrogen, methane, and propane. The San Diego mechanism will also be utilised for all simulations.

The setup is that of a simple coflow burner, where a central jet is issuing into a hot air coflow where the equivalence ratio of the fuel in the jet to the air in the coflow is taken to be $\varphi = 0.2$ for all simulations. It should be noted that this chapter is only utilising a 0-D reactor which is simulated to be perfectly mixed and homogenous, and so mixing and diffusion of the jet and coflow do not impact the calculations and results. The only effect of separating the two is that the coflow is now used to heat up the fuel in the jet from 300K to the nominated coflow temperature as opposed to the fuel starting at the same temperature as the coflow.

Figures 3-1 - 3-6 show the content of several significant species and the reactor temperature and heat release, respectively, in combustion at relatively low temperatures for hydrogen (H₂), methane (CH₄) and propane (C₃H₈) jets respectively. The plots for the high temperatures provide similar results with similar deduction made and have been provided in Appendices B1 to B6. The temperatures used for the coflow are listed in Table 3-1. These temperatures were decided by trialling the simulations so that the low and high temperatures would result in heat release peak times of approximately 25ms and 1ms respectively. The reactor temperature in the plots is also simply the temperature of the mixture in the simulation as it progresses through each timestep.

	H ₂	CH ₄	C ₃ H ₈
Low Temp. (K)	963	1200	1100
High Temp. (K)	975	1500	1300

For the hydrogen jet, only three species are observed compared to the eight for the other two hydrocarbons, as hydrogen does not consist of any carbon and so the radical species formed from carbon are omitted intentionally as they do not form in the combustion of hydrogen.

For hydrogen in Fig. 3-1 all three radicals, those being hydroxyl, hydroperoxyl and hydrogen peroxide peak as a result of autoignition, in line with previous studies [5, 6]. At 963K hydroxyl peaks the latest at 25.43ms, while both other radicals peak together at 25.34ms.

Interestingly, the heat release peaks at 25.42ms which is 0.01ms before the peak of hydroxyl. This feature is common amongst all three fuels, where the peak in mole fraction of hydroxyl occurs in the order of a hundredth to tenths of a millisecond after the peak in heat release. All other radicals peak before heat release. This gives hydroxyl and heat release a unique and interesting relationship. Regardless, despite past literature using hydroxyl as the indicative species [6, 8, 9], the plots shown in this section show otherwise.

Comparing the low and high temperatures, hydroperoxyl and hydrogen peroxide peak relatively faster for a low coflow temperature (963K), whereas for a higher coflow temperature hydroperoxyl peaks before both hydrogen peroxide and hydroxyl. For methane and propane, hydroxyl peaks the latest of all species for both fuels at both low and high coflow temperatures. Peak generation of formaldehyde precedes the peaks of hydroxyl, which validates the findings of Gordon et al. [7]. Formaldehyde, in fact, peaks well before all other observed species and so is the most indicative that autoignition is taking place.

Within this paper, however, hydrogen will be studied, and so, to remain consistent with all fuels, the commencement of autoignition will be defined by the peaks of hydroperoxyl and hydrogen peroxide. It is common among all three fuels being studied for these peaks to occur comparatively earlier than the other radicals. Although it is not clear which of the two is superior as results show that either can occur first, the calculations in the preceding sections will simply use the occurrence of whichever comes first. Using this definition, the ignition delay times of each fuel at each temperature can then be obtained from the plots and are shown in Table 3-2. Further study into the chemical reactions and processes occurring in the fuel may provide a better answer, although, this is not the topic of this thesis and so will not be investigated in any more depth. However, the influence of these species on ignition delay time will be investigated.

 Table 3-2 Ignition delay times of each case tested.

		H ₂	CH ₄	C ₃ H ₈
Ignition delay	Low Temp.	25.34	23.71	27.76
times (ms)	High Temp.	1.89	1.62	1.27

Now that formaldehyde and hydrogen peroxide have been decided as the key species among all three fuels to indicate the onset of autoignition, latter sections will simulate small amounts within a coflow and the influence this has on the delay time. A focus will also be placed on hydroxyl by investigating this radical in parallel with the other two.



Fig. 3-1 Species content in mole fractions versus time for a hydrogen jet issuing into a pure air coflow at 963K with the peak time of each species stated.



Fig. 3-2 Heat release and reactor temperature versus time for a hydrogen jet issuing into a pure air coflow at 963K with the heat release peak time stated.



Fig. 3-3 Species content in mole fractions versus time for a methane jet issuing into a pure air coflow at 1200K with the peak time of each species stated.



Fig. 3-4 Species content in mole fractions versus time for a methane jet issuing into a pure air coflow at 1500K with the peak time of each species stated.



Fig. 3-5 Species content in mole fractions versus time for a propane jet issuing into a pure air coflow at 1100K with the peak time of each species stated.



Fig. 3-6 Species content in mole fractions versus time for a propane jet issuing into a pure air coflow at 1300K with the peak time of each species stated.

Chapter 4.0 – Ignition Delay Times

The aim of this chapter is to investigate the ignition delay time, along with some other influential parameters effecting the delay time, by running numerical simulations to calculate this value for the three fuels studied in a variety of coflow setups. Delay times have been studied in the past with the agreed upon and expected results being that delay times will decrease with an increase in coflow temperature [17, 19, 21]. An interesting finding by Choi et al. [18], however, found that the delay time increased for propene in the range of 960-980K; an example of the phenomena named the negative temperature coefficient (NTC). An inadequacy of this result however is that calculations were only made at the outer bounds of this range. Although, several different mechanisms were tested, and all produced the same results which may prove its accuracy.

Now, an issue with numerical findings is that results have proven to be very inconsistent between each mechanism. Significant variations in results have been found [22-24], especially with respectively large delay times, where a stoichiometric mixture of methane and air burning at 860K has a predicted delay time in the range of 3-50s. Therefore, chosen mechanisms must be carefully considered and caution taken when reproducing calculations.

Some of these variations are a result of the type of reactor used rather than what mechanism was selected. One-dimensional reactors have the effects of mixing and diffusion while zerodimensional reactors are calculated from steady state (i.e., solved spatially with no time components) to be perfectly mixed and homogenous. Ignition delay times are heavily influenced by strain rates and scalar dissipation rates [21], due to diffusion of the turbulent jet into the coflow. Consequently, the type of reactor used for numerical simulations must be noted to understand what is affecting the ignition.

This chapter uses a 0-D reactor solver in Cantera [25] to calculate the delay times. The reactor is homogenous and transient, meaning there is no dissipation of the jet into the coflow, but rather the mixture will simply react as if premixed. Separation of fuel and oxidizer will be done in most sections which is to simply define separate temperature for each.

4.1 – Basic Simulation: Fuel and Oxidizer Combined

The aim of this section is to introduce very basic ignition delay time calculations. Rather than having fuel in the jet heated from 300K by the oxidizer from the hot coflow, both the fuel and oxidizer will be premixed and preheated to the chosen temperature. Results will be plotted in



Fig. 4-1 to visualise how quickly each fuel ignites at each temperature. For this section, an equivalence ratio of 0.2 is used.

Fig. 4-1 Ignition delay time versus jet temperature for hydrogen, methane, and propane premixed at an equivalence ratio of 0.2 (a) For various ranges of jet temperatures (b) For jet temperatures ranging from 1200 to 1500K.

Shown above, Fig. 4-1 presents the delay times, τ (ms) plotted versus the jet temperature, T_{Jet} (K) for the three fuels hydrogen, methane, and propane. Hydrogen clearly ignites much faster than both other higher hydrocarbons, and at lower jet temperatures. Propane and methane then both ignite at similar delay times for temperatures of approximately 1500K and greater,

whereas, for an ignition delay time of 20ms, methane and propane require approximately 1275K and 1125K respectively.

Methane requires the largest initial temperature to ignite, while hydrogen requires the least. This is an expected result as hydrogen has been experimented as an additive for methane and has previously shown to appreciably decrease the lift off height to less than half its original value with a mole fraction of only 2% of hydrogen [20]. Finally, propane lies in between but is evidently much closer to methane than it is to hydrogen.

4.2 – Fuel and Oxidizer Separated

Now, this section investigates the difference in the 0-D reactor when the fuel and oxidizer are split into the jet and coflow respectively. The effect of splitting is that the fuel, now initially at 300K, must be heated by the oxidizer which varies in temperature. Fig. 4-2 shows these plots of delay time versus coflow temperature, T_C for the same fuels, again, at an equivalence ratio of 0.2.

All the fuels behave very similarly to the preceding section. The delay times and temperatures are almost identical except that the same temperatures require a slightly longer delay time. This is due to the small amount of time required for the coflow to heat up the jet to a temperature where autoignition is possible and the mixture is flammable.

4.2.1 – Fuel in Vitiated Oxidizer

Now, a multitude of setups from past research have involved a vitiated coflow of hot combustion products of a hydrogen and air mixture [4-6]. This section utilises the same setup as these studies to observe the influence the vitiated oxidizer has on the delay time. Caution was taken to ensure that the air to fuel ratio was calculated correctly according to eqn. (2.7) where the oxygen content is calculated from the Cantera code [25]. There is a slight inaccuracy in this, that, although the oxygen content is accounted for in the equation, there are other species which can influence the combustion kinetics, and so there are many other variables to the ratio. These variables, however, are negligible and will not be studied within this thesis. Improving the accuracy of future simulations would involve correct calculations of all relevant species to then obtain the correct stoichiometric coefficient. Table 4-1 shows the results of the Cantera calculations, and the mole fractions of the species within the coflow when preheated to 1600K.



Fig. 4-2 Ignition delay time versus coflow temperature for hydrogen, methane, and propane premixed at an equivalence ratio of 0.2 (a) For various ranges of coflow temperatures (b) For coflow temperatures ranging from 1200 to 1500K.

Again, in terms of the relationship from fuel to fuel, all three behave quite similarly to previous results where methane requires the largest coflow temperatures to ignite and hydrogen the least, as seen in Fig. 4-3. In terms of comparing each individual fuel to previous results, the delay times are noticeably quicker. This is directly caused by the addition of new species within the oxidizer, where certain of those that were found will be investigated further in the succeeding sections.

Code was written to calculate the mole fraction of all the species, utilised by the San Diego mechanism, for the products issuing out of the coflow at a temperature of 1600K. Some notable properties were that the nitrogen and oxygen contents dropped to approximately 66% and 9% respectively, compared to the standard 79% and 21% content which exists in air. Another notable feature is that 17% of the coflow exists as water (H₂O). Table 4-1 below has a more detailed list of the contents of certain radicals within the oxidizer.



Fig. 4-3 Ignition delay time versus coflow temperature for hydrogen, methane, and propane issuing into a H_2 /Air coflow premixed at an equivalence ratio of 0.2 for a range of coflow temperatures.

Species	Content (Mole Fraction)	
N_2	0.66	
Н	9.89E-08	
O_2	0.09	
OH	2.09E-04	
0	4.23E-06	
H_2	3.55E-06	
H_2O	0.17	
HO ₂	2.70E-07	
H_2O_2	1.91E-08	

Table 4-1 Mole fraction of species within the 1600K H₂/Air oxidizer.

Chapter 3 discusses the most significant species in indicating ignition. The noticeable radicals worthy of mention were that of hydroxyl (OH), hydroperoxyl (HO₂) and hydrogen peroxide (H_2O_2) . It was found that both hydroperoxyl and hydrogen peroxide were the superior indicator as both peaked in amount before hydroxyl, however, the contents of the combustion products of hydrogen and air show that hydroxyl exists in the greatest amount, compared to all the other radicals (ignoring the water products and unburnt components of air). This may be evidence that, although not the first of the radicals to peak, hydroxyl has the greatest influence on driving ignition.

4.3 – Species Content in Vitiated Oxidizer

The amounts of these radicals were investigated further, by plotting the change of mole fractions of oxygen, water, hydroxyl, hydroperoxyl and hydrogen peroxide with temperatures

ranging from 900-1600K; a study reproduced from Macfarlane [26]. Hydroxyl remains to exist in the greatest amount of the three minor species for all temperatures tested by 3-4 orders of magnitude, as seen in Fig. 4-4. A noticeable characteristic of the growth of these three radicals, however, is that all grow exponentially, increasing at an increasing rate as the temperature of the coflow increases. This means that at the higher temperatures, the kinetics which drive ignition not only act more rapidly, which decreases the delay time, but also produces an increased amount of the important radicals which indicate the start of ignition.



Fig. 4-4 Mole fractions (X) of O₂, H₂O, OH, HO₂, and H₂O₂ from the equilibrated H₂/air coflow at temperatures ranging from 900-1600K. Reproduced from Macfarlane [26].

4.4 – Adding Radicals to a Pure Air Oxidizer

To observe the effect that these radicals have on the ignition delay times, small amounts have been injected into the pure air oxidizer. Both hydroxyl and hydrogen peroxide have been chosen for this section. Mostly because they were already discussed in the preceding chapter, but also because hydroxyl has been studied to be a key driving species in ignition [26], and because hydrogen peroxide exists in smaller amounts than hydroperoxyl, which may help make comparisons more evident. Calculations involve adding increasing amounts of the observed radical to a pure air oxidizer as a mole fraction, starting from the realistic amounts of each which exist in the vitiated oxidizer at a temperature around 1000K. This is so that realistic amounts of the radicals can be compared, while also comparing unrealistically large amounts of each to see which has more of an influence on the delay time, when the same amount of each radical exists in the oxidizer.

Now, by observation of Fig. 4-5 and 4-6, additions of any amounts of hydroxyl and hydrogen peroxide at all coflow temperatures show a decrease in ignition delay time. This is in line with results from Tu et al. [27] who found that additions of hydroxyl in the coflow reduces the ignition temperature and the lift-off heights. Effectively, this means that both species work towards speeding up the ignition process.

Comparing the two radicals to each other with hydrogen as the fuel, hydroxyl clearly has the greatest influence on reducing delay times. When investigating amounts of the same order of magnitude, hydroxyl is superior until about 10⁻⁴ where all the results begin to converge around the same delay times. At temperatures of 1020K and greater, the delay time is no longer dependent on the amounts of radicals that exist in the coflow and any differences are negligible.



Fig. 4-5 Ignition delay time versus coflow temperature for hydrogen issuing into an air coflow with increasing amount of (a) hydroxyl and (b) hydrogen peroxide.

Investigating methane, the hydrocarbon shows a greater sensitivity to hydrogen peroxide, which is opposite to what was found for hydrogen. Fig. 4-6 shows that additions of 1E-3 mole

fractions of hydroxyl and hydrogen peroxide decrease the delay times to approximately 13 and 12ms respectively. Hydrogen peroxide is superior by approximately 1ms. For a more accurate comparison, however, 1E-04 and 1E-08 mole fractions of hydroxyl and hydrogen peroxide respectively, should be compared. This is because these radicals exist in those orders of magnitude in the range of coflow temperatures tested, as seen in the preceding section.



Fig 4-6 Ignition delay time versus coflow temperature for methane issuing into an air coflow with increasing amount of (a) hydroxyl and (b) hydrogen peroxide.

At 1600K, the hydrogen/air coflow was found to contain 2.09E-04 and 1.91E-08 mole fractions of hydroxyl and hydrogen peroxide respectively (see Table 4-1). The figures show that when adding 1E-08 mole fractions of hydrogen peroxide to either hydrocarbon, the delay time is barely affected. Hydroxyl, on the other hand, has a much more noticeable impact when

injected at 1E-04 mole fractions. This is seen in both hydrocarbons and, of course, hydrogen. It can be concluded then, that hydroxyl has the greater influence on ignition for all three fuels compared to the other radical, hydrogen peroxide.

To further validate these findings, a brute force sensitivity analysis may be utilized. This method calculates how sensitive the delay times are to the certain amounts of radicals injected into the coflow. In this case, it is the differentiation of the delay time with respect to the temperature [17]. Fig. 4-7 plots these sensitivities for methane fuel. The brute force sensitivity plots for hydrogen and propane have been provided in appendix C1.



Fig. 4-7 Sensitivity analysis for methane issuing into an air coflow with increasing amounts of (a) hydroxyl and (b) hydrogen peroxide.

Again, 1E-08 mole fractions of hydrogen peroxide has a very small effect on the delay time, while 1E-04 mole fractions of hydroxyl has a much larger sensitivity. This plot also further reinforces that similar amounts of each radical shows that the delay time is more sensitive to hydrogen peroxide. However, it is unrealistic to see the same amount of each radical.
Lastly, the delay times for propane have also been plotted, but the results contribute the same information which was deduced from the methane plots. They are provided in appendix C2.

4.5 – Varying the Oxygen Concentration in the Pure Air Oxidizer

Moving on to other tests with the oxidizer, the air oxidizer was tested by reducing the concentration of the oxygen for all three fuels, reproducing results obtained by Macfarlane [26]. Fig 4-8 shows the plots of the delay times for each fuel with the variations in oxygen content.

From section 4.3, after equilibrating the hydrogen/air coflow at 1600K the mole fraction of oxygen dropped from 0.21 standard in air, to 0.09. Fig. 4-4 also shows that the oxygen levels are all below 21% for the range of temperatures tested from 900K to 1600K. In fact, the oxygen concentrations vary from 0.16 at 900K to 0.09 at 1600K. To test the effects of these variations, the three fuels were then tested within a pure air oxidizer, where the mole fraction of the oxygen in the air was adjusted.

In the preceding section, the effects of the radicals from the coflow were studied. Now, the oxygen content will be adjusted so that the effects of these adjustments can be isolated. This will allow for comparisons to be made between the addition of radicals and the adjustment of oxygen content to observe which of these changes has a greater impact on the delay time.

Fig. 4-8 (a) shows the influence of oxygen concentration for the hydrogen fuel. Interestingly, from 950 to 1250K, decreasing the oxygen concentration also decreases the delay time. By decreasing the concentration, the amount of oxygen in the oxidizer changes so that, ultimately, it is as if the equivalence ratio is increasing. The mass of the coflow still remains the same, meaning the amount of heating done to the jet by the coflow should also remain consistent, ignoring the specific heat of oxygen and nitrogen. This is important because usually increasing the equivalence ratio results in lower temperatures as there is less oxidizer to heat up the increased amount of fuel. Therefore, it is expected for the delay time to decrease due to the combined effect of the resultant increased equivalence ratio and maintained mass of the oxidizer.

The lines for the decreasing oxygen contents then intersect with the original line, from temperatures of 1250K and upwards, so that they all result in longer ignition times. This is interesting because the simulations were run at an equivalence ratio of 0.2 which corresponds to a mixture fraction of approximately 0.005 or 0.5%. It has been found previously that the

most reactive mixture fraction for a methane jet in a hot air coflow is 1% [21]. By decreasing the oxygen content, the mixture fraction will increase according to eqn. (2.7) and tend towards the most reactive mixture fraction of methane.

This explains the pattern for the lower temperatures, but not why the 0.21 mole fraction ends up igniting the quickest of all the cases tested, from 1360K and upwards. It may be worth investigating the reaction of hydrogen at relevantly high temperatures in the future.

Observing methane, the mixture fraction, at an equivalence ratio of 0.2 and oxygen content of 0.21, is approximately 0.011 or 1.1%. For propane, this value is approximately 1.2%. Methane follows the expected results of Arndt et al. [21] as the mixture fraction is already at the most reactive, so by changing the oxygen content, the delay times are expected to increase. Propane also acts quite similarly, except for some overlaps with the 15% oxygen content graph from 1180-1400K. These overlaps result in differences which are negligible and won't be investigated any further.

Relating these findings back to the study done in section 4.5, the reduction in oxygen content has the inverse effect to the addition of hydroxyl and hydrogen peroxide, where, reducing the levels of oxygen increases the ignition delay time. This means that the quicker ignition times seen when using a vitiated oxidizer are due to the hydroxyl, hydrogen peroxide and any other influential radicals, rather than the change in oxygen content.



Fig. 4-8 Ignition delay times for a preheated air coflow with reduced oxygen concentration for (a) hydrogen, (b) methane, and (c) propane. Reproduced from Macfarlane et al. [28].

4.6 – **Diluting the Fuel**

The final change to the standard coflow setup that will be studied within this chapter is the addition of diluents to the fuel in a pure air oxidizer. The addition of diluents will reduce the amounts of fuel in the jets, which will have an impact on the stoichiometric coefficient of the coflow. Therefore, for each addition, a new stoichiometric coefficient will be required depending on what the diluent is. Appendix A1 shows the full calculation of these values from the chemical balance equation.

This section will be split up into sub sections to discuss the influence of nitrogen, hydrogen and finally air additions. Each of these sub section will begin by listing the stoichiometric coefficient equation and the variables within it. Finally, the addition of air will be studied in the most depth where comparisons will be made on the delay times of the flame when the coefficient is corrected, and when it is kept constant at the original value.

4.6.1 – Nitrogen Dilution

The calculation for the stoichiometric coefficient with the addition of nitrogen to the fuel is as follows:

$$a = \frac{\left(1 - X_{N_2}\right)\left[4x + y - 2z\right]}{0.84}$$

Where the variables are the same as in eqn. (2.4).

All three fuels were tested to see what effect nitrogen dilution to the fuel would have on the delay time. Methane is shown below in Fig. 4-9 to have an increased delay time as more nitrogen is added to the fuel. Now, although the idea of less fuel resulting in less of a delay time seems intuitive, it has been found that the most reactive mixture fraction (corresponding to the quickest delay times [29]) is about 1% [21]. So, decreasing the amount of fuel may, in the case where there is too much fuel so that the mixture fraction is above its most reactive value, decrease the delay time.



Fig. 4-9 Ignition delay times for a preheated air coflow with increased amounts of nitrogen dilution to a methane jet.

In this instance however, the stoichiometric coefficient is corrected. This means that, in the context of the coflow setup, the flux of air from the coflow has a mass flow that allows for the equivalence ratio of the fuel in the jet to the air in the coflow to remain at 0.2. The temperature of both molecules in the jet are kept at 300K and are perfectly mixed. Therefore, the only variable at play is the amount of nitrogen mixed with the fuel, where the specific heat of nitrogen then dictates by how much the delay time slowed. The specific heat of nitrogen is relatively low compared to some of the other hydrocarbons and common gases found in the atmosphere [30]. This means the nitrogen dilution won't have an extreme impact on the delay time, however, as seen in Fig. 4-8, the increased amount of nitrogen does in fact slow the ignition time.

Both hydrogen and propane showed quite similar results at relatively low ignition temperatures and the plots are given in appendix C3. At higher temperatures, the delay times would decrease with further dilution. This won't be investigated within this thesis, however, may be worth additional study.

4.6.2 – Hydrogen Addition

The calculation for the stoichiometric coefficient with the addition of hydrogen to the fuel is as follows:

$$a = \frac{(1 - X_{H_2})[4x + y - 2z] + 2X_{H_2}}{0.84}$$

Where the variables are the same as in eqn. (2.5).

Hydrogen has been tested as an additive to methane previously [20] and has shown to decrease the lift off height appreciably. This is expected as both fuels have been tested individually in various simulations done regarding the 0-D reactor within this thesis. All simulations have shown that hydrogen has a much quicker delay time than methane. Fig. 4-10 shows the effects of hydrogen dilution to a methane jet.





Observing the graph, hydrogen does indeed decrease the delay time appreciably. At 1200K, even 10% of hydrogen in the jet decreases the delay time from approximately 35ms to 18ms. This is almost a 50% decrease. The study by Choi et. al. [20] found that at 980K, addition of 1% of hydrogen to a pulsed methane jet, decreased the lift off height by approximately 36%. Therefore, the figure validates the idea found, that hydrogen addition decreases the time taken for the fuel to ignite. Propane showed similar results and is given in appendix C4.

Finally, at 965K, which was the lowest oxidizer temperature tested, the delay time of the fuel is in the range of 13-15ms when the jet is 75-80% hydrogen. Comparing this to an earlier simulation of pure hydrogen, Fig. 4-2, although not igniting below 990K, ignites quicker for all oxidizer temperatures tested. Although, the difference is negligible at relatively high temperatures.

4.6.3 – Air Addition

The calculation for the stoichiometric coefficient with the addition of air to the fuel is as follows:

$$a = \frac{(1 - X_{Air})[4x + y - 2z] - 0.84X_{Air}}{0.84}$$

Where the variables are the same as in eqn. (2.6).

It should be noted that the air added to the fuel is at the same temperature of the fuel, which is 300K.

When running the simulations for the addition of air, the effects of adjusting the stoichiometric coefficient was investigated. The two cases were:

- 1. Correcting the stoichiometric coefficient depending on the amount of air added to the fuel; and
- 2. Fixing the stoichiometric coefficient to the value it would have without considering the air addition.

By correcting the stoichiometric coefficient, in the context of the coflow, the amount of flux of air in the coflow will decrease as the amount of fuel in the jet decreases. Thus, there is less mass of hot air to heat the mixture of the jet. At the fixed coefficient, regardless of air dilution in the jet, the amount of hot air in the coflow remains the same. The value of the coefficient will impact the ignition delay times and will be the first observed variable in this section.

The second variable is the equivalence ratio of the fuel and dilution air within the jet. By adding air, the equivalence ratio decreases, meaning the mixture becomes increasingly leaner. This mixture then heats up from the coflow air. It should be noted that the overall equivalence ratio of jet mixture to coflow air remains constant at 0.2 and is separate to the ratio of the jet.



Fig. 4-11 Ignition delay times for a preheated air coflow with increased amounts of air dilution to a methane jet while either fixing or correcting the stoichiometric coefficient.



Fig. 4-12 Ignition delay times for a preheated air coflow with increased amounts of air dilution to a methane jet while adjusting the overall equivalence ratio and correcting the stoichiometric coefficient of the coflow.

To compare the impact of these two variables, the delay times for a methane jet are plotted, in Fig. 4-11 with a couple of cases of air additions with either a corrected or fixed stoichiometric coefficient.

There is a 'double crossover' feature, where at relatively low and high oxidizer temperatures, fixing the stoichiometric coefficient increases the delay time. The double crossover then causes the mixture to ignite quicker within the range of approximately 1325-1525K and 1400-1525K for air to fuel ratios of 1:1 and 2:1 respectively. This is most likely caused by the two competing variables, the influence of one may take over the other within certain ranges. Both

hydrogen and propane also show crossovers at a varied range of temperatures and will be included within appendix C5.

Finally, the last simulation run within this section was to keep the stoichiometric coefficient corrected, while comparing adjustments to the overall equivalence ratio from 0.2 to 1. Increasing this equivalence ratio decreases the amount of hot air in the coflow which is decreased further by the increased additions of air to the jet. Fig. 4-12 shows the results of these simulations.

The impact of both variables, adjusting the equivalence ratio and adding air to the jet, can be isolated with these graphs. Air additions increase the delay time at all oxidizer temperatures and both equivalence ratios. Increasing the equivalence ratio increases the delay times at relatively low temperatures while increasing the delay time at relatively high temperatures, creating a single intersection point for every case of air addition. Again, this single intersection could be due to the competing effects of varying the amount of total air in the system and varying the amount of heating done as an effect of changing the amount of air in the oxidizer.

4.7 – Investigating the Equivalence Ratio

The final section of this chapter investigates the delay times as a function of the equivalence ratio. The preceding section observed the effects of adjustments from 0.2 to 1. Here, multiple ratios will be tested and plotted in one graph to observe the relationship and impact it has on ignition.

Macfarlane [26] has previously investigated the effects of the equivalence ratio on a range of fuels, including hydrogen, methane, and propane. Fig. 4-13 is reproduced to achieve the same results.

Oxidizer temperatures that do not match the temperatures used throughout the rest of the thesis are used as these temperatures were found to best show the 'U' shape. An interesting finding from this plot is the local peak of delay times at an equivalence ratio of approximately 0.2-0.25. This local peak could help define the findings from the previous sections, because adjustments to the equivalence ratio does not result in a 'smooth' shape, which may indicate that the chemistry of the fuel may react differently at that equivalence ratio. Again, this may be worth further study to help facilitate understanding the 'crossover' of the plots from the preceding section.



Fig. 4-13 Ignition delay time versus equivalence ratio for hydrogen, methane, and propane premixed at a coflow temperature of 1200, 1400, and 1220K respectively. Reproduced from Macfarlane [26].



Fig. 4-14 Ignition delay time versus equivalence ratio for hydrogen, methane, and propane premixed at a mixture temperature of 1200, 1400, and 1220K respectively for equivalence ratios of (a) 0-2, and (b) 0-20.

Now, to isolate the equivalence ratio even further, the temperature of the fuel was increased to the temperature of the oxidizer, effectively resulting in a constant mixture temperature from

the beginning of the thesis. Rather than matching the jet temperature to the coflow temperature, the basic jet used in section 4.1 was reused by setting the overall temperature of the fuel and air mixture to 1200, 1400 and 1220K for hydrogen, methane, and propane respectively. Fig. 4-14 shows the results of this simulation.

Again, the local peak is seen at approximately 0.2. The main difference, however, is the decreased delay times and the ability for all three fuels to be able to ignite even at larger equivalence ratios.

Finally, methane was investigated further by plotting the delay times for several oxidizer temperatures on the same figure, as seen in Fig. 4-15.



Fig. 4-15 Ignition delay time versus equivalence ratio for methane premixed at an oxidizer temperature of 1250, 1400, and 1600K respectively.

The results here are quite interesting because at 1250 and 1600K, the influence of the local peak is quite low, where both plots have a much better 'U' shape compared to 1400K. Again, all these findings seem to have some relation which is not studied here but is an area which is suspected to provide further interesting results. Finally, the delay times decrease as the oxidizer temperature increases, which was expected.

Chapter 5.0 – Sensitivity Analyses

This chapter will now focus on performing sensitivity analyses on some of the fuels, using an in built Cantera function [31]. A sensitivity analysis is used to find which parameter has the greatest influence on a computed solution [10]. The logarithmic sensitivity coefficient S_i is defined as:

$$S_i = \frac{A_i}{y} \frac{\delta y}{\delta A_i} \tag{5.1}$$

Where y is the solution of the simulation and A_i the *i*th parameter which y depends on [10]. In the case of Cantera, this equation becomes:

$$S_{ki} = \frac{p_i}{y_k} \frac{\delta y_k}{\delta p_i}$$
(5.2)

Where y_k is the solution variable and p_i is the sensitivity parameter. Cantera uses the mass, enthalpy or temperature and mass fractions of the species as the input parameters. The SanDiego mechanism is a short C₁-C₃ mechanism which involves 40 species and 235 elementary reaction [32]. The sensitivity function will use these species as the inputs, and the elementary reactions as the solution variables. A non-dimensional number returns which represents the specific elementary reactions sensitivity to the overall reaction, and whether it helps or hinders ignition, being either a chain-initiation, propagation, branching or terminating reaction.

This chapter will use this function to detect the top ten elementary reactions that the simulation is most sensitive too. This will help provide more insight into the chemical kinetics behind some of the most important numerical simulations performed.

5.1 – Comparison of Fuels

In this section, a sensitivity analysis on the three fuels, hydrogen, methane, and propane, will be performed and discussed. The coflow setup is the standard pure air coflow first seen in section 2.2, where the coflow temperature for each fuel is 975, 1500 and 1300K respectively. These temperatures are the same that were used in chapter 1 to obtain ignition delay times of approximately 20-25ms. Fig. 5-1 below shows the results of the sensitivity analysis. Note that

reactions with both a forward and reverse rate appear as a single bar with both a positive and negative value.



Fig. 5-1 Sensitivity analysis of hydrogen, methane and propane issuing into a pure air coflow at 975, 1500 and 1300K respectively.

The sensitivities of the elementary reaction for methane and propane had to be scaled up by an order of 2 for the bars to be visible. The reason for hydrogen having a much larger sensitivity is that it's combustion heavily relies on one forward and one reverse reaction, whereas methane and propane rely on many more. Because of this, the input parameter p_i becomes relatively large.

For hydrogen and propane, the main reaction driving ignition is:

$$H + O_2 \Leftrightarrow O + OH$$
 R1

This means the combustion of the fuels rely heavily on the elementary reaction which forms the hydroxyl radical. The combustion of methane is also quite sensitive to this reaction. This is in line with many previous studies [6, 8, 9] and some of the findings from the preceding chapters of this thesis.

Methane is most reactive to the reaction:

$$CH_3 + O_2 \Leftrightarrow CH_3O + O$$
 R2

This reaction destroys the oxygen molecule using a methyl group (CH_3) to form methoxide (CH_3O) and an oxygen atom. Literature has shown that the CH₃ radical can react to form one of two other molecules, those being CH₃ or C₂H₆, where the latter forms in the presence of a catalyst, as seen in Fig. 3-2 [34].



Fig. 5-2 Flow diagram showing major gas phase reaction pathways in the fuel-rich catalytic partial oxidation of methane (Obtained from Mackie, 1991 [34])

In this case, there is no catalyst, and so all CH₃ would react to form CH₃O, which validates the results of the sensitivity analysis.

To conclude, the OH radical is a key species in the forward and backwards reactions driving ignition for all three fuels. Section 4.4 observed the influence of both OH and H_2O_2 on

ignition and found, graphically and via a brute force sensitivity analysis, that OH has a greater impact, which is reinforced by the findings in this section.

5.2 – Influence of Radical Addition to the Oxidizer

So that this idea can be further emphasized, the sensitivity of a methane jet is investigated in a pure air coflow (as in the preceding section) and compared to a coflow with OH and H_2O_2 added separately, and finally H_2 added to the jet. Fig. 5-3 shows the sensitivity analysis for methane.



Fig. 5-3 Sensitivity analysis of methane issuing into a 1500K coflow, comparing a pure air coflow, with additions of OH and H_2O_2 , and hydrogen additions to the jet.

The coflow is held at 1500K for all cases. The amounts of OH and H_2O_2 added to the coflow were calculated by running the hydrogen coflow simulation from section 4.3 and recording the mole fractions of each. Table 5-1 lists these values. Finally, 5% of hydrogen is added to the jet. This is because larger amounts created large disparities between sensitivities which would require scaling for easier comparison. The following section will investigate larger amounts of hydrogen dilution to compare with the amounts studied in chapter 4.

Table 5-1 Mole fraction of species in hydrogen coflow at 1500K.

Species	Hydroxyl	Hydrogen Peroxide
Content (Mole Fraction)	9.197E-05	1.067E-08

As suspected, the addition of H_2O_2 to the coflow has a small effect on the sensitivities, meaning its addition has little to no influence on the combustion. The addition of OH, on the other hand, decreases the sensitivities of all the reactions, while also converting the main reaction from R2 to R1.

This is the same reaction which was driving the combustion of all three fuels from the preceding section. The addition of 5% hydrogen to the jet also makes the simulation most sensitive to this reaction. In fact, of the 10 most sensitive reactions plotted for the hydrogen addition to the jet, 6 of them have OH in one way or another.

Now, the 5% hydrogen addition changes the sensitivity of R1 from approximately 1.10 to 1.40, making it approximately 27% more reactive to the elementary reaction. Now hydrogen is known to have large impacts on methane jets [20, 36] however, to accurately compare the results of this sensitivity analysis with literature, the combined effect of all reactions should be calculated. This is an avenue for further research which may help better understand the influence hydrogen dilution has on a methane jet.

5.3 – Influence of Dilution to the Fuel

Finally, a sensitivity analysis will be performed on the simulations run in section 4.6, regarding the additions of hydrogen and air to the fuel. Fig. 5-4 shows the sensitivity analysis for (a) hydrogen and (b) air additions. This figure shows the effect of 10, 20 and 50% dilution of hydrogen and air compared to a pure methane jet, with a constant coflow of 1200K.

The coflow is set to 1200K to make visual comparisons between the results of the sensitivity analysis and the results from section 2.6. Fig. 3-4 (a) shows an increase in sensitivity of R1 by approximately 55, 24 and 81% when comparing pure fuel with 10% dilution with 20% dilution with 50% dilution respectively. Table 5-2 lists the sensitivities along with the percentage change. Observing Fig. 4-9 at 1200K, comparing pure fuel with 10% dilution with 20% dilution with 50% dilution, the delay times decrease by 47, 22 and 21% respectively. Table 3-3 lists the delay times along with the percentage change.



Fig. 5-4 Sensitivity analysis of methane issuing into a 1200K coflow, comparing a pure fuel jet with 10, 20 and 50% (a) hydrogen and (b) air dilution.

Now, these comparisons are slightly deficient as all reactions must be considered as a whole, when calculating percentage change of sensitivity. Regardless, what can be deduced from the tables is that the percentage change of the sensitivity to reaction 1, largely outweighs the percentage change of delay time. This implies that the forward rate reaction, which works as a chain branching step, is critical for quickening the ignition delay.

Table 5-2 Percentage change in sensitivity to reaction 1 for each case tested for hydrogen dilution.

Case	Sensitivity (Reaction 1)	Percentage Change (Case by Case)	Percentage Change (Total)
Pure Fuel	3.79	-	-
10% H ₂	5.86	54.62%	54.62%
20% H ₂	7.29	24.40%	92.35%
50% H ₂	13.21	81.21%	248.55%

Table 5-3 Percentage change in delay times at 1200K for each case tested for hydrogen dilution (from Fig. 2-10).

Case	Ignition Delay Time (ms)	Percentage Change (Case by Case)	Percentage Change (Total)
Pure Fuel	34	-	-
10% H ₂	18	47.06%	47.06%
20% H ₂	14	22.22%	58.82%
50% H ₂	11	21.43%	67.65%

Reaction one involves the destruction of a hydrogen atom (H) and oxygen molecule (O_2) to form two radicals, those being the oxygen atom (O) and hydroxyl (OH). Seeing as this is an important reaction, the combination of O and OH may be worth investigating further. The air coflow setups tested throughout the thesis have utilised air which is made up of O_2 . Tests then involved injecting small amount of OH into the coflow. Perhaps it may be worth investigating the effect of injecting the same moles of oxygen atoms as OH. By breaking the bonds of the oxygen molecules and providing the coflow with already split up oxygen atom, combustion may occur at a quicker rate than what was found within this thesis.

Finally, reaction 3, involving the destruction of H_2 and O to form H and OH, is also quite critical.

$$H_2 + O \Leftrightarrow H + OH$$
 R3

The combustion of methane with hydrogen dilution is much more sensitive to reaction 1, however, is still relatively sensitive to reaction 3. This means that it may also be worth investigating the influence of injecting hydrogen atoms into the coflow, in addition to hydroxyl.

Chapter 6.0 – 1D Numerical Simulations

In this chapter, one dimensional simulations of a counter-flow burner will be conducted to observe the influence of strain rate on the combustion of the fuels. The constituents of the 1-D counter flow solver are the same as those from the previous 0-D homogeneous reactor. However, the counter flow setup is simulated by issuing a stream of fuel, which corresponds to a mixture fraction of 1, into the equilibrium products from the H_2 /Air coflow, corresponding to a mixture fraction of 0. This differs from the 0-D reactor where the two streams were homogeneously mixed before ignition in the 0-D simulation. Strain rate is simulated by having the two jets issue and dissipate into one another from opposing sides of the computational domain.

The improvement of 1-D simulations compared to 0-D is that the latter, being homogenous reactors, neglects the influence of diffusion of the two streams. Research has shown that diffusion is important and ubiquitous in autoigniting hydrogen flames [73, 74]. Furthermore, 0-D simulations do not consider strain rates when conducting a sensitivity analysis. Strain rate and scalar dissipation influence the formation of certain radicals, which could, for example, slow down ignition in the case where there is a reduction in the formation of radicals which cause chain-propagating or -branching steps.

6.1 – Ignition Delay Times and Temperature Evolution

This first section will investigate the ignition delay times of certain counterflow setups and will observe the evolution of temperature both temporally and spatially. Single counterflow simulations for each fuel will be run. Table 6-1 shows the input parameters used for each fuel along with the ignition delay time.

Fuel	Hydrogen	Methane	Propane
Temperature (K)	1000	1500	1300
Strain Rate (s ⁻¹)	4000	1000	100
Ignition Delay Time (ms)	7.9	5.2	5.05

Table 6-1 Input parameters used in 1-D simulation and the calculated ignition delay times.

Comparing these to the values of delay times obtained from Table 3-2 (Table 6-2 below is a copy of relevant information from Tables 3-1 and 3-2 for reference), strain rate is shown to have an obvious impact on the ignition delay times. All fuels experience a longer delay time

to ignite. For example, hydrogen ignites in 1.89 ms in the 0-D reactor at 975K, however, this amount increases to 7.2 ms in the 1-D reactor with a strain rate of 7000 s⁻¹ at 1000K. This increase in delay time is seen even when the temperature of the coflow has increased from 975 to 1000 K, which is known to reduce delay times. Furthermore, the coflow stream in the counter flow simulations is a mixture of hydrogen and air. Section 4.6.2 of this thesis displays the effects of hydrogen dilution to a methane and propane jet. Consequently, methane and propane, although maintained at the same temperature, should ignite quicker with the addition of hydrogen to the mixture. Regardless, the strain rates have too large of an influence and the mixture takes longer to ignite.

Fuel	Hydrogen	Methane	Propane
Temperature (K)	975	1500	1300
Ignition Delay Time (ms)	1.89	1.62	1.27

Table 6-2 Copy of relevant information from Tables 3-1 and 3-2.

The counterflow reactor is beneficial for its ability to incorporate strain. Another benefit, being that it calculates in one dimension, is that properties of the flow can be calculated spatially and temporally. Fig. 6-1 shows the evolution in time of the temperature of the mixture for all three fuels along the spatial domain between the two inlet jets. The left side of the plots describe the fuel inlet, and the right is the inlet of the oxidant (coflow). Each plot shows five different instances in time, ranging from pre-ignition (at approximately the time reaction starts to take place) and steady state. Included in these timesteps is the instance where ignition is first reached, which is defined in this case as the point where the maximum temperature first reaches 500 K greater than the oxidizer inlet.

It is evident from all three fuels that the temperature remains quite stagnant leading up to preignition, where it then ignites quickly. Hydrogen ignites in the least amount of time, being approximately 0.1 ms. Ignition time for methane and propane is approximately 0.8 and 0.55 ms respectively. Now, although hydrogen ignites in the shortest amount of time, it takes a relatively long time to reach steady state, being 10.7 ms. For methane and propane, it takes 7.6 and 14.3 ms respectively for them to become steady. In fact, the plot for methane shows that immediately after ignition, the temperature profile has a very negligible difference between each timestep. The temperature profile for propane also does not vary much, whereas

hydrogen seems to be continuously evolving, until the reactor claims it has reached steady state at 10.7 ms.



Fig. 6-1 Temporal evolution of temperature for (a) hydrogen, (b) methane, and (c) propane.

6.2 – Delay Time and the Influence of Strain

The final results of this thesis look at the ignition delay times of all three fuels as functions of the strain rate. Fig. 6-2 shows plots of hydrogen, and another of methane and propane on the same figure, as they operate in comparatively similar strain rates. Common among all three fuels is that as the coflow temperature increases, the strain rates which the fuels can ignite, increases. Since the fuel remains the same, the resistance to dissipation may not necessarily increase. Instead, it is expected that the chemical time scales dominate over the mixing time scales. Essentially, the mixture ignites before it has a chance to mix at these higher temperatures. It isn't until the strain rate has increased to relatively large amounts, at these increased coflow temperatures, that the mixture can then ignite. At these points, the amount of mixing and dissipation that takes place then dominates over the chemical reactions of combustion. Work by Arndt et al. [21] produced similar result with pulsed methane jets, validating the work done here.



Fig. 6-2 Ignition delay times versus strain rate for (a) hydrogen, and (b) methane and propane.



Fig. 6-2 Ignition delay times versus strain rate for all three fuels on the same figure.

Finally, hydrogen is much more reactive than methane and propane, where methane is slightly more reactive than propane. This is evident from Fig. 6-3, where all fuels are plotted on the same figure. Hydrogen can ignite under strain rates which are orders of magnitude larger than the strain rates used for methane and propane. In essence, hydrogen has the greatest resistance to dissipation which also explains why it has the lowest ignition delay time of all three fuels.

Chapter 7.0 – Discussion

This chapter discusses the numerical results of the 0- and 1-D simulations. Initially, the results of each reactor will be explored individually, then comparisons will be made between the two, with an explanation as to why they differ. As a part of the individual investigations, the 0-D reactor will utilise many simulations to test various cases on all 3 fuels. The aim is to isolate certain parameters and adjust certain setup characteristics to reduce the ignition delay times of the fuels. In doing so, ultimately, the most important factors for ignition can be discovered, such as which diluent or radical best influences the combustion process.

1-D simulations are run in parallel to explore the influence of dissipation and mixing of the two streams. Research has been done in this area, however, discussion of the simulation results are still provided within this section to compare the numerical reactors and observe the influence strain has on combustion. The aim here is to highlight what the effect is while also aiming attention to possible future work that can be done on this numerical reactor to investigate what the mixing process does to the formation of the radical pool preceding autoignition.

7.1 – Kernel Contents and Most Important Radical

This thesis first utilized a laminar 0-D isobaric homogenous reactor to simulate the development of the fuel and oxidizer mixtures in time. Mole fractions of the autoignition kernels which form from this reactor were then calculated to investigate their evolution. Gordon et al. [5, 7] found that ignition is preceded by the formation of a pool of radicals, those being HO₂, H₂O₂ and CH₂O among many other minor species. These specific three were identified to play an important part in the autoignition of methane. Hydroxyl (OH), however, has been studied in more detail, with experimental imaging techniques showing that OH forms in the areas where methane is consumed [6].

Many radicals which exist within this pool seem to play an important part in autoignition, being that it peaks in amount first or that the radical itself forms in the areas where the fuel is consumed. This thesis observed these same radicals, including the other minor species, and calculated the times at which they peak along with their amounts. Chapter 3 compares the peak times and finds that CH₂O peaks well before all other radicals, which is in line with other work [7]. For the two hydrocarbons being tested, that is methane and propane, CH₂O may be the foremost radical which can be used to indicate autoignition has occurred.

Although it is quite important to identify the radical which forms first, knowledge of the entire pool of radicals is also beneficial. Knowing the contents of the kernels allows for a better understanding on the assembly of radicals which play a part in autoignition but also which may have the greatest influence. Regarding the assembly, variations in controlling parameters of the simulation, such as temperature or strain rate in 1-D simulations can result in variations to the amounts of each radical. It is known from this thesis and other research on counterflow simulations that increases in strain rate result in longer ignition delay times [21, 26]. In saying this, it should be observed what influence the strain rate has on the formation of each radical. This is an avenue for future work which may provide valuable information. This thesis, however, looked at which radical has the most impact on ignition rather than what has an influence on their formation.

Injection of these radicals into the coflow was investigated in Chapter 4 to find which decreases the ignition delay time the most. Research in this area has investigated the specific chemical reactions which dictate combustion. Chain branching steps which form OH are the most important step in every combustion process involving hydrogen atoms [12], namely:

$$H + O_2 \Leftrightarrow O + OH$$
 R1

OH has also been subject to many investigations in the past [8, 53, 75], however, only as an indicator of autoignition occurring. This thesis observed the influence of OH to ignition delay times by injecting certain amounts to the pure air coflow in the 0-D reactor. It was found that OH, when compared to H_2O_2 , has a much larger impact on combustion, as the delay time reduced drastically. When it comes to combustion, further investigation into the certain species that accelerate the chemical processes is required to quicken ignition in practical applications where this is desirable. The next section of the discussion examines the simulations done within this thesis relating to delay times and what speeds it up.

7.2 – Combustion Kinetics and Ignition Delay Time

This section dives deeper into most of the results obtained from Chapter 4. Various simulations were run, such as comparing an air and vitiated coflow, testing the addition of certain radicals to an air coflow and diluting the jet with certain species such as fuel or the inert, nitrogen.

Firstly, many research papers have investigated the vitiated coflow [5-7, 19] with it being

agreed upon that the use of the combustion products of hydrogen and air quickens the ignition delay time for most fuels. Among the combustion products exist any unburnt hydrogen, and OH which formed from the combustion. As the vitiated coflow quickens combustion, it must be because of the introduction of these new species, compared to a purely air coflow, which speed up the kinetics of combustion.

Injection of small amounts of OH and H_2O_2 was tested in Chapter 4. It was found that, when comparing realistic amounts of each, OH had a much larger influence on ignition delay times. In fact, looking at the brute force sensitivity diagram from Fig. 4-7, H_2O_2 has a sensitivity of approximately 0.01 msK⁻¹ (milliseconds per Kelvin) and less for all coflow temperatures tested. On the other hand, OH has a sensitivity of approximately 0.36 msK⁻¹ at 1250K, dropping to its lowest value, within the temperature range, of 0.3 msK⁻¹ at 1600K. The brute force sensitivity equation used was inspired by a study by Choi et al. [17], which found the ratio of the change in delay time and change in temperature to define sensitivity.

Next, the oxygen concentration in the air coflow was adjusted to observe the effect it has on the delay times. Although not the exact focus of literature, this has been studied inadvertently by investigation done using 1-D reactors to find the most reactive mixture fraction [21], where adjustments to mixture fraction unintentionally correlates with adjustments to the oxygen concentration. Arndt et al. [21] found that the most reactive mixture fraction is approximately 1% of the stoichiometric mixture fraction, translating to a very lean mixture in the homogenous reactor. Results from Chapter 4 show that as the concentration of oxygen decreases, the delay time increases for methane and propane. The effect is the opposite for hydrogen, except for at relatively high temperatures (~1300K and greater).

Decreasing the oxygen concentration in the air coflow creates a richer mixture, which goes against the findings stated above. However, the equivalence ratio of the flow is 0.2, meaning the mixture is already quite lean to begin with. Therefore, creating a richer mixture may in fact approach the most reactive mixture fraction. It may be worth investigating these results further to validate the work of Arndt et al. [21], however, the impact on the delay times is not as large as the additions of OH seen above and so is not explored any further in this thesis.

Another parameter which was investigated, was the adjustment of the equivalence ratio, which also relates to the work of Arndt et al. [21]. All the figures show that there is a peak equivalence ratio, where the time taken to ignite is the quickest. An interesting result from these figures is the local peak which can be seen in most of the plots. This may be due to two competing variables, which will be discussed in the next part regarding air dilution to the jet.

Air and nitrogen dilution to all 3 fuels, and hydrogen dilution to methane and propane were also tested to observe the effects. Now, air and hydrogen dilution produced results with the most changes to the ignition delay times. Starting with air dilution, strange effects were observed. When diluting the jet with air, the stoichiometric coefficient must be adjusted according to eqn. (2.6). This thesis observed the effects of adjusting the coefficient and compared results with keeping this value constant (as if no air was added). Fig. 4-11 showed a double crossover of these plots, which could most likely be attributed to two competing variables. When the stoichiometric coefficient is fixed, the equivalence ratio decreases as the mixture becomes leaner which works to speed up ignition. However, when corrected, the equivalence ratio stays constant at 0.2, but the mixture has less coflow air for heating which slows ignition. This is a possible explanation for the results obtained in Fig. 4-11. Regardless, the dilution of air did not produce clear results of speeding up the ignition process.

Finally, hydrogen dilution to a methane jet, as shown in Fig. 10, decreased the delay time appreciably. In fact, it was found that the delay time decreases from 35 to 18 ms at 1200K for 10% hydrogen dilution. This is expected as hydrogen is known to be more reactive than methane and ignite at lower coflow temperatures. Work by Choi et al. [20] also produced similar results, where the lift off height decreased by approximately 36% at 1% hydrogen dilution and a 980K coflow.

Of all the variations done to the simulations, hydrogen dilution had the greatest impact on the delay time by far. To better understand how hydrogen dilution, and addition of other radicals, accelerate the combustion process, a sensitivity analysis of the chemical reactions must be performed.

7.3 – Chemical Reactions

This section of the discussion chapter presents and examines the sensitivity of the chemical reactions which take place during combustion. The results of the sensitivity analyses performed are given in Chapter 5, where mainly results for methane are shown. To begin, all three fuels are compared to observe how the sensitivity of reactions changes. Chosen temperatures are the same as the "high" temperatures chosen in Chapter 3. It should be noted that the temperature itself does not have an influence on the sensitivity of each reaction [12]. A reaction that methane combustion is most sensitive at 1200K would also be the most sensitive at 1500K, however, the change in temperature causes the physical processes and

number of reactions which take place to change.

To begin, R1, which forms OH through the destruction of an oxygen molecule merging with a hydrogen atom, is the most sensitive reaction in hydrogen and propane combustion, and second most for methane. Methane is most sensitive to a reaction which destroys CH_3 , which highlights the usefulness of this radical in the combustion of hydrocarbons. In fact, CH_3 , and many products of the destruction of this radical, are seen in plenty of the ten most sensitive reactions for methane and propane. This is an area for future work, as this thesis only investigated the effect of radicals which exist in hydrogen as well, so OH and H_2O_2 were the focus and CH_3 didn't get much attention within this work.

Now, looking at the sensitivity of reactions with additions of radicals to the coflow, immediately, Fig. 5-3 shows that H_2O_2 , although a good indicator of autoignition, changes the sensitivities by a negligible amount. Additions of small amounts of OH to the coflow change the foremost sensitive reaction from R2 to R1. Essentially, the combustion process is now most sensitive to the formation of OH, rather than the destruction of CH₃.

Further investigation also shows that any reactions involving the destruction of the OH radical, has a negative temperature sensitivity, meaning it inhibits the combustion process. It can then be deduced that the formation and maintenance of OH is key for ignition, which also validates the findings of Chapter 3, which show the mole fractions of OH remains the greatest of all radicals after ignition has occurred. This is all in line with work by Gordon et al. [5] who found that OH peaks at autoignition and maintains this peak well into the steady flame.

Regarding jet dilution, the dilution of hydrogen to a methane jet showed the most changes to the sensitivity of the combustion. At only 10% dilution, the main reactions driving the combustion vary completely, with this changing even more at 50%. Regardless of amount of dilution, R1 is almost always the reaction which combustion is most sensitive to, further validating the importance of the OH radical.

Combining all the results of these sensitivity reactions, a prime combination of OH addition to the coflow and hydrogen dilution to a methane jet will result in the greatest sensitivity in R1. However, this may not necessarily result in a faster ignition, as all sensitivities will need to be observed. This is because the addition of some species may result in many negative reactions inhibiting combustion. For best results, all reactions must be calculated including their sum effect. This way, the perfect amount of each radical can then be added allowing for quickest ignition times of the mixture. Although, there are some possible downsides to this which

haven't been investigated in this thesis, such as the amount of pollutants forming from this type of combustion or the possibility of engine damage over long periods of time due to the new chemical reactions and sensitivities.

Finally, air dilution was also investigated in the hopes of providing meaningful results and explanations to the double crossover feature seen in Fig. 4-11 and the single crossover of Fig. 4-12. However, the only real result of air dilution is that increasing the amount of air, decreases the sensitivity of all reaction by a greater degree. Almost all 10 most sensitive reactions remain the same. What could possibly be investigated is the point where the maximum sensitivity to all reactions exists. This would relate very closely to the work done by Arndt et al. [21] regarding the most sensitive mixture fraction. Instead of diluting the jet with air, the equivalence ratio could be adjusted and plotted using a sensitivity analysis, to find at which ratio (corresponding to different degrees of coflow air to fuel from the jet) is the combustion most sensitive to all reactions.

Similar to section 7.3, hydrogen dilution was found to have the greatest influence on the combustion process, further solidifying its superiority as a diluent to methane and propane. This provides and explanation as to why it is studied so extensively and why future study in this area could prove to be extremely useful for combustion research.

7.4 – Influence of Dissipation of Streams into One Another

On the topic of ignition delay, dissipation and mixing of the streams influences the time taken for the mixture to ignite. 1-D reactors carry out the simulations similar to 0-D reactors, except now another variable is introduced to the calculations. This variable, being strain rate, effects the ignition. Increasing the amount of strain imposed by the two jets increases the force and velocity of each jet at their point of contact resulting in more mixing. Flame stability, in this setup, is achieved by the balance of diffusion, chemical reaction, and convection of heat throughout the mixture [75].

Results begin by displaying the temporal evolution of flames in the counterflow burner. The benefit of plotting this is that it visually shows how the temperature of the mixture at the reaction zone evolves in a similar way to the homogenous reactor tested previously. Although, a point that should be highlighted is that for similar temperatures and fuels tested, the counterflow reactor takes longer to ignite. This is directly attributed to the influence of strain. Work by Arndt et al. [21] on a pulsed methane jet highlights that autoignition had an increased probability of occurring in areas with lower strain rate, validating the findings in

this thesis for all three fuels.

Furthermore, delay times were plotted against strain rate in Fig. 6-2. This further solidifies the idea that increasing the strain rate increases the time taken to ignite. At these high strain rates, the chemical time scales for combustion no longer dominate ignition and instead is governed by the mixing time scales and other flow characteristics. These characteristics can inhibit autoignition from occurring as the movement of the mixture caused by the steep strain rates causes the species and heat to be transported away from a point within the mixture which has the possibility of igniting [8].

7.5 – Comparing the Numerical Reactors

Finally, comparison of the numerical reactors show that both produce quite similar results. A key point of focus of this thesis is the ignition delay time, and both 0- and 1-D simulations bring to light a key characteristic of flames and flow which have an influence on this time. For the 0-D homogenous simulations, it is the species which exist in the mixture, be it in the jet or coflow, including any additions to either. On the other hand, 1-D simulations highlight the influence of strain rate and how mixing of the fuel and oxidant can impact ignition which is a more realistic replication of physical flow and ignition. This does not take away from the credibility and usefulness of the 0-D reactor, however. This thesis shows how effective both can be, with each having its own advantages and disadvantages. In fact, the homogenous reactor is much easier to use and produces relevant information such as the temperature range that should be used in experimental studies. In this case, it would be unnecessary and a waste of computational effort to run a coflow reactor.

7.6 – Concluding Remarks

To obtain the most accurate results, 3-D simulations should be run, which solve the combustion of the flame while accounting for all flow characteristics and chemical reactions of the flame. Regardless, the results provided should still somewhat resemble physical flames and can be used to validate other experimental results. It should also be noted that the specific mechanism used in the simulations of this thesis is the SanDiego mechanism [37].

Now, the reactors utilise these mechanisms to conduct the calculations and reproduce the chemical reactions which take place in the physical world.

Adjusting the mechanism used has shown to produce varied results as inconsistencies exist between data sources used to create each one [11]. Therefore, it is important to note which

one is being used in each paper especially when trying to reproduce results. Whilst investigation into the mechanisms is not the topic of this thesis, it should be expressed that combustion research would benefit tremendously from a more global approach of sharing data to produce a mechanism that can be used for all simulations. Although, it may be many years before this ever comes to fruition.

Chapter 8.0 – Conclusion

This thesis presented a comprehensive study of autoignition using numerical reactors. Hydrogen, methane, and propane were tested in 0-D coflow simulations to investigate the contents of autoignition kernels within the flame, the ignition delay times, and the sensitivity of the chemical reactions governing the combustion. In conjunction, 1-D simulations of the counterflow burner were produced to investigate the influence of dissipation of the two streams. The following conclusions are obtained from this thesis:

- Common to all three fuels, H₂O₂ and HO₂ are better indicators of autoignition than OH. However, CH₃O peaks well before all other radicals for methane and propane and so is the superior indicator for those two fuels.
- Use of a vitiated coflow quickens the ignition delay time. Investigation shows that OH exists in the largest amount and has the most influence on the delay. Injecting realistic amounts of OH and H₂O₂ to a pure air coflow show that OH decreases the delay time by the largest amount. A brute force sensitivity was also performed which validates this claim.
- Diluting the jet with other species also influences the delay times. Adding hydrogen to a methane or propane jet decreases this time appreciably, which is in line with other literature. Dilution of air produces 'double crossover' features in the delay time plots, which is attributed to the calculation of the stoichiometric coefficient. Adjusting this value according to the amount of air added to the jet decreases the air in the coflow, resulting in less heating being done. If the stoichiometric coefficient is fixed, the amount of heating also remains constant, but the amount of air increases with more dilution. These two competing variables are most likely the cause of the 'double crossover'
- The choice of equivalence ratio also effects the ignition delay time, with fastest ignition occurring at approximately 0.2 for all fuels, and not actually occurring at the stoichiometric equivalence ratio. These plots also produce 'local peaks' where the ignition delay time slows down in the range of approximately 0.25-0.3 which was an unexpected result.
- Adjusting the oxygen concentration in a pure air coflow decreases the delay time for hydrogen and increases it for methane and propane. This relates to the equivalence

ratio results, as adjusting this ratio adjust the amount of oxygen in the mixture.

- A 'perfect' combination of adjusting the equivalence ratio, diluting the jet and additions of radicals to the coflow will result in the quickest ignition delay time which would be preferable in some real-world applications. Trends are shown and summarised in this section; however, this 'perfect' combination was not found here.
- Sensitivity analyses of the chemical reaction of combustion for all three fuels validate that OH varies the sensitivities of each reaction by the greatest degree. Other species which have a great influence on combustion include oxygen atoms (O), hydrogen atoms (H) and CH₃.
- Introducing strain rates to the simulations increases the ignition delay times for all the cases tested.
- Steepening the strain rate imposed on the flow increases movement of the mixture which increases the chance of species and heat being transported away from a point of possible ignition, due to flow characteristics.
- Further work can be conducted in 3-D to produce more accurate result; however, computational efficiency will be an issue, and choice of mechanism will influence the results produced.

Through the comprehensive numerical simulations conducted in this thesis, a better understanding of autoignition has been established. Ignition delay times, sensitivity analyses and numerical reactors have been the focus of this work. Although quite extensive, many aspects of this thesis have potential for future work.

To conclude the work of this thesis, this final section will outline some of the potential areas of further study that have been uncovered.

Firstly, this thesis investigated the mole fractions of certain radicals that exist within the autoignition kernels of each fuel. It was decided that common amongst hydrogen, methane and propane, hydrogen peroxide and hydroperoxyl would be used as the best form of indicators. However, neither of the two seemed superior as in some cases one would ignite before the other, and other cases, the order would be reversed. An area of possible work could be to study these chemical reactions and processes further, to identify which of these two radicals is the better indicator of autoignition and why one peaks earlier than the other in different cases of fuel and coflow temperature.

Moving on to the delay time calculations, to begin, the simulations conducted were not always perfect. This was seen in section 4.2.1 where the calculation of the stoichiometric coefficient disregarded the species assumed to be negligible. The vitiated coflow is a combination of many species created from the combustion of hydrogen and air. The stoichiometric coefficient is influenced by these as the air to fuel ratio will change according to the amount of air existing in the coflow. Further study would involve calculating the delay times using the correct calculations. In this way, results would be more accurate, helping combustion research to progress further in the correct direction.

Additional areas for investigation relate to some of the strange findings for certain fuel at certain temperatures. In section 4.5, it was found that hydrogen at relatively high temperatures (approximately 1360K and higher) ignited faster when less oxygen was present. Section 4.6.1 also discovered that both hydrogen and propane ignite quicker with more dilution of nitrogen to the jet within certain range of coflow temperatures. Investigating why this occurs may be of some benefit to further our understanding of nitrogen dilution.

Furthermore, the equivalence ratio plots of section 4.7 found a local peak in delay times at an equivalence ratio of approximately 0.15-0.25. This is suspected to be due to the definition of autoignition used within the simulations which depends on detecting the peaks of the mole fractions of certain species within the kernels. A possibility is that the simulation may detect a peak, when in reality the mole fractions of the observed radicals are still growing. Therefore, it is surmised that looking into the definition of autoignition may further our understanding of computational simulation or may uncover another useful piece of information which describes why the equivalence ratio plots exhibit the local peak.

Regarding the sensitivity analyses conducted, this thesis investigated a single reaction at a time rather than considering them as a whole. The overall influence of all reactions together, is more useful in understanding how the combustion of the whole mixture should change according to the change of the certain parameter being tested, say, temperature. Future work should involve comparing the entire sensitivity analysis with the results obtained for ignition delay times, and with results obtained in other literature such as the lift-off height and acoustic emissions of flames.

Additionally, the sensitivity analyses showed that the chemical reactions which form and destroy an oxygen atom are quite important for causing the mixture to combust. Although not as commonly seen as hydroxyl, it may still be worthwhile investigating the addition of oxygen

atoms to a mixture and how this effects the delay times. It is possible that the destruction of oxygen molecules into singular atoms may take valuable time which slows the ignition process.

Moving on to the 1-D simulations, many improvements can be made to the work of this thesis. To begin, computational efficiency should be the focus of further work. Simulations took many hours to run simple calculations because the hardware used was not of a good enough quality to keep up with computational demands. With the aim to quicken the computational time, the number of profiles saved was reduced, and the timestep of calculations was also increased. This greatly reduces the accuracy of results, sacrificing meaningful findings for quicker simulations.

Variations to the burner setup is another avenue for further work. Chapter 4 investigates various coflow setups, equivalence ratios, temperatures, additions to the coflow and dilutions to the jet. This thesis lacks the same investigation in the 1-D simulations. Doing so will allow for more comparisons between the two numerical reactors to help further understand the influence dissipation of the two streams has on certain flow and combustion characteristics.

Finally, in the beginning of the year, it was planned for the numerical simulations to be done in conjunction with physical experiments, however, this thesis only utilised the former. Further work in this field would benefit greatly from reproducing the numerical simulations as physical experiments. Comparisons can then be made with each method, and validation provided to the results obtained within this thesis.

Chapter 9.0 – Appendix

A1

Adding N₂ to the Jet:

$$(1-k)C_{x}H_{y}O_{z} + kN_{2} + a(0.21O_{2} + 0.79N_{2}) \rightarrow bCO_{2} + cH_{2}O + dN_{2}$$

$$C: (1-k)x = b$$

$$H: (1-k)y = 2c \Rightarrow c = \frac{(1-k)y}{2}$$

$$O: (1-k)z + 0.42a = 2b + c$$

$$= (1-k)\left(2x + \frac{y}{2}\right)$$

$$\therefore a = \frac{(1-k)[4x + y - 2z]}{0.84}$$

Adding H₂ to the Jet:

$$(1-k)C_{x}H_{y}O_{z} + kH_{2} + a(0.21O_{2} + 0.79N_{2}) \rightarrow bCO_{2} + cH_{2}O + dN_{2}$$

$$C: (1-k)x = b$$

$$H: (1-k)y + 2k = 2c \Rightarrow c = \frac{(1-k)y}{2} + k$$

$$O: (1-k)z + 0.42a = 2b + c$$

$$= (1-k)\left(2x + \frac{y}{2}\right) + k$$

$$\therefore a = \frac{(1-k)[4x + y - 2z] + 2k}{0.84}$$
Adding Air to the Jet:

$$(1-k)C_{x}H_{y}O_{z} + k(0.21O_{2} + 0.79N_{2}) + a(0.21O_{2} + 0.79N_{2}) \rightarrow bCO_{2} + cH_{2}O + dN_{2}$$

$$C: (1-k)x = b$$

$$H: (1-k)y = 2c \Rightarrow c = \frac{(1-k)y}{2}$$

$$O: (1-k)z + 0.42k + 0.42a = 2b + c$$

$$= (1-k)\left(2x + \frac{y}{2}\right)$$

$$\therefore a = \frac{(1-k)[4x + y - 2z] - 0.84k}{0.84}$$

Varying O₂ Content in Coflow:

$$C_x H_y O_z + a \left(\frac{X_{O_2} O_2 + (1 - X_{O_2}) N_2}{0} \right) \rightarrow b C O_2 + c H_2 O + d N_2$$

$$C: x = b$$

$$H: y = 2c \Rightarrow c = \frac{y}{2}$$

$$O: z + 2X_{O_2} a = 2b + c$$

$$= 2x + \frac{y}{2}$$

$$\therefore a = \frac{4x + y - 2z}{4X_{O_2}}$$



B1-1 Species content in mole fractions versus time for a hydrogen jet issuing into a pure air coflow at 975K with the peak time of each species stated.



B1-2 Heat release and reactor temperature versus time for a hydrogen jet issuing into a pure air coflow at 975K with the heat release peak time stated.



B1-3 Species content in mole fractions versus time for a methane jet issuing into a pure air coflow at 1500K with the peak time of each species stated.



B1-4 Heat release and reactor temperature versus time for a methane jet issuing into a pure air coflow at 1500K with the heat release peak time stated.



B1-5 Species content in mole fractions versus time for a propane jet issuing into a pure air coflow at 1300K with the peak time of each species stated.



B1-6 Heat release and reactor temperature versus time for a propane jet issuing into a pure air coflow at 1300K with the heat release peak time stated.



C1-1 Brute force sensitivity analysis for hydrogen issuing into an air coflow with increasing amounts of (a) hydroxyl and (b) hydrogen peroxide.



C1-2 Brute force sensitivity analysis for propane issuing into an air coflow with increasing amounts of (a) hydroxyl and (b) hydrogen peroxide.



Ignition delay time versus coflow temperature for methane issuing into an air coflow with increasing amount of (a) hydroxyl and (b) hydrogen peroxide.



C3-1 Ignition delay times for a preheated air coflow with increased amounts of nitrogen dilution to a hydrogen jet.



C3-2 Ignition delay times for a preheated air coflow with increased amounts of nitrogen dilution to a propane jet.



C4 Ignition delay times for a preheated air coflow with increased amounts of hydrogen dilution to a propane jet.



C5-1 Ignition delay times for a preheated air coflow with increased amounts of air dilution to a hydrogen jet while either fixing or correcting the stoichiometric coefficient.



C5-2 Ignition delay times for a preheated air coflow with increased amounts of air dilution to

a propane jet while either fixing or correcting the stoichiometric coefficient.

Chapter 10.0 – References

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