**Combustion ME 5446 Project 2**

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*A. Introduction*

Combustion reactor modelling is an important area of study in combustion science. Further, the development of these models has obvious implications for electrical grids, manufacturing infrastructure, and transportation methods around the world. The ability to effectively model the development of combustion reactions in different conditions and from different fuel mixtures is essential for the study of efficient and clean energy generation, as well as safe handling and storage of combustive mixtures (i.e. “accidental” combustion reactors). This report centers on some basic applications of different combustion reactor models using the reactor modelling software Cantera.

*B. Methods*

The Cantera combustion modelling library for Python has powerful reaction and reactor modelling capabilities, including plug flow reactors (PFRs) and continuous stirred tank reactors (CSTRs) which are the primary reactors studied in this report.

Reactors can be described using balance equations for energy, composition, and mass, all of which may be derived from an overall material and energy balance for fluids.

The coupled sets of equations for each type of reactor (PFR and CSTR) are listed below:

*where*

To determine the solution of these sets of coupled nonlinear equations, Cantera uses a modified damped Newton-Raphson solution method with numerically-determined derivatives. Cantera provides tools to convert experimental mechanism and thermodynamic files of many formats to a Cantera-compatible file format. In this report, PFR modelling utilized the most recent [University of California-San Diego (UCSD) combustion mechanism](http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html) while CSTR modelling was performed using the traditional [GRI-30 reaction mechanism from UC-Berkeley](http://combustion.berkeley.edu/gri-mech/version30/text30.html).

To implement these reactor models, a reaction network is generated and initialized with a gas of the desired composition, temperature, and pressure.

PFR and CSTR models are assumed to be ideal, which involves different assumptions for each type of reactor; axial mixing, flow velocity gradients, and heat loss to environment are assumed to be negligible in the PFR reactor, and CSTR reactors are assumed to be homogenous with respect to temperature and composition as well as adiabatic. For the purposes of study in this report, all CSTRs were approximated to be at steady state condition. All gas mixtures were assumed to be ideal given the elevated temperatures and moderate pressures present in reactor models.

Auto-ignition delay, for the purpose of this report, is defined as the time required to generate a temperature rise of 150 K from initial temperature. This represents the amount of time an adiabatic fuel-oxidizer mixture at a given temperature takes to undergo an explosion spontaneously.

*C. Results and Discussion*

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Description automatically generatedAuto-ignition delay of a fuel-air mixture can be easily determined by evaluating an ideal model of a PFR reactor. To demonstrate this method, auto-ignition of methane-air mixtures were studied using an ideal gas, constant pressure PFR. Since auto-ignition at low temperature takes inordinate amounts of time to take place, initial temperatures were assumed to be high, between 1100 and 1500 K. Pressures were varied between 1 and 10 atm, with equivalence ratios (ɸ) between 0.3 and 1.5. For the three pressures, five temperatures, and four equivalence ratios studied, this results in (3) x (5) x (4) = 60 auto-ignition delays, visualized below:

**Fig 1 | Variance in auto-ignition delay [s] with respect to pressure [atm] starting temperature [K] and equivalence ratio** ɸ **[unitless]**

These results provide several well-defined trends that match theoretical work regarding combustion kinetics. While ignition delay shows a relatively weak dependence on ɸ, with large changes in ɸ (ɸ = 0.3 ɸ = 1.5) inducing less than a 10% difference in auto-ignition delay. This is due to “wet” combustion, combustion in the presence of hydrogen and oxygen radicals such as H and OH, dominating even when hydrogen and oxygen species are present at very low quantities. Since these radicals are always present in very small relative quantities, even large changes in equivalence ratio do not strongly affect their generation.

However, auto-ignition delay periods show much stronger dependence on reactor pressure and initial temperature. Theoretical work implies the following dependence of characteristic combustion reaction time () on pressure and temperature:

Where the pressure and temperature dependence are derived from the Arrhenius model of chemical reaction. Both of these correlations imply that, as pressure and temperature increase, the characteristic time of reaction decreases for the reaction, which is shown on the graphs in figure 1. Pressure increase from 1 atm to 10 atm decreases auto-ignition delay by nearly an order of magnitude for equivalent ɸ and initial temperature conditions, while initial temperature increase from 1100 K to 1500 K decreases auto-ignition temperature by nearly two orders of magnitude for equivalent pressure and ɸ conditions.

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Description automatically generatedIt is worthwhile, however, to investigate more deeply the trends in species concentrations and temperature with respect to time in an ideal PFR reactor model. This is performed below for a representative combustion example, with ɸ = 1.0, initial temperature of 1100 K, and pressure of 1 atm for the same methane-air combustion mixture. Thus, the concentrations of minor and major species and reactor temperature with respect to residence time are shown graphically below:

**Fig 2 | Major and minor species compositions with respect to residence times in the ideal PFR reactor** **with equivalence ratio ɸ = 1.0, initial temperature = 1100 K, and pressure = 1 atm**

Note, importantly, the difference in scales on the vertical axes on the major and minor species graphs, where minor species are much less abundant than major combustion species. The same relationship with residence time may be displayed for reaction temperature.

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**Fig 3 | Combustion temperature with respect to residence time in the reactor in the ideal PFR reactor** **with equivalence ratio ɸ = 1.0, initial temperature = 1100 K, and pressure = 1 atm**

In this example, the ignition delay is approximately 0.057 seconds. In this simulation, the onset of combustion appears instantaneous due to nearly negligible amounts of reactive radicals in the reaction mixture before the onset of rapid combustion. A view of solely the point of ignition may shed more light on this rapid process:

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**Fig 4 | Radical oxyhydrogen species with respect to residence time in the reactor in the ideal PFR reactor** **with equivalence ratio ɸ = 1.0, initial temperature = 1100 K, and pressure = 1 atm at the point of ignition**

The accumulation of reactive oxyhydrogen radicals can be more effectively diagnosed by showing minor species accumulation on a logarithmic scale:

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**Fig 5 | Accumulation of oxyhydrogen radicals in the ideal PFR reactor** **with equivalence ratio ɸ = 1.0, initial temperature = 1100 K, and pressure = 1 atm on logarithmic scale**

The constant accumulation of oxyhydrogen radicals and the relationship between these radicals and the initiation of rapid combustion reaction (i.e. ignition) is much more evident when displayed on a logarithmic scale. Since radicals are generated and terminated via an equilibrium reaction, the composition of the reaction mixture with respect to radical species displays a hysteresis, which is nonetheless monotonically increasing for the entirety of the residence time within the PFR. Oxyhydrogen species compositions rapidly rise to quasiequilibrium levels, defined by their equilibrium production and termination rate, represented by the initial rapid rise in the hysteresis curve. Then, the rise in concentrations of these species slows as major species are consumed and the quasiequilibrium levels of these reactive radicals slowly shifts. Finally, a combination of temperature rise and fuel consumption continues to accelerate radical generation to the point of complete combustion.

The concentrations of these reactive radicals are the root cause of rapid ignition. Once highly reactive radical species rise sufficiently to catalyze significant fuel consumption, their rate of generation also rises rapidly, causing a runaway reaction.

Their importance to induction delay can be further emphasized by evaluating the effect on auto-ignition of several oxidizers of different compositions of oxygen and reactive radicals. These initial oxidizer concentrations are tabulated below:

**Table 1 | Simulated initial oxidizer compositions**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Initial Oxidizer Composition** |  |  |  |  |
| air | 0.21 | 0.79 | -- | -- |
| oxygen | 1.0 | -- | -- | -- |
| O radicals | 0.207 | 0.79 | 0.003 | -- |
| OH radicals | 0.207 | 0.79 | -- | 0.003 |

The simulation displayed in figure 1 was performed again for ɸ = 0.5, initial temperature of 1300 K, and pressure of 1 atm. The auto-ignition delay of each of these initial oxidizer compositions are visualized below:

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**Fig 6 | Auto-ignition delay as a function of inlet oxidizer concentration**

The effect of initial oxyhydrogen radicals in the oxidizer input to the reaction mixture on the auto-ignition delay can be most easily understood by considering whether this change brings the reaction mixture closer to the composition that enables rapid ignition. Since a reaction mixture with high levels of O and OH in the reaction mixture are characteristic of a rapid ignition reaction, combustion using an oxidizer with O and OH already present serves to speed the onset of auto-ignition (see figure 5).

As for the shorter auto-ignition delay using pure oxygen as oxidizer, the removal of nitrogen, which is a nonreactive diluent, serves to selectively speed radical generation reactions, while the removal of nitrogen slows the rate of third-body termination reactions. This speeds the generation of oxyhydrogen radicals and the onset of combustion overall.

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**Fig 1 | (L) Adiabatic flame temperature for propane-air mixture as a function of equivalence ratio** ɸ **(R) Equilibrium concentrations for major species in adiabatic flame as a function of equivalence ratio** ɸ

Clearly shown on Fig 1-L is the peak flame temperature, near ɸ = 1.04, T = 2290 K. The decline of temperatures away from this maximum is also intuitive given that reaction is either incomplete due to fuel or oxidant limitations. Fig 1-R displays how the trend of H2O follows the trend of reaction completeness, while other reagents rise or fall dependent on fuel or oxidant limitations. For example, when oxidant-limited, CO and H2 fractions rise, while fuel-limited reactions show higher presence of O2. Excluded from Fig 1-R is N2, which is generally inert and present in very high concentrations in air-fed combustion.

The same equilibration procedure may be repeated in a constant-volume configuration, with all other characteristics the same:

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**Fig 2 | (L) Adiabatic combustion temperature for propane-air mixture as a function of equivalence ratio** ɸ **(R) Equilibrium concentrations for major species in adiabatic combustion as a function of equivalence ratio** ɸ

While results are qualitatively similar to the constant-pressure condition, there are some significant differences. Most importantly, while the temperature trend is roughly equivalent, the maximum combustion temperature shown on Fig 2-L is significantly higher than flame temperature from Fig 1-L, at 2670 K rather than 2290 K. This is explained by the inability to lose temperature energy as expansive work in a constant volume condition (where work *w = PdV*) and a subsequently higher temperature.

Since pressure is no longer held constant, pressure can also be evaluated in the constant-volume model:

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**Fig 3 | Constant-volume adiabatic combustion pressure as a function of equivalence ratio** ɸ

While the pressure relationship in Fig 3 roughly mirrors the combustion temperature in Fig 2-L, the maximum combustion pressure occurs at a significantly higher ɸ = 1.21 rather than the maximum temperature ɸ = 1.04. This can be explained by considering the ideal gas law:

where it is apparent pressure is positively dependent on temperature (T) but also the number of molecules (n). So, while temperature peaks at a much lower ɸ value, the number of molecules in the mixture continues to increase for higher values of ɸ due to decomposition of hydrocarbon molecules. This results in a pressure maximum at a slightly more fuel-rich ratio. Also relevant is the decreased specific heat of the mixture as the relative amount of diluting N2 decreases.

Temperature and pressure can also affect the composition results of equilibrium models. To illustrate these effects, the following models were equilibrated using ranges of temperatures and pressures that span the absolute extremes of temperature and pressure found on Earth and their major species (H2O, H2, O2, CO, CO2) were plotted. Even if the outer edges of these ranges are far outside the conditions that will ever be encountered, these ranges illustrate the trends in equilibrium concentrations caused by temperature and pressure. Temperature was varied between 184 K (Antarctic low) and 330 K (Death Valley high). Pressure was varied between 33.7 kPa (Mount Everest low) and 108.5 kPa (Siberian high).

Since there are many possible variations of these parameters, only some will be included here for illustrative purposes, with the rest shown in the appendix section of this report.

First, the most striking result is how the equilibrium species concentrations are largely invariant to both temperature and pressure changes, never shifting more than 0.2% for any species in the mixture:

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**Fig 4 | (L) Major species mol% at equilibrium for equivalence ratio** ɸ **= 0.7 as a function of starting pressure (R) Major species mol% at equilibrium for equivalence ratio** ɸ **= 0.7 as a function of starting temperature**

Table

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**Fig 5 | (L) Major species mol% at equilibrium for equivalence ratio** ɸ **= 1.4 as a function of starting pressure (R) Major species mol% at equilibrium for equivalence ratio** ɸ **= 1.4 as a function of starting temperature**

Even for these extreme pressure and temperature changes, to the extremes of environmental temperature and pressure conditions found on Earth, the equilibrium composition of flame products is essentially identical, for both fuel-rich and fuel-lean mixtures, across both Fig 5 and Fig 6.

The equivalence ratio of the mixture combusted more strongly controls the outcome of the reaction than the starting temperature and pressure, given the higher magnitude of effects shown in Fig 1-L and Fig-2 from those in Fig 4 and 5.

However, although flame products are essentially identical across wide ranges of starting pressures and temperatures, the equilibrium flame temperature can be more significantly affected:

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**Fig 5 | Relationship between equilibrium flame temperature and initial pressure for various values of the equivalence ratio** ɸ

With the initial pressure plotted on a logarithmic scale, there is a clear positive relationship between initial pressure and equilibrium flame temperature shown on Fig 5. More interestingly is the difference in magnitude of this effect at different values of ɸ. The span of equilibrium temperature changes (ΔT) over the range of initial pressures (ΔP) is shown below for different values of ɸ:

|  |  |  |  |
| --- | --- | --- | --- |
| ɸ | 0.7 | 1.0 | 1.4 |
| ΔT (K) | 2.5 | 33 | 3 |

Notably, the induced change in flame temperature is an order of magnitude higher at a stoichiometric fuel-air ratio. This effect can be explained by considering the fact that at an equivalence ratio of ɸ = 1.0, the reaction is just at the border between fuel-rich and fuel-lean. The previous Fig 2-R shows that the major products of combustion change drastically across this border region. Thus, a smaller change in the equilibrium condition, in this case by a change in pressure, can have a larger effect on the overall outcome of the reaction and thus the heat released during combustion.

This modelling procedure is also not limited to propane-air as the fuel-oxidant mixture: to illustrate, the constant-pressure procedure displayed in Fig 1 was repeated for a methane-oxygen (CH4-O2) fuel mixture:

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**Fig 6 | (L) Major species mol% at equilibrium for equivalence ratio** ɸ **= 0.7 as a function of starting pressure (R) Major species mol% at equilibrium for equivalence ratio** ɸ **= 0.7 as a function of starting temperature**

The most prominent difference between a methane-oxygen and propane-air combustion mixture is caused by the lack of nitrogen in an oxygen-fed combustion reaction. The effect of this change is clearly evident in Fig 6, where the flame temperature and equilibrium composition graphs display a much more rounded relationship with equivalence ratio. While N2 is mostly chemically inert in reaction, the heat capacity of the large amounts of nitrogen introduced to the fuel-oxidant mixture can have significant effects on flame temperature and the outcome of the reaction. As a result, with the effects of N2 removed, the effect of equivalence ratio ɸ on flame temperature and equilibrium molar composition is much more gradual, without the sharp changes found on Fig 1 and 2 near a value of ɸ = 1.

*D. Summary and Conclusion*

These simple computational models are easy to generate with the Cantera module and can offer valuable insight that can be applied even to more complex, real-world examples. At the very least, the ability to rapidly generate and visualize models for any fuel and oxidant combination serve as a useful starting point in assessing the equilibrium combustion conditions of a system under study.

*E. Appendix*

Python-Cantera programs: <https://github.com/hankdikeman/CombustionProj2>

All graphs: <https://github.com/hankdikeman/CombustionProj2/tree/master/Figures>