Combustion ME 5446 Project 2

Henry Dikeman
Student ID: 5305384
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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 Reynold's transport theorem. Since a CSTR approaches a stable equilibrium state in long times for most reactor cases, the steady state system of equations with no time dependence is listed for this reactor.

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

Balance Equation	PFR	CSTR
Mass	$$\frac{d(\rho u_x A)}{dx} = 0$$	$$0 = \dot{m}_{in} - \dot{m}_{out}$$
Species	$$(\rho u_x)\frac{d(Y_i)}{dx} = \dot{\omega}_i \bar{W}_i$$	$$0 = \frac{\dot{m}_{in}}{\rho V}\left(Y_{i,in} - Y_i\right) + \frac{\dot{\omega}_i \bar{W}_i}{\rho}$$
Energy	$$(\rho u_x c_{Pmix})\frac{dT}{dx} = \dot{q}_i''' - \sum_i h_i \dot{\omega}_i \bar{W}_i$$	$$0 = \frac{\dot{m}_{in}}{\rho V}\sum_i Y_{i,in}(h_{i,in} - h) - \frac{\sum_i^N h_i \dot{\omega}_i \bar{W}_i}{\rho} + \frac{\dot{q}_i'''}{\rho}$$
Momentum	$$(\rho u_x A)\frac{du_x}{dx} = -A\frac{dp}{dx} - \tau_w P$$	[--]

A solution is found to these sets of nonlinear solutions using a numerical solver.

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 while CSTR modelling was performed using the traditional GRI-30 reaction mechanism from UC-Berkeley.

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

PFR and CSTR models are assumed to be ideal and adiabatic, which involves different assumptions for each type of reactor; in the PFR, axial mixing, flow velocity gradients, and heat loss to environment are assumed to be negligible, and CSTR reactors are assumed to be homogeneous with respect to temperature and composition as well as adiabatic with no heat loss to the environment. For the purposes of this report, all CSTRs were approximated to be at steady state condition, meaning that outlet conditions of the reactor have no time dependence. All gas mixtures were assumed to be ideal given the elevated temperatures and moderate pressures present in reactor models.

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

C. Results and Discussion
Auto-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 (ϕ) 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:
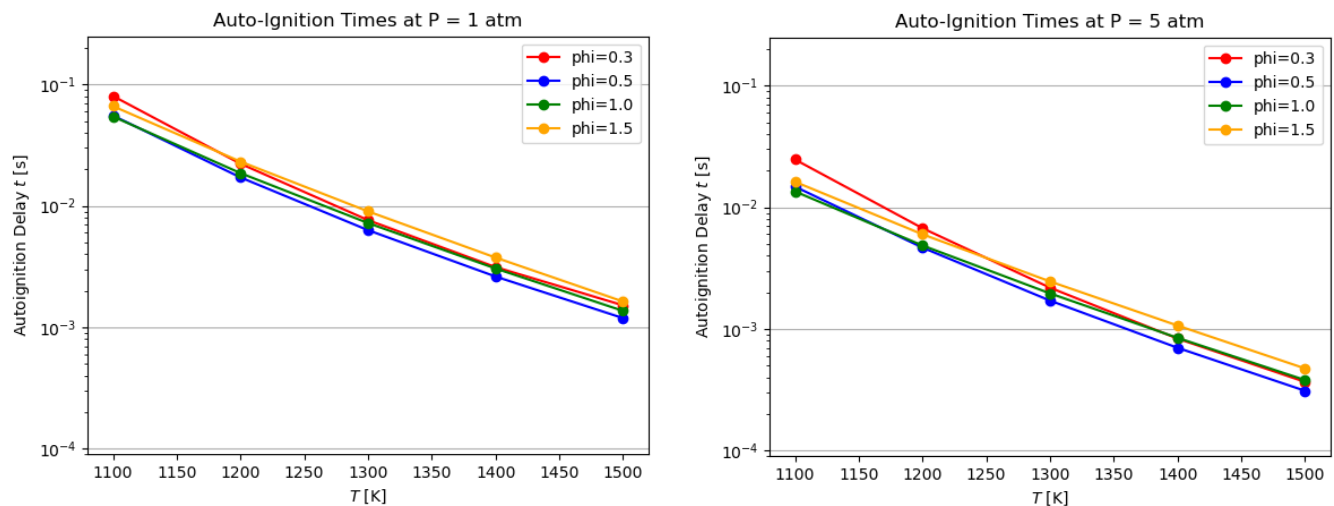
Fig 1 | Variance in auto-ignition delay [s] with respect to pressure [atm] starting temperature [K] and equivalence ratio ϕ [unitless]
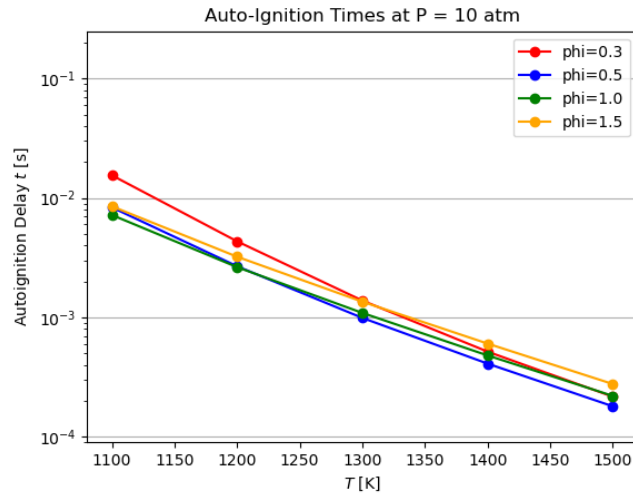
Fig 1 (cont'd) | Variance in auto-ignition delay [s] with respect to pressure [atm] starting temperature [K] and equivalence ratio ϕ [unitless]

These results provide several well-defined trends that match theoretical work regarding combustion kinetics. While ignition delay shows a relatively weak dependence on ϕ, with large changes in ϕ (ϕ = 0.3 → ϕ = 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 quantities relative to other species in the mixture, even large changes in equivalence ratio do not strongly affect the generation of these radical species.

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 (τ_{chem}) on pressure and temperature:

$$\tau_{chem} \propto P^{-n} \quad 0.8 < n < 0.85$$

$$\tau_{chem} \propto \exp(1/T)$$

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 ϕ 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 ϕ conditions, matching the expected correlations given above.

It 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 ϕ = 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:
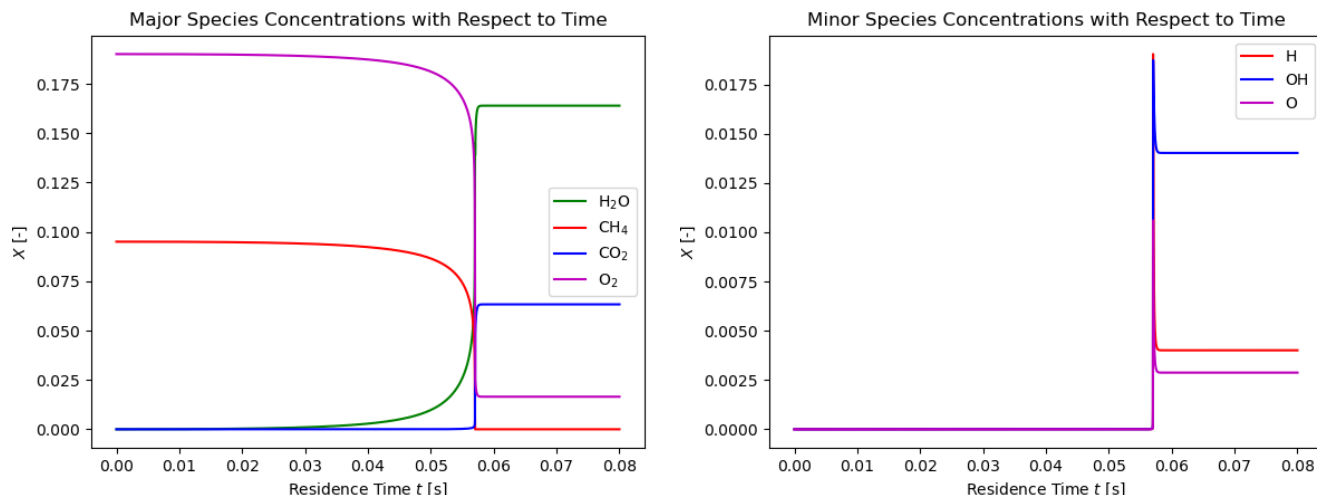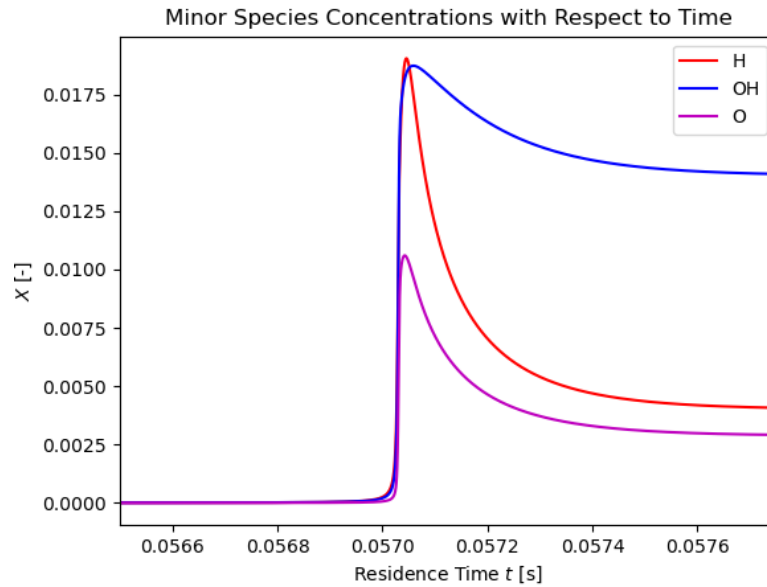

Fig 2 | Major and minor species compositions with respect to residence times in the ideal PFR reactor with equivalence ratio φ = 1.0, initial temperature = 1100 K, and pressure = 1 atm

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.
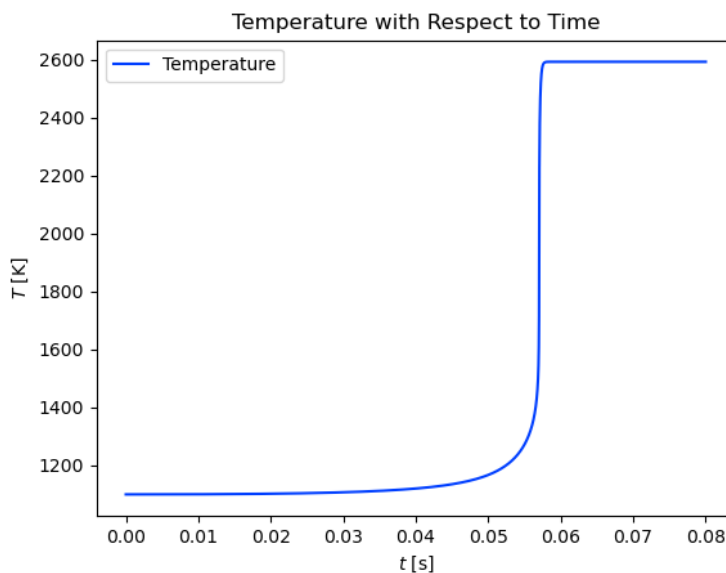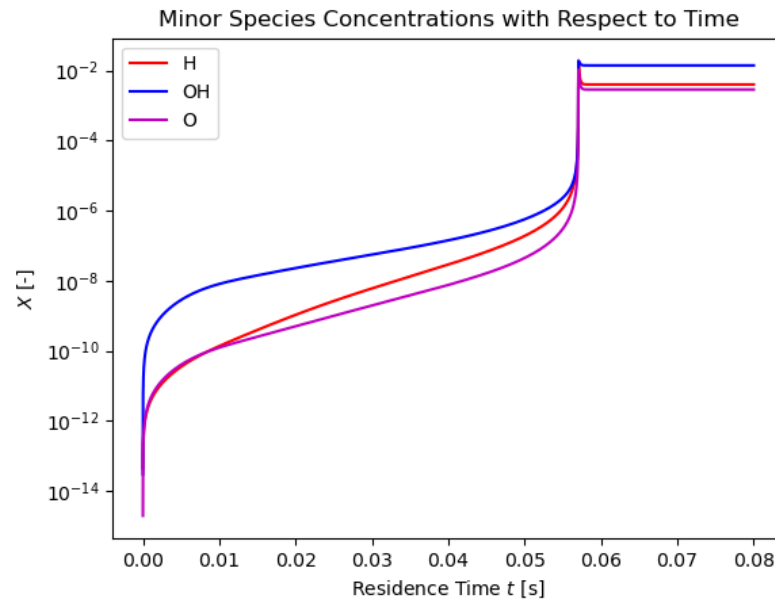

Fig 3 | Combustion temperature with respect to residence time in the reactor in the ideal PFR reactor with equivalence ratio φ = 1.0, initial temperature = 1100 K, and pressure = 1 atm

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 closer view of the point of ignition may shed more light on this rapid process:

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

The accumulation of reactive oxyhydrogen radicals such as H, OH, and O can also be more effectively diagnosed by showing minor species accumulation on a logarithmic scale:

Fig 5 | Accumulation of oxyhydrogen radicals in the ideal PFR reactor with equivalence ratio φ = 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 but still increases 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	χ_{O2}	χ_{N2}	χ_O	χ_{OH}
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 ϕ = 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:
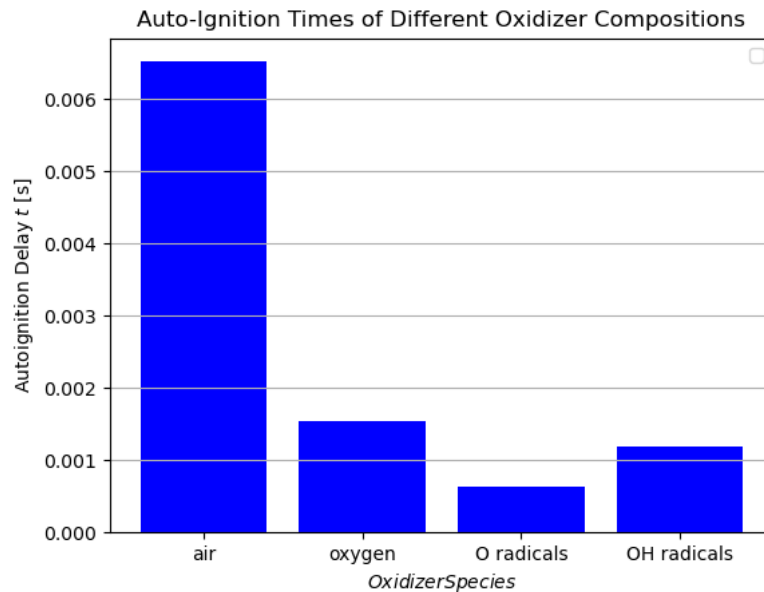
Fig 6 | Auto-ignition delay as a function of inlet oxidizer concentration

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, since the removal of nitrogen slows the rate of third-body termination reactions and increases the concentration of oxyhydrogen species in the mixture. This speeds the generation of oxyhydrogen radicals and the onset of rapid combustion overall.

For combustion applications where reactors are well-mixed, meaning that reactants entering the system are thoroughly homogenized with the product mixture before there is sufficient time for them to react, a PFR is a poor model. In these cases, a CSTR is a more effective model for reactor dynamics.

Here, CSTR models are employed to determine the steady state emission of the important pollutants NO and CO. Cantera is again used, but this time with the simplified GRI-30 combustion mechanism from UC Berkeley.

For combustion reactors where scale or propulsion considerations makes the addition of emission-reducing catalysts infeasible, such as aircraft engines or large power generation turbines, reactor residence time is the most powerful method for controlling the emission of NOx and CO species as well as combustor efficiency. By tightly controlling the amount of time combustion species remain in the reactor, the amount of NO and CO produced by combustion can be limited to legally permitted levels.

To perform this reactor modelling, a mass flowrate controlled CSTR was initialized in Cantera, where the mass flowrate was set as a function of the desired residence time using the corresponding equation:

$$1/\tau_{res} = \dot{m}/\rho V \;\; \Rightarrow \;\; \dot{m} = \rho V/\tau_{res}$$

The inlet stream to the reactor was a methane-air mixture at 650 K, 1 atm, and an equivalence ratio of ϕ = 0.85. The reactor was simulated for sufficient time to allow it to reach steady state, where the composition and temperature of the interior product mixture were no longer changing with time. In order to initiate combustion quickly, the CSTR was initialized containing a methane-air mixture at 1 atm, ϕ = 0.85, and at a high temperature of 2000 K in order to initiate auto-ignition immediately and bring the CSTR to steady state much more rapidly.

For the following analysis, a distinction must be made between the _steady state_ reactor condition and the _equilibrium_ reactor composition. The _steady state_ composition is the state at which the following condition is satisfied for all species within the reactor mixture:

$$(\text{rate of consumption}) + (\text{rate of removal}) = (\text{rate of generation}) + (\text{rate of addition})$$

In other words, the steady state condition is a kinetic consideration determined by the residence time and rate of reaction of all species. The _equilibrium_ reactor condition is solely a thermodynamic limitation, where given infinite residence time, all species arrive at an equilibrium composition with only Gibb's energy limiting further changes in composition.

With those clarifications in mind, the following is a normalized relationship between methane-air combustion steady state NO/CO concentrations as a function of CSTR residence times between 0 and 12 seconds. Steady state mole fractions of NO and CO were normalized using the _thermodynamic equilibrium_ compositions, which were determined by the equilibrate functionality within Cantera and the inlet reactor conditions:
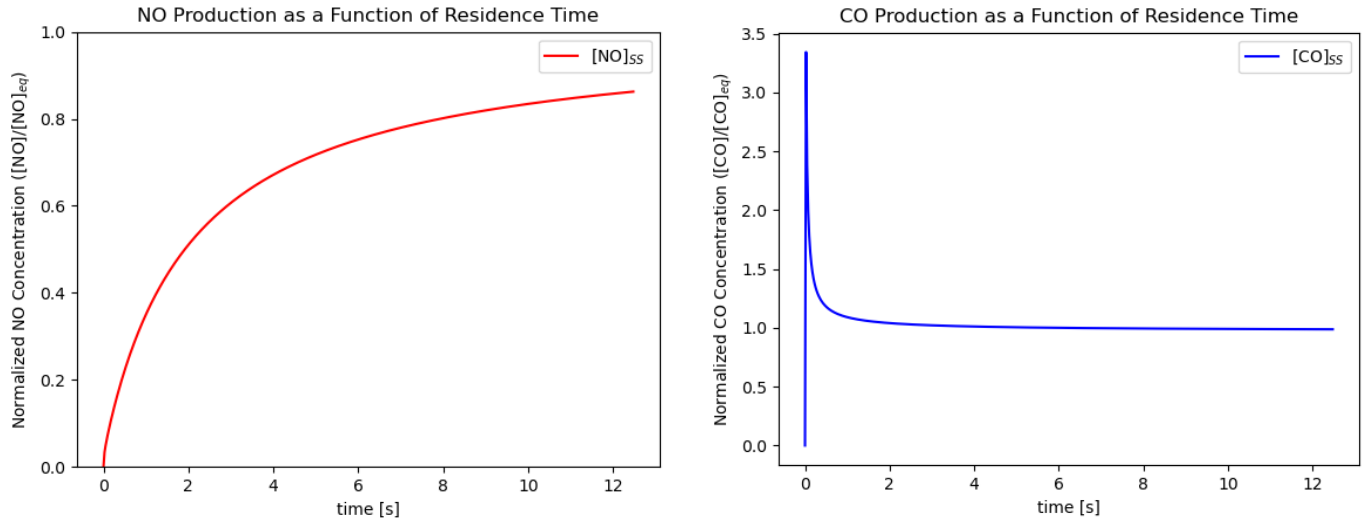
Fig 7 | Normalized CO and NO steady state CSTR outlet concentrations as a function of reactor residence time for a methane-air mixture at T = 650 K, P = 1 atm, and an equivalence ratio of ɸ = 0.85

Under these reactant conditions, the adiabatic, constant pressure thermodynamically equilibrated mole fractions of NO and CO were 0.005 and 0.001, respectively.

While both CO and NO normalized concentrations remain zero at residence times of 0, expected given the reactant mixture has no time to react, the trends in NO and CO steady state outlet concentrations are significantly different at longer residence times. While NO concentration is monotonically increasing with respect to residence time, CO concentration undergoes a sharp maximum of more than three times the thermodynamic equilibrium concentration, before decreasing to equilibrium levels.

As a combustion intermediate in lean mixtures, before hydrocarbon molecules can undergo complete oxidation, it is expected that CO would be generated in large quantities at intermediate residence times. Under these steady state reactor conditions, the reactant mixture is retained with sufficient duration only to undergo partial oxidation of hydrocarbon molecule.

For NO concentration, a monotonic increase with respect to longer residence times is also expected, since the most rapid form of NO generation is via the thermal mechanism, dependent on high temperatures. Since NO generation occurs much more slowly than hydrocarbon combustion, retention of reactant species beyond the short period required for complete combustion enables increased generation of NO species.

An important implication of this result is the trade-off inherent in pollution control using reactor residence time. With insufficient residence time, combustion is incomplete resulting in significant CO emission and greater reactor inefficiency. With long residence times, NO generation is much

more rapid and reactor operation may not meet legally prescribed guidelines for pollutant emission.

Finding a balance between these competing effects of residence time controls is an essential step in designing a combustion reactor that can operate safely, efficiently, and within legal pollutant limits.

D. Summary and Conclusion
Before developing reactor models of greater complexity, a simplified modelling scheme using a PFR or CSTR reactor model can provide valuable insight regarding auto-ignition times, the development of radical species and temperature changes in a batch reactor or storage system, and even the effects of reactor configuration on the emission of important pollutant molecules. Further, although idealized reactor models omit much of the detail of real-world systems, a PFR or CSTR model can serve as an effective starting point for future reaction models of arbitrary complexity.

E. Appendix
Python-Cantera programs: https://github.com/hankdikeman/CombustionProj2
All graphs: https://github.com/hankdikeman/CombustionProj2/tree/master/Figures