**Combustion ME 5446 Project 3**

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*A. Introduction*

The mechanics of hydrocarbon detonation shed light on many of the complex processes occurring during a combustion reaction. Modelling the structure and mechanics of detonation are also important in their own right, since hydrocarbon detonation has the potential to be an extremely dangerous event if unexpected. Understanding the detonation process at a microscopic and theoretical level enables researchers and industry engineers to properly understand the safety risk and physical phenomena present due to a hydrocarbon detonation. Additionally, the future of efficient combustive engine design is likely to be reliant upon detonation, and the success of future research is grounded upon a competent understanding of the backbone of detonation mechanism. This report determines the theoretical characteristics of propane-air combustion at a variety of initial conditions and mixing ratios, as well as simulating the induction period for propane-air mixtures at the detonation limits of the mixture.

*B. Methods*

This report employs the Cantera combustion simulation library as a backbone for most major analysis, including induction time simulation and reaction kinetics simulations.

Induction time was determined using a PFR reactor module within the Cantera library, with mechanics dictated by the coupled series of governing equations below:

|  |  |  |
| --- | --- | --- |
| **Balance Equation** | **PFR** | **CSTR** |
| Mass |  |  |
| Species |  |  |
| Energy |  |  |
| Momentum |  | [--] |

This sets of equations are integrated with respect to time to yield an estimation of the progression of the reaction as a function of residence time. This residence time is used as a proxy for the autoinduction time for the gas mixture used as the entry mixture, since this ideal reactor model neglects axial mixing and assumes uniform plug flow. Autoinduction period, for the purposes of this report, is considered a rise in temperature of 150 K from the PFR entrance condition of the gas mixture.

To construct the chemical source term estimation for this simulation, the [GRI-30 reaction mechanism from UC-Berkeley](http://combustion.berkeley.edu/gri-mech/version30/text30.html) was used to evaluate hydrocarbon combustion.

In addition to the core Cantera package, the SDToolbox module from CalTech was used to determine the gas condition after the detonation shock and subsequent reaction. This toolbox contains several useful functions for detonation analysis, all of which were implemented in Python using the robust Cantera equilibrium and kinetics solvers as a structural backbone with the SciPy package performing much of the nonlinear optimizations necessary.

The SDToolbox library includes functions for solution of the Chapman-Jouget (CJ) detonation speed, calculation of the speed of sound at any gas condition, and physical gas conditions following a pressure shock. While the Python implementation of these utilities is less robust than their Cantera counterparts, the ability to seamlessly integrate detonation analysis with standard Cantera equilibrium and reaction kinetics simulations is extremely practical for detonation analysis.

Detonation can be considered an equilibrium process between heat released upon combustion and the pressure wave that this reaction generates and is sustained by. Calculation of the detonation speed is reliant upon the simultaneous solution of the following sets of equations:

However, since there exist in this set of equations 6 unknowns and only 5 equations, a final specification must be made that the product flowrate downstream of the detonation zone has a Mach number equal to 1. This condition generates a unique solution for detonation, which is referred to as the upper CJ point. This point is also the unique point where the Rayleigh mass transfer relationship is tangent to the Hugoniot heat release relationship.

Solution of this set of now 6 equations and 6 unknowns is performed by the SDToolbox library and yields a detonation condition considered to be the minimum and equilibrium detonation speed at a given initial condition.

To determine the solution of these sets of coupled nonlinear differential equations, Cantera uses the CVODES solver from the SUNDIALS package, implemented in C++, to integrate the system of stiff ODEs above. Cantera also 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 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 evaluated at steady state condition, meaning that the 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 and for simplicity.

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*

In this report, detonation of a propane-air mixture at a range of different starting conditions were considered. Propane-air mixtures were evaluated for 2.2 to 9.2 mol% propane in air, which represent the experimental detonation limits determined for propane-air mixtures initially at 300 K and 1 atm.

Detonation speed was first determined for the mixtures:

Diagram

Description automatically generated

**Fig 1 | Variance in detonation speed as a function of initial physical state and composition**

While detonation speed is only loosely coupled to the initial pressure, speed is more strongly dependent on the initial temperature of the reactant gas mixture. This is evident in the small changes in detonation speed between the reactant mixtures at 100 kPa and 500 kPa, while a significant deviation in the detonation speed trend is present when the initial temperature is doubled to 600 K.

At the outer limits of inlet composition, speed also decreases due to the lower heat release available to sustain the shockwave, since the concentration of oxidant and fuel is nonideal for heat release. This rigorous calculation can be compared with a simplified approximation for detonation speed, which is shown below:

Using physical values for N2 at 2700 K ( 1.29, 28) since N2 is the majority of the reactant mixture, the rigorously calculated values from the plot above when outlet temperature is 2700 K (values plotted below) are compared to the simplified approximation at the same temperature, tabulated below:

**Table 1 | Simplified detonation speed calculations**

|  |  |  |  |
| --- | --- | --- | --- |
| **Inlet Concentration** | **SDToolbox (m/s)** | **Simplified (m/s)** | **Deviation** |
| T=300 K, P=100 kPa | 1798 | 1805 | 0.4% |
| T=300 K, P=500 kPa | 1833 | 1805 | 1.6% |
| T=600 K, P=100 kPa | 1798 | 1805 | 0.4% |

As shown in Table 1 above, the deviation in detonation pressures from the simplified estimation is nearly negligible for all reaction mixtures. This is especially remarkable given the highly simplified assumptions used when constructing the above model, not least approximating the mixture as a pure N2 stream. While this simplified detonation speed approximation is useful for quick estimations of detonation speed, for full estimations of the conditions inside the 1-dimensional ZND detonation wave, including induction time, pressure, temperature, and Mach number, the full simulation must be evaluated.

This speed is directly related to the Mach number for detonation, which corresponds to the ratio between the reactant flow and the speed of sound in the reactant mixture:

Chart

Description automatically generated

**Fig 2 | Variance in Mach number as a function of initial physical state and composition**

From this plot, it becomes clear the near-negligible effect that initial pressure holds on the reactant feed Mach number for detonation. However, temperature shows a much stronger effect on Mach number.

An intuitive explanation for this phenomenon is uncovered by considering the structure of a Zeldovich-von Neumann-Doering (ZND) detonation wave. This wave consists of a supersonic reactant zone, shock zone with elevated temperature and pressure, reaction zone where combustion rapidly occurs, and equilibrated product flow. The ZND detonation wave propagates using the temperature and pressure rise from the shock to rapidly trigger autoignition. This autoignition process, like typical autoignition, is highly dependent on temperature to encourage the production of reactive radical species. When the inlet temperature to the detonation process is elevated, so is the temperature within the induction region, and thus the width of the induction zone is smaller due to the much faster autoignition process, which decreases the speed necessary to maintain sonic flow downstream of the rapid combustion reaction.

Further insight can be gained on the combustion process by evaluating the pressure, temperature and specific heat downstream of the combustion reaction at each initial condition. These were evaluated at the outlet gas concentration, after the combustion reaction has already occurred.

Chart, line chart

Description automatically generatedDiagram

Description automatically generated with medium confidenceChart

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**Fig 3 | Variance in product specific heat ratio, pressure, and temperature as a function of composition and reactant feed condition**

As expected, the pressure and temperature are elevated within the detonation of the reactant mixture which enters at 5 atm, with an extremely dramatic increase in pressure downstream from the reaction. This is understandable given the dependence of autoignition reaction upon temperature: when initial pressure is higher, pressure must increase dramatically to reach a temperature capable of sustaining rapid combustion reaction, here reaching a peak of over 80 atm. Pressure remains lower when the reaction mixture enters at 600 K for a similar reason: reactant pressure must increase to a lesser degree to initiate rapid combustion.

[specific heat ratio]

Finally, temperature follows a similar trend to that seen for detonation speed, with temperature reaching a maximum near 4 mol% propane and decreasing as the composition approaches the lean and rich detonation limits. However, for the reactant mixture that enters the detonation at elevated temperature, with T0 = 600 K, outlet temperature is correspondingly higher. The same detonation speed trend is again seen for this reaction mixture, where higher entrance pressure triggers a higher peak detonation product temperature.

It is also worth investigating the autoignition delays at the lean and rich detonation limits for propane-air at an initial temperature of 300 K and initial pressure of 100 kPa. For these initial conditions, experimental data reports that the lean and rich detonation limits are 2.2 mol% and 9.2 mol% propane, respectively.

The autoignition delay was performed as indicated in the Methods section, where a constant pressure PFR was loaded with a Cantera gas mixture and the reactor was advanced through time using the GRI-30 mechanism until a rapid temperature increase occurred (here, evaluated as a temperature rise of 150 K over inlet conditions). The time at which this temperature increase occurs is considered the autoignition time. The time step for this iteration may be iteratively adjusted until the magnitude of the timestep is much less than the induction period () to ensure sufficient precision for autoignition measurement.

**Table 2 | Autoinduction times for rich (9.2 mol%) and lean (2.2 mol%) detonation limits**

|  |  |  |  |
| --- | --- | --- | --- |
| **Inlet Concentration (mol%)** | **Inlet P (atm)** | **Inlet T (K)** | **Induction Delay (s)** |
| 9.2 mol% (rich limit) | 30.15 | 1280 | 2.13 x 104 |
| 5 mol% (intermediate) | 35.13 | 1560 | 4.83 x 10-6 |
| 2.2 mol% (lean limit) | 23.50 | 1266 | 2.69 x 104 |

The rich and lean detonation limits signify the molar concentrations past which detonation can no longer occur, instead favoring deflagration. This is evident when comparing the rich and lean limit autoignition time to the autoignition period for an intermediate composition value. The time delay is on the order of 100 times larger at the lean and rich detonation limits, supporting the experimental observation that sustained, steady detonation is unfavorable past these limits.

This has important implications for future development of detonation-driven combustion engines, where some fuel mixtures that may be favorable with other engine configurations are no longer feasible when detonation is desired. This analysis is a necessity when assessing the feasibility of premixed fuel-air mixtures at the running pressure of a detonation engine or any detonation-driven process. Simplified, zero-dimensional calculations such as those shown above form a convenient complement with more intensive multi-dimensional direct numerical simulation methods when performing any rigorous combustion analysis.

*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>