Exercise 6 - Determination of ignition delay time of methane-air mixture using Cantera

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1. Introduction & Problem

Ignition delay refers to the time interval between the injection of fuel and the onset of combustion in an internal combustion engine. During this period, the injected fuel mixes with hot, compressed air and vaporizes. Once sufficient mixing and vaporization occur, spontaneous ignition takes place, initiating the combustion process.

The duration of ignition delay plays a crucial role in engine performance and emissions. A longer ignition delay allows more fuel to accumulate and vaporize within the combustion chamber, often resulting in a sudden and intense combustion event. This rapid combustion can generate high-pressure shock waves and extremely elevated surface temperatures, which may contribute to mechanical stress on engine components. Prolonged ignition delays are associated with increased loading on the piston crown, potential breakage of piston rings, and material degradation due to erosion caused by hot gas flow.

Moreover, the elevated temperatures resulting from extended ignition delay can lead to higher emissions of nitrogen oxides (NO_x), a major environmental pollutant. Understanding and accurately predicting ignition delay is therefore essential for optimizing engine design, improving fuel efficiency, and controlling emissions.

This report focuses on analyzing ignition delay as a factor of equivalence ratio, temperature and pressure and comparing it to experimental data so see the accuracy of the model.

2. Theory and Method

IDT is experimentally determined using two primary experimental facilities, each designed for different temperature regimes. Rapid Compression Machines (RCM) are employed for low-temperature studies (typically 600-1000K), where the fuel-air mixture is compressed adiabatically to achieve the desired thermodynamic conditions. The compression process heats the mixture to ignition temperatures while maintaining controlled temperature histories. Shock Tubes are utilized for high-temperature investigations (1000-2500K and above), where reflected shock waves instantaneously heat the test mixture to the target conditions. The shock tube provides precise control over initial temperature and pressure while eliminating gradual heating effects that could influence the ignition process.

IDT determination uses a zero-dimensional (0D) reactor model, which assumes the system has a uniform thermodynamic state everywhere. This means there are no spatial differences or transport effects, so the complex equations are simplified to ordinary differential equations. As temperature, species concentration and pressure/volume (depending on reactor model) changes due to chemical reactions taking place during the ignition, changes in time can be observed and collected for future analysis.

Figure 1 illustrates the pressure and species changes that take place during a shock tube experiment. The incident shock is when the pressure rise in the driver gets high enough to break the diaphragm. When the incident shock reaches the end

of the tube and gets reflected, this results in a pressure increase called the reflected shock. The reflected shock provides the energy required to start the chemical reaction and ignition. Initially, this compression creates a relatively stable environment where slow induction chemistry dominates, with chain-branching reactions gradually building up radical while competing with termination processes until the ignition points which results in a rapid pressure rise. Thus when calculating IDT, when the reflected shock reaches its maximum pressure is often used as the time point zero for IDT calculations.

There are several definitions for IDT and methods to calculate the point of ignition. They are based on the different parameters observed in the shock tube. It can be calculated between the reflected shock and when the pressure rises from chemical reactions (bottom of ignition in figure 1), or from temperature jumps due to exothermic reactions. It can also be calculated from the peaks of selected radical species, such as OH, CH, OH*, and CH* seen in figure 1, or by tracking rapid fuel consumption. Additional methods include direct visualization using high-speed cameras to detect chemiluminescence ($\lambda_{OH^*} = 308$ nm and $\lambda_{CH^*} = 430$ nm) and flame appearance. Cantera uses the species concentration method and defines the IDT at specified ground-state species peak concentration.

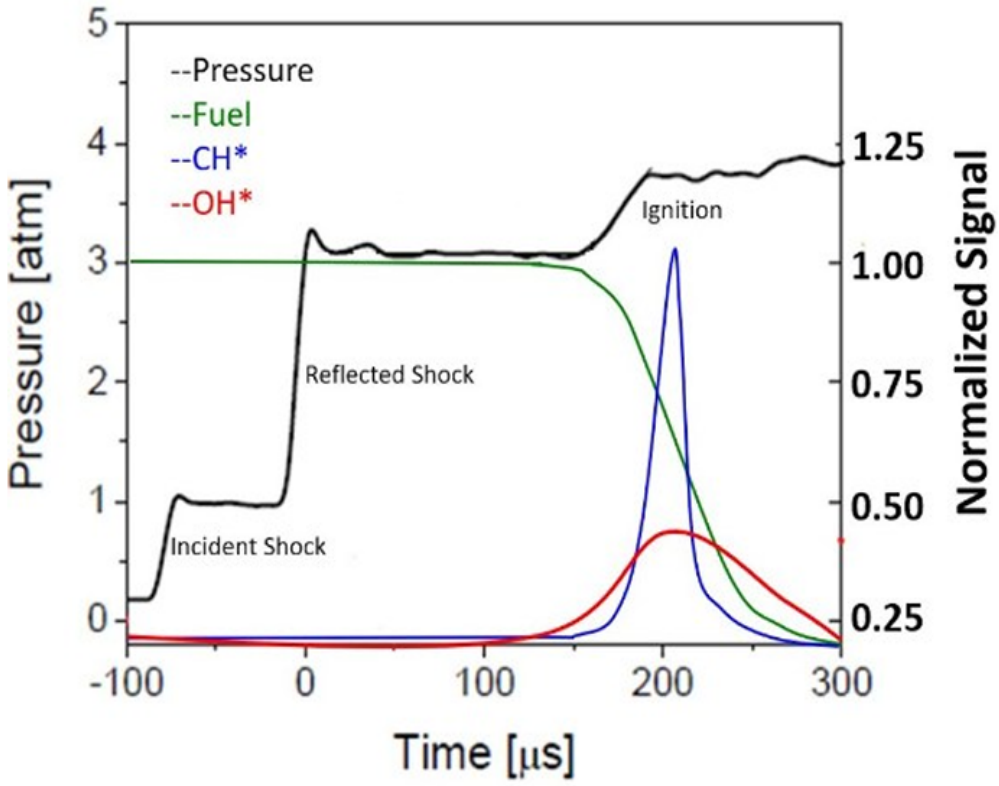

Figure 1: Pressure and species concentration changes over time for a shock tube experiment. The black line represents the pressure changes inside the shock tube. Split into different shock sections that occur during the experiment. Green, blue and red represent different species normalized concentration signals (between 0-1).

3. Results

Three cases for ignition delay time were calculated and compared to experimental results. All cases calculated the IDT in the temperature range of 800-2000K with different equivalence values of 0.5 for case one, 1.0 for case two and 2.0 for case three. The initial pressure varied between 1, 3, 5, 10, 25 and 44 atm, see figures 2 to 4. Table 1 presents the ignition delay time for all three cases at the point where the temperature fulfills the condition of 1000/T = 0.55.

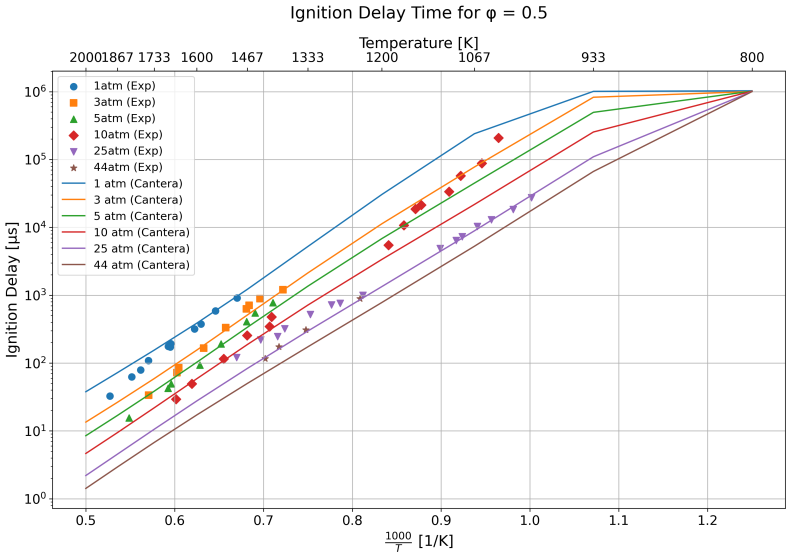

Figure 2: Cantera calculations for Ignition delay time compared with experimental data with equivalence ratio of 0.5 against the inverse logarithm of temperature. Lines represent canteras calculated values and markers represent experimental data.

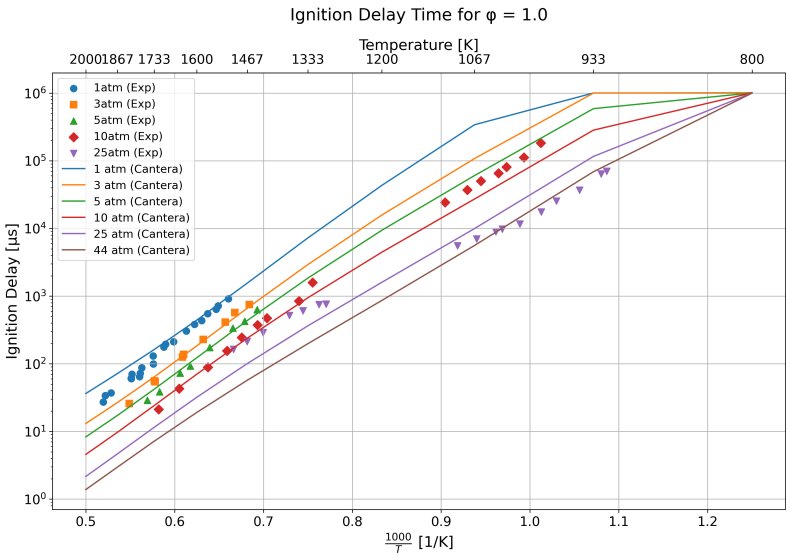

Figure 3: Cantera calculations for Ignition delay time compared with experimental data with equivalence ratio of 1.0 against the inverse logarithm of temperature. Lines represent canteras calculated values and markers represent experimental data.

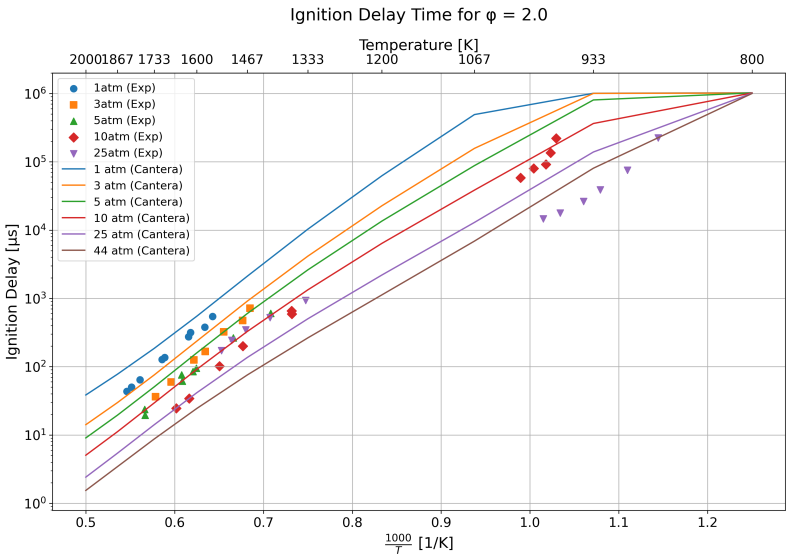

Figure 4: Cantera calculations for Ignition delay time compared with experimental data with equivalence ratio of 2.0 against the inverse logarithm of temperature. Lines represent canteras calculated values and markers represent experimental data.

Table 1: Ignition delay time [μs] at 1000/T = 0.55 at varying pressures and equivalence ratios

φ	1 atm	3 atm	5 atm	10 atm
0.5	118.46 [μs]	44.40 [μs]	28.75 [μs]	16.28 [μs]
1.0	121.51 [μs]	46.82 [μs]	30.66 [μs]	17.51 [μs]
2.0	135.54 [μs]	54.16 [μs]	36.00 [μs]	20.88 [μs]

4. Discussion and Conclusion

First to note is the plateau seen when the IDT reaches 1s. This is an numerical error from the script generating the plots as the estimated IDT value is set to 1s and works as a hard upper limit in the calculations. As our experimental data doesn't go over this value, this error can for the present be ignored but would need to be fixed for calculations and simulations of lower temperature environments.

From the results we can observe three different effects caused by the changes of equivalence ratio, pressure and temperature.

4.1 Effect of Temperature on IDT

We see that for all equivalence ratios and pressures, an increase in temperature results in a decrease in IDT. This behaviour follows Arrhenius kinetics as higher temperatures both result in more energy in the system, allowing for more chain-branching reactions to pass the activation energy barrier as well as a higher temperature results in faster reaction rates.

4.2 Effect of Pressure on IDT

Pressure difference shows a consistent pattern across all equivalence ratios, with higher pressures leading to shorter IDT. This is most likely due to a higher pressure resulting in an increased molecular density. At elevated pressures, molecules are compressed into a smaller volume resulting in an increase in collision frequency which increases the overall reaction rates.

4.3 Effect of Equivalence Ratio (φ) on IDT

Equivalence ratio effects show distinct patterns with $\varphi = 0.5$ producing the shortest IDT values, followed by $\varphi = 1.0$, and $\varphi = 2.0$ showing the longest delays, see table 1 for reference. This occurs because lean conditions provide abundant oxygen for efficient chain-branching reactions, with the excess oxidizer effect overcoming fuel dilution and pushing the equilibrium towards the radicals. Rich mixtures suffer from oxygen limitation, forcing slower alternative reaction pathways that require higher thermal energy to achieve ignition.

We also observe a slope variation, with rich mixtures exhibit the steepest slope, then stoichiometric mixture and lean mixture the most gentle slope. This shows that rich mixtures are more temperature sensitive, with a small change in temperature resulting in a larger difference of IDT. This occurs because different mixture compositions promote distinct reaction pathways with varying activation energy requirements, effectively changing the overall energy barrier as a weighted combination of all active pathways.

4.4 Cantera vs Experimental Data

The comparison between Cantera simulations and experimental data demonstrates good fitting and accuracy for lean and stoichiometric conditions ($\varphi = 0.5$ and 1.0) for high temperturs (T>1400K) and pressures below 10 atm. However, some deviation is observed for rich conditions ($\varphi = 2.0$) and pressure 25 respectively 44 atm. These deviations may occur for various reasons. One might be that the method of calculating IDT is varying. The IDT values may vary up to 10% depending on the definition and method for calculating the IDT values. However, this is an unlikely cause due to the fitting of the lean and stoichiometric conditions.

Another possibility is that the GRI-3.0 mechanism has limitations under rich and high pressure combustion conditions. While GRI is designed for $\varphi = 0.1 - 5$, most experimental data is around $\varphi = 1$, so it misses important information/parameters for higher ratios, leading to incorrect radical formation and difference between Cantera and experimental

data. GRI-3.0 is also desgined for temperture intervals between 1000-2500K and pressure ranges between 10 Torr (0.013158 atm) to 10 atm. This would explain why our Cantera calculations and experimental data dosen't match for pressues above 10 atm, which we can see in figures 2 to 4 where 25 atm and 44 atm is inconsistent with experimental data.

The unique behavior of experimental data for 10 atm at $\varphi = 0.5$ for lower temperatures in figure 2 stands out from the the rest IDT-values. As these conditions are within the pressure range and temperature range of GRI-3.0 and the model would need to cross over the IDT-values of lower pressures to fit the data. The likely cause for this inconsistency is experimental errors during experimental data collection.