Effects of mixture composition, dilution level and pressure on auto-ignition delay times of propane mixtures

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HIGHLIGHTS

- The ignition process of propane mixtures is investigated at intermediate temperatures.
- The activation energy of the ignition process changes from intermediate to high temperatures.
- Such behavior strongly depends on the mixture dilution levels, stoichiometry and system pressure.
- The kinetics of the ignition process is numerically exploited.
- The competition between oxidative and recombination/pyrolytic routes promotes this behavior.

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ABSTRACT

The auto-ignition process of propane/oxygen mixtures has been widely studied in several facilities. Literature on shock tubes and tubular flow reactors has shown a change in the activation energy of the ignition process in the transition region from intermediate to high-temperature chemistry. Although fuel ignition chemistry has been widely exploited at low and high temperatures, further studies are required at intermediate temperatures. Based on previously published experimental results, this paper aimed to investigate the kinetics responsible for such a phenomenology, through a detailed kinetic analysis of the main pathways involved in the ignition process of propane mixtures. Simulations were performed over a wide range of temperatures (from low to high), changing the dilution levels of the mixture from "air" conditions to 97%, the pressure from 0.1 up to 3 MPa, and the mixture compositions from lean in fuel to rich in fuel. The analysis suggests that the phenomenology strongly depends on the mixture dilution levels and pressure. In particular, the differences in the ignition chemistry between low to intermediate temperatures and between intermediate to high temperatures is more evident for systems that are highly diluted and at low pressure. Such results are supported by data from the literature.

This aspect explains why such a behavior is not reported for any experimental configurations and partially justifies the differences among the data obtained in several facilities, which is commonly addressed by the non-idealities of systems.

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1. Introduction

Understanding the characteristic auto-ignition times and their relationship with operating conditions is vital for the successful design and dimensioning of combustion systems. This is particularly true for MILD combustion processes [1], in which highly diluted mixtures with inlet temperatures higher than that of fuel auto-ignition are used, thus giving rise to a combustion mode that is drastically different from that of traditional diffusive/deflagrative flames. In these applications, large mixture dilution levels are used to maintain working temperatures below critical values for the formation of pollutants species while high inlet temperatures are used to promote and sustain the oxidation process that occurs in homogeneous and nearly isothermal conditions [1–4]. In these conditions, the combustion regime is primarily controlled by a distributed auto-ignition process, which represents a key parameter in determining combustion behaviors [3–8]. However, high initial temperatures (above the auto-ignition value) and diluted conditions have significant effects on the chemical kinetics, affecting the auto-ignition chemistry [9–13]. Fuel nature, mixture

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composition, temperature and pressure represent the main controlling parameters of the ongoing chemical reactions in a combustion process. Many detailed studies have described the complex relationships of these parameters and their respective roles in determining combustion behavior. However, reports on these parameters under MILD conditions are scarce, and many chemical kinetics effects that are specific to these conditions must be further clarified. This information is essential for developing predictive, effective and robust numerical models for practical device design.

Combined experimental and modeling efforts are required to elucidate the auto-ignition dependence on the operating parameters and to develop robust and predictable chemical kinetics models of MILD combustion processes. Many experimental and model aspects must be fixed to ensure the meaningfulness of obtained results.

For instance, on the experimental side, the ignition process of hydrocarbons has been extensively studied over a wide range of operating conditions (pressure, temperature and mixture composition) and in many experimental facilities. Shock tubes [14–20], flow reactors [10,21–30] and rapid compression machines (RCM) [31,32] are commonly used to evaluate the ignition process. Although each of these methodologies has its merits, their utility is restricted to well-defined ranges of pressure, temperature and ignition times. Therefore, several experimental approaches have to be pursued in parallel.

By combining data from different sources, the auto-ignition process of fuel/oxygen mixtures over a wide range of temperatures and pressures can be investigated. However, comparisons among data obtained through different experimental configurations or empirical/numerical methods must be made carefully.

Interesting and even unexpected behaviors can emerge when the ignition process is experimentally studied under non-conventional conditions. Sabia et al. [10] numerically investigated methane oxidation under MILD conditions. They identified a phenomenology resembling "NTC" behavior of methane under MILD conditions at intermediate temperatures, and they identified the kinetics responsible for the behavior [9]. This phenomenology was previously experimentally identified by Huang et al. [20] in shock tubes for lean to rich methane/air mixtures but under different reference conditions, namely at high pressures (1.6–4.0 MPa) and at intermediate temperatures.

Similarly, we previously [29] studied the propane auto-ignition process in a tubular flow reactor for highly diluted mixtures that were pre-heated to a wide range of temperatures. For mixtures characterized by fuel/oxygen ratios close to the stoichiometric conditions and diluted in N_2 at 90%, at intermediate temperatures auto-ignition, delay times were almost independent of the inlet temperature. For high temperatures (T_{in} > 1100 K), the delay times linearly changed with the inlet temperature according to the Arrhenius plot.

Previous reports of ignition delays from TFRs that obtained data for stoichiometric propane/air mixtures at several pressures have indicated a linear dependency on ignition delay temperature. Other recent studies [14–19] on propane auto-ignition in shock tubes have reported a sudden change in the activation energy when temperatures shift from intermediate to high at elevated pressures.

In particular, Cadman et al. [14] measured propane ignition delay times at elevated pressures (0.5–4 MPa) for temperatures in the range of 850–1100 K for fuel-lean and stoichiometric mixtures in a shock tube. They compared the acquired ignition delay times with previous high temperature data provided by Burcart et al. [15,16], identifying a decrease in the ignition process activation energy in the range of 850 K < T < 1100 K. A sensitivity analysis demonstrated the importance of hydroperoxyl, propyl and methyl radicals at these intermediates temperatures. Similar

considerations were made by Herzler et al. [17]. They measured the ignition delay times of lean propane–air mixtures in the temperature range of 740–1300 K at pressures of 1 and 3 MPa in a shock tube facility. The experiments confirmed that the activation energy of the ignition delay time decreases at approximately 1050 K.

Zhukov et al. [18] measured the ignition delay times behind reflected shock waves for lean propane–air mixtures in the temperature range of 800–1500 K and in the pressure range of 0.2–50 MPa. They identified two different activation energies for the auto-ignition process that could be expressed as Arrhenius-dependent, at intermediate and high temperature ranges. They also updated a detailed kinetic mechanism based on their experimental data. Penyazkov et al. [19] measured the ignition delay times for lean, stoichiometric, and rich propane–air mixtures within the temperature range of 1000–1800 K at a pressure range of 0.2–2.0 MPa. They identified two different slopes for temperatures lower and higher than 1300 K.

Healy et al. [31] performed several experiments in an RCM facility of mixtures composed of different proportions of methane/propane and methane/ethane/propane and investigated the effect of pressure on the ignition delay time. They compared their results with shock tube data obtained at high temperatures, observing a marked change in "activation energy" as a function of temperature in the transition region from intermediate- to high-temperature chemistry.

In summary, propane reactivity is sensitive to changes from intermediate to high temperatures. This property is of interest regarding the ignition chemistry of hydrocarbons because propane exhibits thermo-chemical and combustion properties of larger hydrocarbon fuels more closely than either methane or ethane. Furthermore, propane oxidation is a sub-scheme of larger hydrocarbons, and thus understanding the ignition chemistry of such a reference fuel can provide useful information for a larger class of fuels.

According to the previous considerations, the present work aimed to better define the oxidation chemistry of propane auto-ignition delay times by utilizing an extensive simulation of the chemical kinetics and comparing the numerical results with experimental data reported in the literature for several facilities and over a large range of operating conditions. The study focuses on the effects of the fuel/oxygen ratio, mixture dilution level and pressure at low, intermediate and high (750–1400 K) inlet temperature ranges. The objective is to identify possible chemical pathways responsible for the different auto-ignition trends observed across the various temperature ranges.

2. Critical analyses of test facilities

Prior to analyzing the effects of mixture composition, dilution and pressure on the ignition data, a critical review on the reliability of ignition data is mandatory because non-idealities and perturbations may alter the data quality obtained from the reference facilities (shock tubes, tubular flow reactors and RCMs).

A shock tube uses the compressive heating of a shock wave to rapidly increase the temperature and pressure of a premixed combustible mixture. Shock tubes are used to study the ignition process within short periods of times (on the order of tens of microseconds). Problems related to shock tubes have been widely discussed in the literature [32–35]. Recently, Davidson and Hanson [34] provided a clear and exhaustive analysis of shock tube performances. They identified the formation of a viscous boundary layer behind incident and reflected shock waves as a perturbing effect. This non-ideality causes a temperature and pressure increase in the core of the flow and attenuation of an incident shock wave,