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An experimental and kinetic study of alkane autoignition at high pressures and intermediate temperatures

David J. Beerer, Vincent G. McDonell *

UCI Combustion Laboratory, Department of Mechanical and Aerospace Engineering, University of California Irvine, CA 92697-3550, USA

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Abstract

Autoignition delay times of individual alkanes and mixtures of alkanes were measured experimentally in a high pressure, intermediate temperature, turbulent flow reactor. The mixtures are intended to simulate various natural gas compositions from around the world. Testing was conducted from 7 to 15 atm and from 785 to 935 K which mimic the inlet conditions to the premixing zone in many modern lean premixed gas turbine engines. It is also in the kinetics region where reactions involving RO_2 and H_2O_2 control the ignition process. The results are compared to higher temperature autoignition data from the literature which reveals several interesting differences between the two regimes. Finally, the data are compared to simulations using comprehensive chemical kinetics mechanisms to elucidate the dominant reactions at these conditions.

Keywords: Autoignition; Ignition delay; Natural gas; High pressure; Flow reactor

1. Introduction

Autoignition is a spontaneous process whereby a mixture of fuel and air undergoes a chemical reaction leading to ignition and combustion without the aid of an external source such as a flame or spark. A common term associated with autoignition is the ignition delay time. This is the period of time between creation of the combustible mixture (e.g. injection of fuel into an airstream) and ignition. Ignition delay measurements are valuable for gas turbine engine design as well as for chemical kinetics research. Many modern gas turbine engines utilize a lean premixed combustion strategy where a premixing chamber upstream of the combustor mixes the fuel and air prior to combustion. Design engineers must ensure that the time spent by the fuel and air in the premixer is less than the ignition delay time in order to prevent autoignition. Typical inlet conditions to the premixer are between 5 and 30 atm and temperatures from 600 to 1000 K [1]. For kinetics research, the ignition delay time represents one type of experimental data which is useful in validating chemical kinetics mechanisms. In both applications, accurate knowledge of ignition delay as a function of pressure, temperature, equivalence ratio and fuel composition is required. Therefore, the goal of the present study is to quantify experimentally the ignition

* Corresponding author. Fax: +1 949 824 7423.
E-mail address: mcdonell@uicl.uci.edu (V.G. McDonell).

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delay times of several fuels at these elevated pressure and temperature conditions. The fuels of interest in this paper are alkane blends which represent various natural gas compositions from around the world, especially those with larger fractions of ethane and propane [2].

2. Background

The most common experimental devices for ignition delay measurements are shock tubes, rapid compression machines (RCMs) and flow reactors. Shock tubes work well at high temperatures ($T > 1200$ K) because of their ability to rapidly bring their mixture to test conditions. But they are limited to test times on the order of a few milliseconds, so are not capable of testing at lower temperatures [3]. RCMs have been widely used in the low to intermediate temperature region ($1100\ \text{K} > T > 700\ \text{K}$) and have garnered valuable ignition delay data [4]. One difficulty with RCMs is the inevitable heat loss to the walls which limits test times to typically around a 100 ms. Flow reactors mimic the flow conditions inside gas turbine premixers so their data has been used for both gas turbine design [5] as well as chemical kinetics research [6]. In order to obtain useful kinetics data from flow reactor experiments, many of the secondary effects such as mixing time, heat loss and diffusion of species must be rendered negligible in order to model the experiment as a plug flow. Heater and facility capabilities limit experiments to temperatures of around 1000 K and pressures from 1 to 30 atm.

One of the first comprehensive studies relevant to natural gas autoignition was that of Burcat et al. [7] who measured ignition delay times of alkanes C_1 through C_5 in a shock tube at temperatures between 1200 and 1900 K. Burcat et al.'s [7] measurements found methane to have the longest ignition delay of any alkane. Propane, butane and pentane all had similar ignition delays times which were between 5 and 10 times shorter than methane depending on the temperature. Somewhat peculiarly, ethane's ignition delay was shortest, being roughly half that of the heavier alkanes at these conditions, the reason for which will be discussed later. The measured overall activation energies of ethane through pentane ranged from 155 to 167 kJ/mol, while methane's activation energy was 209 kJ/mol. Crossley et al. [8] continued this work with shock tube measurements of mixtures of methane with fractions of alkanes, ethane through pentane, in quantities of up to 20%. Eubank et al. [9] along with Spadaccini and Colket [10] also independently studied methane/higher alkane mixtures in shock tubes. The temperatures for all these experiments ranged from 1200 to 1800 K with pressures between 1 and 5 atm. Ignition delay times ranged from 15 μs to 2 ms. Westbrook and Pitz [11,12] have developed several comprehensive chemical mechanism for high temperature natural gas ignition. Simulations with their mechanisms can reproduce the experimental data of Burcat et al. [7] and have identified many of the controlling chemical reactions and species leading to ignition at high temperatures.

Recently, the research groups of Petersen and Curran [4,13] together have measured ignition delay times of alkane mixtures in shock tubes and RCMs for both high and intermediate temperatures. Conditions in the RCM ranged from 10 to 40 atm and from 700 to 1000 K with measured delay times between 5 and 300 ms. Shock tube testing have been conducted between 1 and 40 atm and temperatures from 1100 to 1600 K with measured delay times between 20 μs and 2 ms. They have also developed several comprehensive kinetics mechanisms that can accurately reproduce their experimental findings at both high and intermediate temperatures.

Ignition delay times have also been measured quite extensively with flow reactors in past decades. Lezberg [14] measured delay times of propane at atmospheric pressure between 1030 and 1135 K, while Lefebvre et al. [15,16] measured delay times of methane and propane at pressures between 1 and 10 atm and temperatures from 800 to 1100 K. Ignition delay measurements of binary and ternary mixtures of alkanes have been studied recently at atmospheric pressure by Holton et al. [17] at temperatures between 930 and 1100 K. Measured delay times in these studies ranged from 20 to 200 ms.

The primary goal of the current study is to quantify the effects of adding higher alkanes to methane at intermediate temperatures and pressures up to 15 atm. This is accomplished in a high pressure, turbulent flow reactor with residence times of up to 700 ms which allows for ignition delay measurements at conditions outside the capabilities of other comparable flow reactor, RCM, or shock tube experiments.

3. Experiment

The flow reactor used in the present study is designed to measure ignition delay times of gaseous fuels inside a turbulent air flow at pressures and temperatures up to 15 atm and 950 K, respectively. A more detailed description of the flow reactor can be found elsewhere [18,19] however a short summary is presented here.

The flow reactor test section consists of a stainless steel cylindrical duct with an inner diameter of 38 mm and a length of 3.90 m. Fuel is injected by way of eight radially inward pointing jets (0.8 mm diameter) in the converging section of a venturi at the beginning of the test section and mixed with the oncoming air. The fuel/air mixture flows down