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Predicting ignition delay times of C1-C3 alkanes/hydrogen blends at gas engine conditions

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ABSTRACT

A comprehensive ignition delay time database of 3.1 million points using detailed chemistry is generated. The database includes ignition delay times for pure methane, ethane, propane and hydrogen, as well as for gas blends comprising of the mentioned gases. The database covers a broad range of gas engine applications; pressure 1–20 MPa, temperature 900–2500 K, air–fuel equivalence ratio (λ) 0.9–2.5 and exhaust gas recirculation (EGR) 0–30 m%. For gas blends up to 60 vol% to methane, it is observed that different gas blends with the same HC-ratios/methane-numbers, show similar ignition delay times. Ignition delay time correlations for pure CH_4, C_2H_6, C_3H_8, H_2 and the gas blends are suggested with mean deviation being as low as about 7%. A new blending methodology is developed to describe the C1-C3 alkanes/H_2 blends at elevated pressure and temperature conditions. Correlations describing the effect of EGR on the ignition delay time are further developed.

1. Introduction

Natural gas engines provide an attractive alternative to the existing technologies both in the transport and power generation sector. Natural gas allows CO_2 emission reduction in the range of 20% compared to conventional fuels like gasoline and diesel due to the lower C/H ratio of the fuel. Also gas engines operate without soot and for lean operation conditions with relatively low NO_x emissions. Natural gas can be supplied from large fossil reserves, from biomass and in the future also from “methanisation” of hydrogen generated from renewable electricity. The main constituent of natural gas is methane, with small amounts of heavier hydrocarbons, which are mainly C2-C3 alkanes. This fraction can significantly vary depending on the source of natural gas up to 18 vol% [1]. The influence of these compounds has a significant effect on the reactivity of natural gas [2]. Further, processes such as gasification of coal or biomass can produce fuels with high hydrogen content and other components up to 38 vol% that are more reactive than methane [3]. Apart from the availability of natural gas surrogate mixtures with other compounds, blending of natural gas with reactive gases such as ethane or hydrogen is an attractive option to the gas turbine and engine industry. These additions of higher hydrocarbons or hydrogen can greatly accelerate the ignition process of the methane based fuel due to changes in the combustion chemistry [4]. Gas blending can have a dramatic impact on the design of the combustion system. Hence, it is of primary importance to consider these effects for the design and operating conditions of the engine.

Ignition delay is a fundamental parameter often used for developing chemical reaction mechanisms. The ignition delay includes the time lag due to the mixing of fuel and oxidizer known as the physical ignition delay time and then the time required for the beginning of the chemical reactions governed by chain-branching mechanisms, this is known as the chemical ignition delay time. In the case of premixed combustion, the ignition delay time is equal to the chemical ignition delay time. In this work, the chemical ignition delay time will be referred simply as ignition delay. Ignition delay is dependent on the fuel composition, mixture stoichiometry, temperature, pressure and exhaust gas recirculation. The term “autoignition” refers to a problem specific to engines employing premixed combustion, where the mixture ignites prior to the flame front causing an abrupt rise in in-cylinder pressure often leading to engine damage. This phenomenon is referred to as “knocking”. The definition of ignition delay depends on the criteria defined, as shown in Fig. 1. The criteria could be, the maximum temperature gradient, maximum concentration (OH, CH) or maximum total heat release rate. The ignition delay provided by most criteria are almost identical [5].

Shock tubes and rapid compression machines are the widely used experimental facilities to measure ignition delays [3,6,7]. High pressure shock tube methane ignition delay measurement data is available in literature [4,7,8]. Cheng and Oppenheim [9] measured ignition delay of CH_4/H_2 mixtures with H_2 varying from 0–100 vol%. Zhang et al. [10] and Donohoe et al. [6] measured ignition delay times of CH_4/H_2 blends at elevated pressures. Petersen et al. [4] performed shock tube

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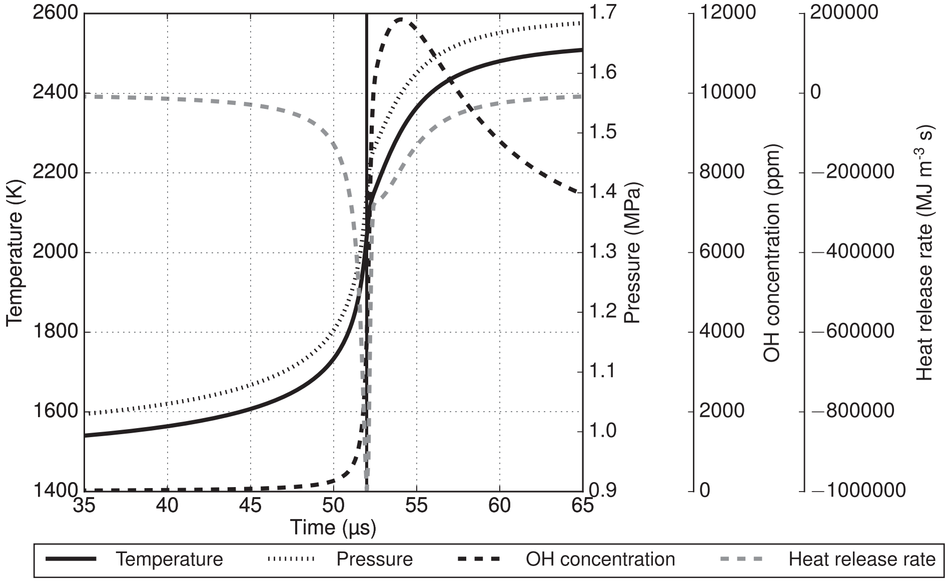

Fig. 1. Ignition delay time profile of CH_4/air mixture.

experiments to measure the ignition delay times of CH_4/C_2H_6, CH_4/C_3H_8, CH_4/H_2 in ratios ranging up to 60/40% at elevated pressures up to 30 atm. The igniton delay decreased with increasing levels of hydrogen and C2-C3 alkanes. This acceleration of the methane ignition process with addition of fuel species is due to the rapid supply of extra radicals to the preignition radical pool. Healy et al. [3] conducted rapid compression machine (RCM) and shock tube experiments for natural gas surrogates at elevated pressure conditions. They observed a "turnover" in the reactivity at about 1250 K for the investigated gas blends, i.e., at temperatures below turnover, fuel-rich mixtures are fastest and fuel-lean slowest to ignite. But at temperatures above 1250 K, the effect is opposite. This difference is due to different chemical kinetic behavior at various temperature regimes. It is concluded that the fuel lean mixtures are most reactive at high temperatures.

2. Influence of HC Ratio

Warnatz [11] suggested the reactions $\dot{H} + O_2 = \dot{O} + \dot{O}H$ and $CO + \dot{O}\,H = CO_2 + \dot{H}$, as the most fundamental reactions for the combustion of any hydrocarbon fuel up to 16 carbon atoms. The other major sensible reaction being $\dot{H} + O_2\,(+M) = H\dot{O}_2\,(+M)$. Kochar et al. [12] conducted sensitivity analysis for their experiments for pure methane, ethane, propane and the blends CH_4/C_2H_6: 60/40 vol% and CH_4/C_3H_8: 60/40 vol% at 298 K and 5 atm. It is seen that the first chain branching reaction is the most important at high temperatures. It shows the highest sensitivity for the case of pure methane and the sensitivity decreases when one moves towards ethane/propane. The sensitivity analysis showed that no reactions involving the parent molecules C_2H_6 or C_3H_8 were present. The abstraction and recombination reactions, $CH_4 + \dot{H} = \dot{C}H_3 + H_2$ and $CH_3 + \dot{H}\,(+M) = CH_4\,(+M)$, being significant reactions involving parent CH_4 molecule for all blends. Metcalfe et al. [13] suggested the importance of C3 and C4 chemistry to describe the kinetics of CH_4 and C_2H_6, with the recombination reactions, $\dot{C}H_3 + \dot{C}_2H_5 = C_3H_8$ and $\dot{C}_2H_5 + \dot{C}_2H_5 = nC_4H_{10}$. These reactions are however, significant for fuel rich conditions. It can be concluded from the literature, that for the lean gas engine conditions, that the chemistry of small species is fundamental for the description of combustion for larger hydrocarbons.

The availability of these radicals can be described in terms of the ratio of C and H atoms in the mixture pool. The HC-ratio or HC is defined as the ratio of the total number of hydrogen atoms to the total number of carbon atoms per mole of a hydrocarbon gas mixture.

$$HC = \frac{4\cdot X_{CH_4} + 6\cdot X_{C_2H_6} + 8\cdot X_{C_3H_8}}{1\cdot X_{CH_4} + 2\cdot X_{C_2H_6} + 3\cdot X_{C_3H_8}} \tag{1}$$

For a given hydrocarbon gas mixture, $X_{CH_4} + X_{C_2H_6} + X_{C_3H_8} = 1$, where $X_{C_xH_y}$ denotes the mole fraction of the respective hydrocarbon.

The methane-number (MN) describes the gas qualities in terms of the knocking in engines [14] and the correlation for the methane-number is defined as a function of HC-ratio in [15,16]. The knocking ability is a function of the ignition delay for a given mixture [14].

In Fig. 2, the ignition delay of different gas mixtures for $HC \approx 3.9231$ or $MN \approx 98.1003$ at stoichiometric conditions are plotted for varying temperatures at 1 MPa, it is seen that the ignition delay of all the three different gas compositions are almost identical throughout. A similar behavior can be seen for another mixture with $HC \approx 3.7391$ or

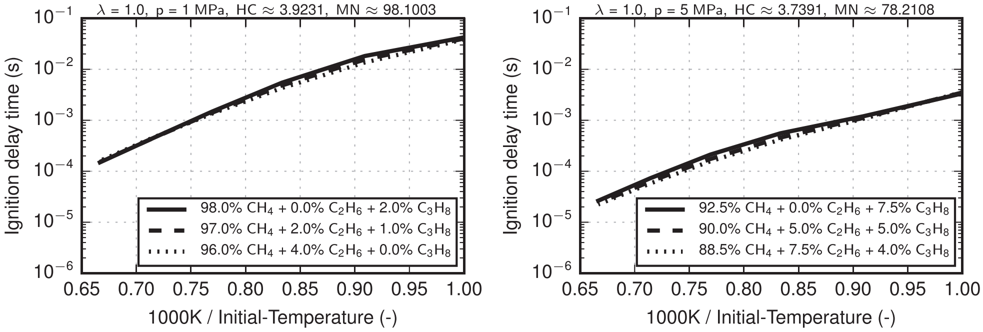

Fig. 2. Ignition delay time of different gas blends at a constant HC-ratio.