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Combustion chemistry of iso-octane/ethanol blends: Effects on ignition and reaction pathways

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ABSTRACT

This work presents new experimental data on the ignition of iso-octane and ethanol fuel blends, including measurements of pollutant species and precursors, using the University of Michigan Rapid Compression Facility (UM RCF). Ignition delay times were determined from pressure–time histories of ignition experiments for stoichiometric mixtures of iso-octane, ethanol, and 5, 11, 26, 50 and 67% by volume iso-octane and ethanol blends with air. A range of temperatures (900–1080 K) were studied at a pressure of 10 atm. Speciation experiments were performed for pure iso-octane (E0), pure ethanol (E100) and a 50% by volume blend of the two fuels (E50) at 10 atm and ~930 K. Fast-gas sampling, gas chromatography and mass spectrometry were used to identify and quantify 14 stable intermediate species formed during the ignition delay periods for the three fuels. The measurements of eight stable intermediates: iso-butene (i-C_4H_8, 2-methyl-1-propene), propene (C_3H_6), ethanal (CH_3CHO), ethene (C_2H_4), ethane (C_2H_6), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2) were considered in detail and were used to describe reaction pathways important during iso-octane and ethanol ignition and how they were altered for iso-octane/ethanol blends. Simulations were carried out using a detailed reaction mechanism for gasoline surrogates available in the literature and the agreement with the ignition and speciation experiments was generally excellent (within the experimental uncertainty and expected computational uncertainty) for ignition delay times and for the species time-histories, with a few small discrepancies. The results indicate the reaction pathways of iso-octane and ethanol in the blend develop in parallel with a shared radical pool with no significant fuel-to-fuel interactions.

1. Introduction

Ethanol remains the leading biofuel in the transportation sector, where it is primarily used as an anti-knock additive in reformulated gasoline in the U.S. and as the main transportation fuel in Brazil [1]. In the U.S., the increase in ethanol consumption has been driven by biofuel policies such as the Renewable Fuel Standard [2] and the California's Low Carbon Fuel Standard [3]. Although commercially limited by the so-called "blend wall" and currently blended in the U.S. at 10% ethanol with gasoline, blends of gasoline and ethanol with higher amounts of ethanol (e.g. 20–85% by volume) show promising results regarding efficiency and tailpipe CO_2 emissions when used in turbocharged engines with high compression ratios [4]. Gasoline/ethanol blends with higher amounts of ethanol can also significantly reduce the formation of soot particulates and NO_X exhaust emissions in direct injection spark ignition engines [5,6]. Understanding the combustion chemistry of ethanol blends can help the successful integration of ethanol into the transportation fueling infrastructure. Based on this motivation, the current work is a comparative study of the low temperature chemical kinetics of ethanol and iso-octane fuel blends.

Iso-octane is an important primary reference fuel and is often used as a simple chemical surrogate for gasoline. Numerous experimental studies of the low temperature (600–1300 K) ignition chemistry of iso-octane can be found in the literature, in particular where shock tubes and rapid compression machines (RCMs) were used to create the desired state conditions. Examples of studies at the pressure relevant to the current work are briefly summarized here. Shen et al. [7] used a shock tube to measure ignition delay times of stoichiometric iso-octane/air mixtures at 10 atm and 950–1250 K, and compared the results with shock-tube data by Fieweger et al. [8] and Davidson et al. [9] at similar conditions. In those studies, no negative temperature coefficient (NTC) behavior was observed for temperatures above 910 K, and good agreement was achieved between the different experimental data sets and be-

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tween the experimental data and modeling results based on the iso-octane kinetic mechanism by Curran et al. [10]. Ignition of iso-octane/air mixtures at $\phi = 1$ and P = 10 atm have also been studied in RCMs by Minetti et al. [11] at T = 660–890 K, and Griffiths et al. [12] at 900–950 K. The RCM data suggested the onset of NTC behavior for iso-octane was between 800 and 850 K for P = 10 atm, which corresponded well with simulation results based on the Mehl et al. [13] reaction mechanism for gasoline surrogates and gasoline fuel mixtures (which includes the Curran et al. [10] sub-mechanism). Iso-octane ignition has been extensively studied using the University of Michigan rapid compression facility (UM RCF) through ignition delay time [14], OH time history [15] and intermediate species [16] measurements, and by characterizing the weak and strong ignition behavior using high-speed imaging [17,18] for a range of conditions ($\phi = 0.2$–2.0, P = 5–23 atm, T = 810–1100 K). Low temperature shock tube, RCM, RCF, and other important experimental and computational chemistry studies have led to quantitative predictive understanding of iso-octane combustion chemistry over a broad range of pressures, temperatures and mixture compositions. Such accurate understanding of iso-octane ignition is invaluable for quantifying the effects of iso-octane as a binary blend component.

Ethanol chemistry has also been extensively studied as presented by Sarathy et al. [19] in their comprehensive summary of the combustion literature on ethanol and other alcohols. Like iso-octane, previous work includes experimental studies in a wide variety of facilities and kinetic modeling and elementary reaction rate studies. Numerous ignition delay measurements at low to moderately high temperatures (T = 650–1900 K) are available in the literature for ethanol from shock tubes and RCMs at a range of equivalence ratios ($\phi = 0.25$–2.0) and for a large range of pressures (P = 0.2–92 atm) [19]. In a recent UM RCF study by Barraza-Botet et al. [20], ignition delay times were measured for stoichiometric ($\phi = 1.0$) ethanol mixtures at 3–10 atm and 880–1150 K. In the same study, stable intermediate species were measured during ignition at 10 atm and ~930 K for $\phi = 1.0$. Comparing and correlating the UM RCF data together with previous ignition data on stoichiometric ethanol mixtures revealed good agreement between data sets and the experimental data were well reproduced using the reaction mechanism by Burke et al. [21]. As expected, no NTC behavior was observed from ethanol from the composite data which spanned 1–92 atm and 750–1700 K [20]. As for iso-octane, such an accurate understanding of the baseline behavior of neat ethanol (100% ethanol) fuel is critical to evaluating the chemical kinetics of a fuel blend.

To our knowledge, only two studies in the literature have reported ignition data of binary iso-octane/ethanol blends. Cancino et al. [22] measured ignition delay times in a shock tube for stoichiometric ethanol and blend of 25% by volume ethanol (E25) at 30 bar and 750–1200 K. They found the iso-octane reduced the reactivity of the ethanol for T > 1000, and proposed a kinetic model that agreed well with their experimental data. Song and Song [23] used an RCM to measure the ignition delay times of pure iso-octane (E0), E10 and E20 at 27 bar and 750–900 K, and demonstrated the opposite trend—where the ethanol addition suppressed iso-octane reactivity at low temperatures (T < 870 K), particularly in the NTC region. Additionally, shock-tube ignition data of stoichiometric multi-component surrogate mixtures blended with 40, 20 and 10% ethanol by Fikri et al. [24] and Cancino et al. [22,25] at 10–50 atm and 690–1220 K are available, although the effects of ethanol addition to a fixed surrogate mixture were not measured. Yahyaoui et al. [26] evaluated the changes in reactivity of a surrogate mixture of iso-octane, toluene and 1-hexene when adding ethanol up to 85% by volume at $\phi = 1$, P = 2 atm and T = 1200–2000 K, and concluded ethanol addition consistently increased the blend reactivity at the conditions studied. Up to date, no measurements of stable intermediate species produced during the ignition of ethanol/iso-octane blends currently exist in the literature. Such data provide direct insight into the dominate reaction pathways of ignition of ethanol/iso-octane blends and provide high fidelity validation of our current understanding of the reaction chemistry of these important fuel blends.

The aim of this work is to understand the effects of ethanol on the reaction pathways important during iso-octane ignition, and to specifically identify any synergies or other interactions between the two fuel compounds. The technical approach was to provide new experimental ignition and speciation data on stoichiometric iso-octane/ethanol blends using the UM RCF. The current work includes ignition data for E0, and E5, E11, E26, E50 and E67 blends (by liquid fuel volume) at moderate levels of dilution (inert gas/O_2 molar ratios of 8.74:1), temperatures ranging from 900 to 1080 K and a nominal pressure of 10 atm. Speciation data were obtained for E0 and E50 at the same conditions (10 atm, 930 K and inert gas/O_2 molar ratios of 7.5:1) of a prior 100% ethanol study conducted using the UM RCF [20]. High-speed imaging was used to record chemiluminescence during ignition, and fast-gas sampling coupled with gas chromatography and mass spectrometry were used to identify and quantify stable species during the ignition delay time. The experimental results were compared with simulation results which used the kinetic model for gasoline surrogates and mixtures developed by Mehl et al. [13] at Lawrence Livermore National Laboratory. Although various detailed kinetic models for fuel blends that include ethanol can be found in the literature, the Mehl et al. mechanism [13] is widely accepted and has been extensively validated for gasoline surrogates. The results are discussed in terms of the major reaction pathways and the changes in the reaction processes based on the blend of ethanol with iso-octane.

2. Experimental methods

Through measurements of ignition delay times (τ_{ign}) in RCMs, shock tubes, the UM RCF and using other experimental methods, the global reactivity of individual surrogate compounds and their blends have been determined for a wide range of thermodynamic states. The identification of important reaction pathways is also possible by measuring the concentrations of radical and stable intermediate species formed during ignition, which allows the development of combustion theory and validation and improvement of chemical kinetic models. A broad range of experimental conditions can be achieved using the UM RCF for a variety of fuels and multicomponent blends, including end-of-compression pressures and temperatures ranging from 0.5 to 30 atm and 500–1800 K, and test times from 5 to 50 ms [20]. In this study, ignition delay times, high-speed imaging and stable intermediate species measurements were applied to ethanol/iso-octane blends and compared with similar data for 100% ethanol and 100% iso-octane.

2.1. Ignition and high-speed imaging

The UM RCF consists of five major components: the driven section, driver section, test section, sabot (free piston) and the hydraulic control valve. The driver section—filled with high-pressure air—and the stainless steel driven section—filled with the test mixture at low pressure—are initially isolated from each other by the hydraulic control valve and a thin polyester (Mylar®) film. The two-piece sabot assembly consists of a deformable ultra-high molecular weight polyethylene nosecone and a brass counter-weighted body (Delrin®) in a tight contact with the internal walls of the driven section.

A pre-defined mixture with composition determined by target values of molar equivalence ratio, molar dilution ratio, pressure and temperature is prepared in a dedicated mixing tank. An intake