Full Length Article

The impact of physicochemical property interactions of *iso*-octane/ethanol blends on ignition timescales

Cesar L. Barraza-Botet[a,*], Jon Luecke[b], Bradley T. Zigler[b], Margaret S. Wooldridge[a,c]

[a] Department of Mechanical Engineering, University of Michigan, 2350 Hayward Street, Ann Arbor, MI 48109-2125, USA
[b] National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA
[c] Department of Aerospace Engineering, University of Michigan, 1320 Beal Avenue, Ann Arbor, MI 48109-2140, USA

A B S T R A C T

This work presents new measurements of liquid fuel ignition delay times of *iso*-octane and ethanol fuel blends obtained from an ignition quality tester at the National Renewable Energy Laboratory (NREL IQT), which are compared to previous ignition delay data from the University of Michigan rapid compression facility (UM RCF), at the same experimental conditions. Pressure-time histories were used to determine liquid fuel ignition delays at global stoichiometric non-premixed conditions for *iso*-octane, ethanol and *iso*-octane/ethanol blends of 25, 50, 75% by volume in mixtures of 10% oxygen diluted in nitrogen. Temperatures ranging from 880 to 970 K were studied at a pressure of 10 atm. By comparing total ignition delay times from the NREL IQT with chemical ignition delay times from the UM RCF, the contributions of physical phenomena were quantified as representative time scales for spray injection, breakup and evaporation processes, and for gas-phase turbulent mixing. Regression analyses were developed for ignition time scales as function of blend level and charge temperature. Non-dimensional analyses were also carried out to determine the relative effects of physical time scales with respect to chemical ignition delay times.

1. Introduction

Ethanol remains the most widely used biofuel for transportation purposes, being primarily an anti-knock additive in reformulated gasoline in the U.S. and the main transportation fuel in Brazil [1]. In the U.S., the increased use of ethanol has been driven by biofuel policies such as the Renewable Fuel Standard [2] and the California's Low Carbon Fuel Standard [3]. Higher ethanol-content blends with gasoline (e.g. 20–85% by volume) have shown promising results for efficiency and tailpipe CO_2 emissions 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 and physics of ethanol blends is vital for the successful integration of ethanol into the transportation sector.

Iso-octane is an important primary reference fuel and is often used as a simple chemical surrogate for gasoline. Numerous experimental studies of the ignition chemistry of *iso*-octane at homogenous conditions can be found in the literature, in particular in shock tubes and rapid compression machines (RCMs) [7]. Ethanol chemistry has also

been extensively studied as presented by Sarathy et al. [8] in their comprehensive summary of the alcohol combustion literature. In two recent UM RCF studies by Barraza-Botet et al. [7,9], ignition delay times and stable intermediate species were measured for homogenous stoichiometric mixtures ($\phi = 1.0$) of ethanol, *iso*-octane and *iso*-octane/ethanol blends at 10 atm and 900–1080 K.

The ignition of liquid fuels in ICEs, however, involves overlapping physical processes that produce an auto-ignitable mixture and chemical reactions that transform reactants into intermediates and products. The distinction between the physical and chemical processes in direct-injection engines is difficult to assess experimentally due to the complex geometry of the combustion chamber and the high turbulence in the charge, which affect fuel distribution, spray evaporation and mixing with the air [10]. Additionally, the changing properties of the compressed air during the ignition delay period complicate the quantification of the effects of engine charge temperature and pressure on the total ignition delay. Constant-volume devices, on the other hand, provide a nominally quiescent environment before the start of injection and much smaller changes in the charge temperature and pressure during the ignition delay period than piston engines [10]. Such characteristics make them suitable tools to quantify the contributions of

physical phenomena to the ignition time scales of ethanol/*iso*-octane blends.

Direct-injection constant-volume combustion chambers, like ignition quality testers (IQTs), are powerful experimental tools. They have been utilized to measure liquid fuel ignition delays of low-volatility fuels and surrogates to observe NTC behavior [11–16], to calculate low- and high-temperature apparent heat release [10,11], to develop correlations for research and motor octane numbers (RON and MON) [17–19], to assist the validation of chemical kinetic [11,20] and CFD [16,21] models, and to estimate physical and chemical effects on delay periods [10,20,22,23].

IQT data have also been used to evaluate the chemical and physical contributions to ignition behavior. Zheng et al. [10] used an IQT to determine the physical and chemical delay periods of ultra-low sulfur diesel fuel, jet propellant-8 fuel, and two synthetic fuels by comparing the results of injecting the fuels into air (according to the ASTM D6890-10a standard [24]) and injecting the fuels into nitrogen at the same charge conditions. They defined the end of the physical delay period as the point at which the two resulting pressure traces separated, and the researchers developed Arrhenius correlations for total, physical and chemical ignition delays to evaluate the apparent activation energies of each fuel [10]. They concluded the physical delay period was a significant part of the total delay period, and the chemical activation energy had an inverse relationship with the cetane number for all the fuels tested [10]. However, Kim et al. [25] suggested using noticeable heat release as the physics-to-chemistry transition criterion inherently overestimates the physical delay by attributing part of the chemical delay to physical phenomena. IQT studies of isomeric fuels [20,22,23] have concluded that oxidation chemistry—instead of physical property variations—is the dominating factor in changes in total ignition delay at ASTM conditions.

There are several previous studies of neat fuels and fuel blends using IQT systems, including studies of *iso*-octane and ethanol. Osecky et al. [16] used the NREL IQT to observe the NTC behavior of *iso*-octane at global equivalence ratios between 0.7 and 1.05, pressures of 1.0 and 1.5 MPa, and temperatures ranging from 653 to 996 K; and to validate single-, multi-zone and CFD models predicting well-mixed conditions in the main part of the chamber at ~30 ms after SOI. At similar conditions, Yang et al. [15] utilized an IQT to correlate temperature, pressure and global equivalence ratio with *iso*-octane total ignition delay, obtaining an inverse relationship between global equivalence ratio and total ignition delay in the intermediate-temperature regime. Haas et al. [22] measured the cetane number of binary blends of ethanol with n-heptane and CF13 (a real distillate diesel fuel) in an IQT as the physical properties of the blends varied, and demonstrated that blending up to 10% vol. alcohol into the base hydrocarbon resulted in modest reductions of the cetane number. Bogin et al. [12] investigated the reduction of low-temperature heat release and NTC behavior with increasing ethanol blending in *iso*-octane using the NREL IQT at near-stoichiometric conditions, pressures of 0.5–1.5 and a temperature range of 623–993 K. They concluded that NTC behavior was observed for blends up to E20, that ethanol addition produced consistently shorter ignition delays in the high-temperature region, and that increasing ethanol content from E0 to E10 had lesser impact on ignition delays than increasing from E10 to E20 [12].

The aim of this work is to quantify the effects of spray physics and turbulent mixing on the global ignition chemistry of ethanol, *iso*-octane and ethanol/*iso*-octane blends at the same experimental conditions of previous studies of homogeneous ethanol and blend mixtures [7,9]. The NREL IQT was utilized to measure liquid fuel ignition delays, $\tau_{ign,liq}$, of stoichiometric ethanol/*iso*-octane blends—including E0, E25, E50, E75 and E100—at moderate dilution levels (N_2:O_2 molar ratios of 9:1), pressures of 10 atm, and temperatures ranging from 880 to 970 K. The overall contribution of spray and mixing physics to the global ignition time scales were determined as a function of blend levels and charge temperatures by directly comparing the IQT liquid fuel ignition delay measurements with the chemistry-driven ignition data acquired in the RCF studies [7,9]. By further interrogating the pressure time histories of the IQT experiments, time scales and apparent thermal effects of physical phenomena such as spray injection, breakup, evaporation, turbulent mixing and heat release were also quantified. Regression analyses provided best-fit Arrhenius correlations for total, physical and mixing time scales as functions of charge temperature and molar carbon content in the blend (as surrogates of the different blend levels), which complement the correlation obtained in previous work for homogeneous blend ignition [7]. Non-dimensional analyses connected findings on ignition time scales to fuel properties, experimental conditions, and known physical principles. The results are discussed on a comparative basis between premixed and non-premixed global reactivity of ethanol and *iso*-octane blends.

2. Materials and methods

Two facilities were utilized to carry out the experimental studies on the chemistry and physics of ethanol and ethanol blends in this work—the NREL IQT and the UM RCF. The fundamental difference between the IQT and RCF experimental approaches is that liquid fuels are injected, vaporized and mixed in situ in IQT studies while gas-phase reactants are pre-mixed for RCF experiments. At the same experimental conditions, the IQT allows the effects of spray and mixing physics on the overall reactivity of ethanol blends to be quantified whereas the RCF provides insights on the global reactivity and pollutant formation under homogenous conditions. The different approaches are used to quantify the physical and chemical interactions of the fuel spray and mixing in the IQT results by isolating the effects of chemistry in the RCF results.

2.1. Ignition quality tester (IQT)

The NREL IQT is a bench-scale device consisting of a stainless-steel constant-volume combustion chamber with a fuel spray injection system that enables the direct measurement of liquid fuel ignition delay time, $\tau_{ign,liq}$. Experimental conditions such as initial charge air pressure and temperature, global equivalence ratio and dilution level are well controlled. The fuel is injected into the chamber through a single-hole S-type delayed (inward-opening) pintle nozzle connected to a pneumatically-driven mechanical fuel pump using a 1.5 mm (ID) fuel line. A piezo-electric pressure transducer (Kistler 601B1 with coolant jacket) installed at the opposite end of the injector measures the charge-air pressure during the experiment. The 0.21 L chamber is pressurized with a mixture of 10% O_2 in N_2 (Scott Specialty Gas Certified Master Class purity, ± 2% analytical accuracy) to a charge air pressure of 10 ± 0.07 atm (absolute) prior to the injection of a pre-determined amount of fuel resulting in an overall equivalence ratio of ~1.0 for each blend. Fuel injection pressures of ~177 atm (manometric) were used for the experiments in this study.

Nine electric cartridge heaters (Watlow Firerod, J4D-4441, each 300 W) are embedded in the outer wall of the combustion chamber to maintain a constant temperature representative of the bulk air prior to injection in the main portion of the chamber. Omega K-type thermocouples are used for temperature measurements in the IQT. The charge air temperature (T_{charge}) reported with each result corresponds to the measurement of the air back thermocouple just before the start of injection (SOI), although the gas temperature during the ignition delay period is lower due to the evaporative cooling of the fuel. The air back thermocouple is used because its location closer matches the location where combustion is more likely to start, as indicated by previous CFD modeling [20]. A second thermocouple located 70 mm closer to the injector nozzle along the axis of the chamber typically indicates temperature gradients of 40–50 K exist in the chamber with respect to the location of the air back thermocouple. The temperature gradient is caused by heat transfer to the cooling system of the injector nozzle and