

Tailoring Ethanol High Temperature Ignition by Means of Chemical Additives and Water Content

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ABSTRACT

The quest for sustainable alternatives to fossil fuels leads to a growing diversification of the molecular structures of fuel sources. Since ignition is a vital property in the choice of an engine combustion concept, the ability to tailor the ignition behavior of various fuel sources by means of fuel additives is expected to aid the development of fuel-flexible engines. Ethanol is one of the biofuels with a potential to play an important role in the transportation fuel mix of the future. One of the final processes during ethanol production involves distillation in order to minimize the water content. Using wet ethanol in combustion engines could lead to a reduction in the energy consumption during fuel processing. An understanding of fundamental combustion properties of ethanol in the presence of water vapor such as ignition behavior is expected to aid in the design of efficient engine combustion processes.

In this work, the effect of two esters, isopropyl nitrate (IPN) and isopropyl formate (IPF), on the high temperature shock ignition of ethanol is investigated. Furthermore, the ignition of wet ethanol is investigated in order to shed light on the effect of water vapor content on the ignition chemistry of ethanol. New ethanol ignition data at 10 atm are also reported. Experiments are carried out in a shock tube at average pressures of 2, 10 and 12 atm over a temperature range of 949-1650 K. The ethanol and ethanol/additives are mixed with oxygen and argon. Ignition delay times are obtained behind reflected shock waves by means of pressure and light emission profiles.

It is observed that while IPN addition to ethanol results in shorter ignition delay times, IPF addition leads to longer delay times. In case of water addition, it is found that for the same post-reflected temperatures and pressure, shorter ignition delay times are observed. However, this effect must

be considered together with other physical processes of wet ethanol combustion such as heating and vaporization.

INTRODUCTION

There is a growing need for flexible fuels to meet the world's need for diversified sustainable fuel sources. Coupled with this fuel diversification is the emergence of improved combustion technologies aimed at higher efficiencies, low pollutant formation and fuel-flexibility. Ethanol (EtOH) is increasingly being used in sparkignition engines either blended with gasoline or in its pure form. Concerns about the sustainability of ethanol production prompt the investigation of wet ethanol combustion which could reduce production costs and improve the environmental impact of the bioethanol cycle. The ignition properties of a fuel are very important in the choice of an engine design. By means of ignition promotion additives, ethanol is also being successfully used in compression ignition engines [1,2]. These ignition improvers are peroxides, alkyl nitrates or amides. On the other hand, when self-ignition of a fuel is undesirable as in spark-ignition engines, some ethers such as methyl tert-butyl ether (MTBE) and alcohols such as EtOH have been used as anti-knock additives.

The use of chemical additives based on a fundamental understanding of their chemical interactions with the baseline fuel presents great opportunities and challenges for the development of fuel-flexible vehicles. The mechanism by which alkyl nitrates accelerate ignition in hydrocarbons has been the subject of many studies [3,4,5,6,7,8], however gaps still exist in our understanding of their effects at various thermodynamic conditions. Griffiths et al. [3] studied the pyrolysis of isopropyl nitrate (IPN) at low temperatures and pressures [3] and high temperatures (1300 K - 1500 K) and pressures (greater than 14 atm) [9] in continuous flow and constant volume reactors. Based on analysis of the products, they observe that the decomposition proceeds through the

generally accepted mechanism of initiation through cleavage of the O - NO₂ bond in alkyl nitrates. They further observed that depending on the reactor temperature and pressure, the subsequent reactions and products of NO₂ and the isopropoxy radical can vary. For instance, they found that above 1400 K, NO could not be detected but both H₂ and CH₄ concentrations changed considerably. Because of the different ways by which alkyl nitrates can modify the chemistry of the main fuel, fuel-specific studies at varied conditions are necessary to establish their ignition-promoting ability.

There are few studies of the high temperature ignition of EtOH in shock tubes [10,11] which have aided the development of detailed chemical kinetic mechanisms for its oxidation [12,13]. Apart from its use as a fuel for spark-ignition engines, it is of interest as an anti-knock additive. Other anti-knock additives are ethers such as MTBE and ETBE [14,15,16]. Because of environmental concerns about the use of MTBE as a fuel additive (e.g. ground water contamination), alternatives have been suggested and are mostly other ethers and alcohols. It is possible that other oxygenated hydrocarbons such as alkyl esters could be good anti-knock additives as well.

In this work, we explore the effect of a branched chain alkyl ester, isopropyl formate (IPF), on the ignition of EtOH. IPF pyrolysis and combustion has not been extensively studied. Anderson and Rowley [17] investigated the kinetics of the decomposition of n-propyl and isopropyl formates. They found that the decomposition proceeds by ester rearrangement to yield formic acid and propene, an observation later confirmed by Blades [18] in a similar study. In high temperature oxidation, however, it would be expected that other reactions such as hydrogen abstractions and bimolecular reactions with oxygen present competing pathways for the ester oxidation.

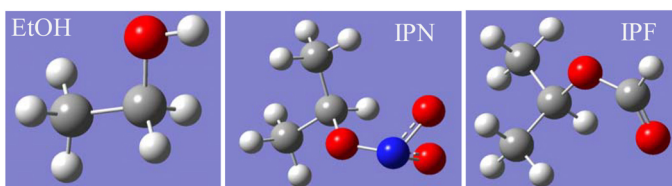


Figure 1. Structures of ethanol (EtOH), isopropyl nitrate (IPN) and isopropyl formate (IPF), with the following atoms: C - dark grey, H - light grey, O - red and N - blue.

In the area of wet ethanol combustion, previous studies have focused on system level combustion studies. Mack et al. [19] and Martinez-Frias et al. [20] have demonstrated the use of wet ethanol in homogeneous charge compression ignition (HCCI) engines as a means of improving the life cycle efficiency of bioethanol. They found that smooth combustion

was sustained using wet ethanol with up to 60% water content by volume. However, higher intake temperatures were required.

In this work, the effect of IPN and IPF on high temperature EtOH ignition in a shock tube is studied. The ethanol and its blends with the various additives are mixed with oxygen and diluted with argon. Ignition delay times for EtOH are obtained and compared to previously published data at 2 atm and to simulations. Ignition delay times of IPF and IPN are also obtained and compared to those of EtOH. Blends of EtOH with these esters (10 and 20% IPN by liquid volume; 10, 20 and 50% IPF by liquid volume) are then studied at constant equivalence ratios, ϕ , constant argon/oxygen ratios, D , and average pressures, p . The pressures investigated in this study range from 2-12 atm, within the pressure limit of the current facility. Though these moderate pressures are lower than are normally observed in engines, they permit the investigation of the kinetics underpinning the ignition processes of the fuels studied. In the case of pure IPN ignition, a lean mixture, $\phi = 0.8$ was investigated as it was difficult to obtain reasonable ignition delay times without direct initiation of IPN mixtures detonation at 10 atm for stoichiometric mixtures. The argon/oxygen, D , ratio is maintained constant to capture the ignition behavior in “synthetic air”, which has a fixed nitrogen/oxygen ratio. The ignition of wet ethanol is also investigated for stoichiometric mixtures with 0%, 10% and 30% water content by liquid volume as well as for lean mixtures with 0%, 30% and 50% water content. In the same manner, the argon/oxygen ratio, D , is maintained constant while the fuel concentration is chosen such that the required equivalence ratio is obtained. The homogeneous gas phase ignition data obtained from the shock tube shed light on relative chemical reactivity of these fuels in practical engines as well as aid in improved chemical kinetic modeling for engine combustion simulations.

EXPERIMENTAL METHOD

Auto-ignition is observed behind reflected shock waves in a 5.0 cm inner diameter shock tube. Details of the facility and the data acquisition system are given elsewhere [21]. The fuels used in this study have the following purities: anhydrous EtOH - 95%, IPN - 97%, and IPF - 98%. In all mixture preparations, final fuel pressures were below 70% of the vapor pressure at room temperature to avoid condensation of the fuel in the mixing tank.

The ignition delay time is obtained from light emission at the endwall with the shock arrival time determined from the end-wall pressure trace. Light emission is observed using a photodiode equipped with a normal band pass filter centered at 430 nm with a 10 nm bandwidth, corresponding to a chemiluminescence emission band of the CH radical. As illustrated in Figure 2, the ignition delay time is obtained by the intersection of the line of maximum slope of the CH

signal with the average photodiode signal prior to ignition onset as discussed in Ref. [21].

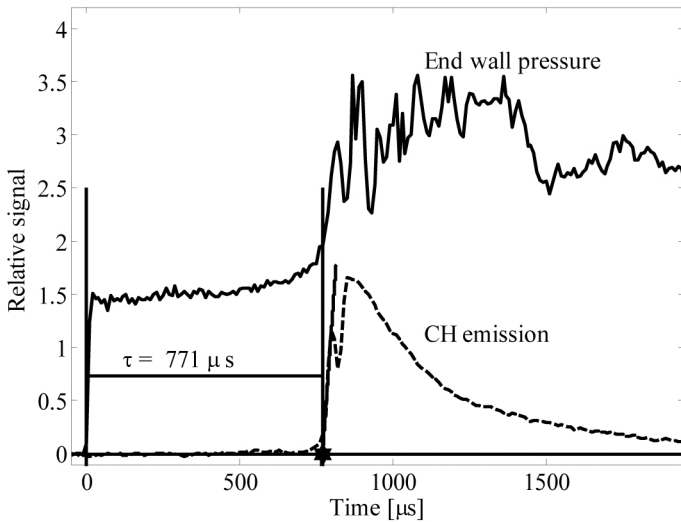


Figure 2. End-wall pressure and chemiluminescence of the CH radical (430 nm) histories and resulting ignition delay time for a mixture of 20 % IPF and 80 % EtOH ($\phi = 1.0$, $D = 12.0$) at 10.2 atm and 1125 K.

The post-reflected shock temperature in this study was calculated using GasEq [22] with mixture compositions, shock velocity and initial pressure and temperature as input quantities. Thermodynamic data for EtOH were taken from the mechanism by Marinov [12], while data for oxygen and argon were taken from the thermodynamic database in GasEq. The data for IPN and IPF are obtained using the thermo-chemical data estimator software, THERM [23]. A main source of uncertainty in shock tube ignition data is uncertainty in temperature which is largely controlled by the uncertainty in the shock speed. In this study the temperature uncertainty is estimated to be in the range 10-25 K, which is typical for shock tube facilities. This estimate is based on estimation of uncertainty in shock speed, pressure transducer separation, time resolution of the data acquisition system and the method of extrapolating the speed to the endwall. This uncertainty does not compromise the relative behavior addressed in this study. Ignition delay time simulations are performed using the CANTERA software package [24].

RESULTS AND DISCUSSION

Results of the ignition of ethanol and the additives, IPN and IPF, are presented followed by ignition delay times of blends of ethanol and the respective additives. The results of the effect of water on ethanol ignition are presented towards the end of this section. The ignition delay time, τ , is plotted against the inverse temperature, T at a constant average pressure, p . Variations in the post-reflected shock pressure are corrected by a power law relation:

$$\tau \propto p^{-1} \quad (1)$$

A set of ethanol ignition experiments in the literature were chosen for validation of the present shock tube technique. An example of these verifications is shown in Figure 3 for a lean mixture at 3.3 atm whereby the present data are compared with those reported by Dunphy and Simmie [10] as well as with simulated ignition delay times using the mechanism by Marinov [12]. It is observed that there is reasonable agreement with the literature data within the limit of uncertainty as well as with the simulation. However, on account of the lower global activation energy or temperature sensitivity in the correlation by Dunphy and Simmie [10], there are marked deviations between the correlation and the Marinov mechanism predictions at lower and higher temperatures. Global activation or temperature sensitivity is proportional to the slope of the logarithmic plot of the ignition delay time against inverse temperature.

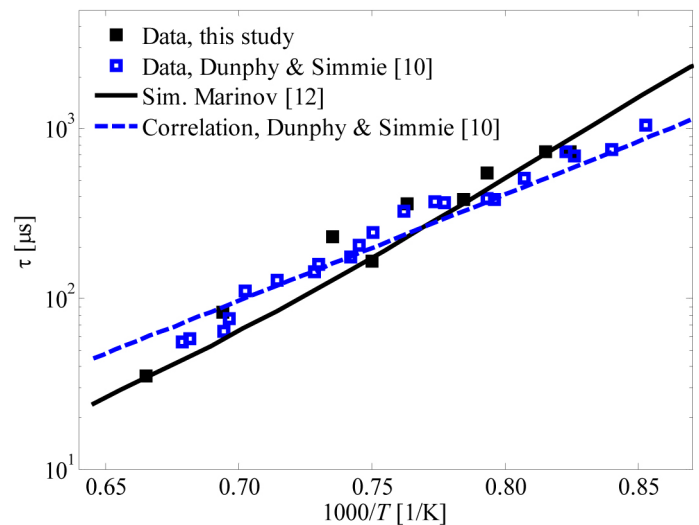


Figure 3. Comparison of present EtOH ignition data with literature data and simulation at 3.3 atm ($\phi = 0.5$, $D = 12.2$).

EFFECT OF ISOPROPYL NITRATE (IPN)

Figure 4 shows that IPN is more reactive than EtOH at lower temperatures, which are accessible in the shock tube at higher pressures as a result of the limited observation time in conventional shock tubes (1-2 ms). At lower pressures, higher temperatures are required for ignition and the ignition delay times of IPN tend to be comparable to those of EtOH. At about 1400 K (corresponds to about 0.7 on the abscissa) the ignition delay times of both substances become comparable. This change in relative behavior is thought to be associated with a change in the relative competing chain branching

reactions either brought about by IPN decomposition or other radicals such as OH, H, etc, as discussed later.

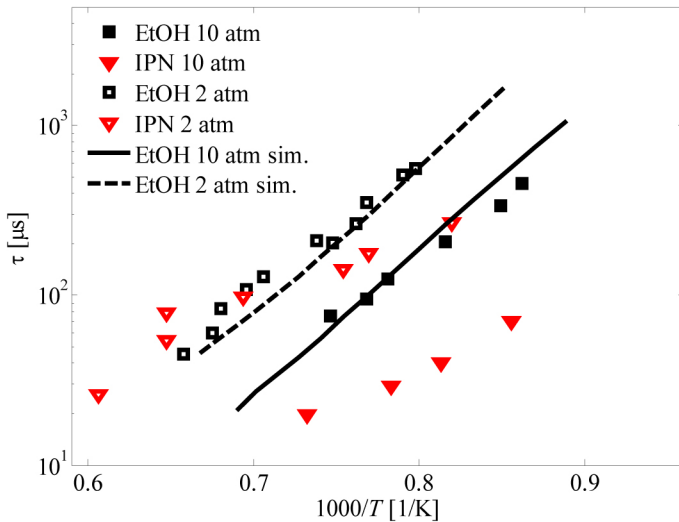


Figure 4. Pure IPN ($\phi = 0.8$) and EtOH ($\phi = 1.0$) ignition compared at $D = 12$. Simulations are carried out using mechanism by Marinov [12].

Figure 5 shows the effect of adding IPN to EtOH on ignition. As could be expected, the ignition delay times of the blends are intermediate between pure EtOH and IPN, with temperature sensitivity less than that of pure EtOH. At the lower pressure of 2 atm (higher temperatures), the ignition delay times of the blends are comparable with those of ethanol though they are slightly longer delay times than ethanol at temperatures above 1400 K (see Figure 6).

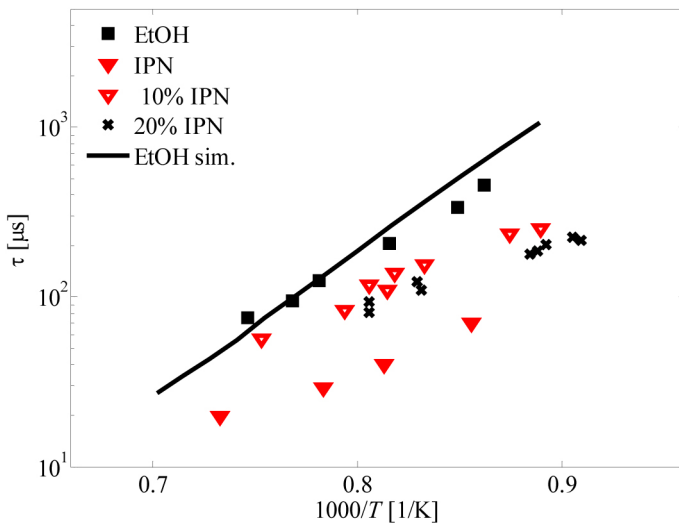


Figure 5. Effect of IPN additive on ethanol ignition at an average pressure of 10 atm ($\phi = 1.0$, $D = 12$).

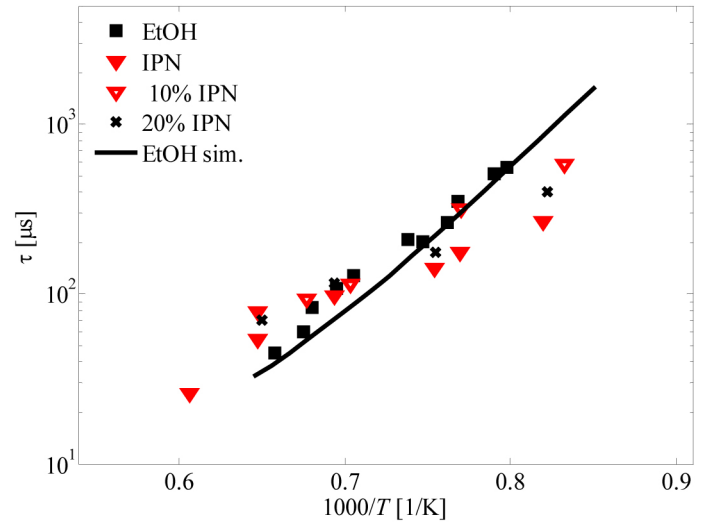
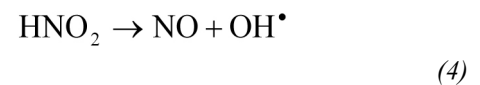
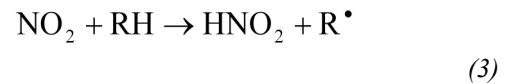
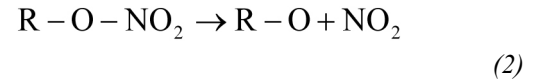
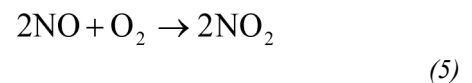


Figure 6. Effect of IPN additive on ethanol ignition at an average pressure of 2 atm ($\phi = 1.0$, $D = 12$).

As discussed in the introduction, IPN decomposition proceeds through cleavage of the O - NO₂ bond forming NO₂ and isopropoxy radical. The increased reactivity of hydrocarbons with nitrate additives is attributed to the further participation of NO₂ in chain reactions leading to OH radical formation as per the sub-mechanism [6]:



NO₂ is regenerated from the reaction:



The weaker temperature sensitivity and the reduced effectiveness of IPN as a booster at very high temperatures is attributed to a change in the dominant oxidation mechanism, as proposed by Pinard et al. [7]. At higher temperatures the relative competition of other H-abstraction reactions with the reaction pathway discussed above becomes important:

