



Chemical interaction of dual-fuel mixtures in low-temperature oxidation, comparing *n*-pentane/dimethyl ether and *n*-pentane/ethanol



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ABSTRACT

With the aim to study potential cooperative effects in the low-temperature oxidation of dual-fuel combinations, we have investigated prototypical hydrocarbon (C₅H₁₂) / oxygenated (C₂H₆O) fuel mixtures by doping *n*-pentane with either dimethyl ether (DME) or ethanol (EtOH). Species measurements were performed in a flow reactor at an equivalence ratio of $\phi = 0.7$, at a pressure of $p = 970$ mbar, and in the temperature range of 450–930 K using electron ionization molecular-beam mass spectrometry (EI-MBMS). Series of different blending ratios were studied including the three pure fuels and mixtures of *n*-pentane containing 25% and 50% of C₂H₆O. Mole fractions and signals of a significant number of species with elemental composition C_nH_{2n+x}O_y ($n = 1-5$, $x = 0-(n+2)$, $y = 0-3$) were analyzed to characterize the behavior of the mixtures in comparison to that of the individual components. Not unexpectedly, the overall reactivity of *n*-pentane is decreased when doping with ethanol, while it is promoted by the addition of DME. Interestingly, the present experiments reveal synergistic interactions between *n*-pentane and DME, showing a stronger effect on the negative temperature coefficient (NTC) for the mixture than for each of the individual components. Reasons for this behavior were investigated and show several oxygenated intermediates to be involved in enhanced OH radical production. Conversely, ethanol is activated by the addition of *n*-pentane, again involving key OH radical reactions. Although the main focus here is on the experimental results, we have attempted, in a first approximation, to complement the experimental observations by simulations with recent kinetic models. Interesting differences were observed in this comparison for both, fuel consumption and intermediate species production. The inhibition effect of ethanol is not predicted fully, and the synergistic effect of DME is not captured satisfactorily. The exploratory analysis of the experimental results with current models suggests that deeper knowledge of the reaction chemistry in the low-temperature regime would be useful and might contribute to improved prediction of the low-temperature oxidation behavior for such fuel mixtures.

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1. Introduction

Adverse effects on the environment and climate caused by the combustion of fossil fuels in conventional engines underline the need for more efficient and cleaner engine–fuel combinations [1,2]. Fuel additives as a component of intelligent fuel design can serve to control the ignition timing in advanced engine concepts using homogeneous charge compression ignition (HCCI), reactivity-

controlled compression ignition (RCCI), and stratified-charge compression ignition (SCCI), with the prospect of cleaner burning processes and higher thermal efficiencies [3,4]. However, the operation of such engine–fuel combinations must rely on the fundamental knowledge of the combustion chemistry that drives the low-temperature auto-ignition of fuel mixtures. Such low-temperature combustion (LTC) strategies can involve mixtures of high-cetane and high-octane fuels with their synergistic combustion characteristics to achieve high thermal efficiencies, and several approaches have been demonstrated, e.g. using primary reference fuels with additives to achieve efficient engine control and ignition timing [5,6]. High-cetane fuels usually auto-ignite early, showing typical low-temperature heat release (LTHR) and high-temperature heat release (HTHR) characteristics. The addition of high-octane fuels

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suppresses the early LTHR, shifting more of the heat release from high-cetane fuels closer to the top dead center of engines, thereby improving the combustion efficiency in internal combustion engines.

Dual-fuel mixtures are a good basis to understand the chemistry of multi-component mixtures. In spite of its importance for practical applications in engines, however, detailed information regarding potential interactions between different fuel components in the LTC regime remains scarce. The auto-ignition of mixtures with simple molecular structures was investigated recently [7,8], including methane/dimethyl ether (DME) and propane/DME blends. These studies have profited from the numerous low-temperature oxidation investigations of light C_3 – C_4 alkanes [8–18] as a substantial basis to examine dual-fuel interactions. Regarding heavier alkanes, *n*-heptane/ethanol (EtOH) blends were investigated by Saisirirat et al. [19,20] under HCCI and jet-stirred reactor (JSR) conditions, with a noted impact of *n*-heptane on ethanol consumption between 600 and 700 K. Their work mainly focused on ignition delay times, however, and only a few intermediates were observed which could not illustrate the nature of the interaction between *n*-heptane and ethanol [19,20]. A challenge to fully understand such interactive effects for fuels of the size of *n*-heptane or *iso*-octane is the large number of isomeric structures that are formed in the low-temperature oxidation reactions via alkyl (R), peroxyalkyl (ROO), and hydroperoxyalkyl (QOOH) radicals. The identification and quantification of these radicals and their subsequent reaction products are often beyond the capability of commonly used diagnostic techniques. Furthermore, significant uncertainties exist in the pressure-dependent kinetic parameters of these reactions [21–25] which limit the further development of accurate kinetic models. As a reasonable compromise, we have therefore chosen *n*-pentane (C_5H_{12}), an alkane component in gasoline, as the primary fuel in this work to explore its interaction with fuel additives of different ignition reactivity.

As for lighter or heavier alkanes [8–18,21–25], a number of studies have been performed of the low-temperature oxidation of *n*-pentane, using rapid compression machine (RCM) [26–35], shock tube (ST) [34–36], and JSR [37–40] experiments. Most of the previous experimental work focused on the macroscopic auto-ignition behavior of *n*-pentane, with detailed speciation reported only in recent publications of Bugler et al. [39] and Rodriguez et al. [40]. Bugler et al. [39] have also developed a mechanism for the auto-ignition of pentane isomers which they examined against JSR data (500–1100 K, 1 and 10 atm) obtained by gas chromatography (GC), cavity ring-down spectroscopy (CRDS), and Fourier transform infrared spectroscopy (FTIR). Rodriguez et al. [40] complemented the atmospheric-pressure JSR experiments in the temperature range of Bugler et al. [39] with measurements using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Their experiment successfully identified and separated contributions of different isomers, especially of saturated, unsaturated, and carbonyl hydroperoxides. These recent investigations support the choice of *n*-pentane as base fuel for the present work.

DME and ethanol have been selected as isomeric fuel additives of different reactivity in this study. They are considered as potential or widely applied biofuels that could reduce the emission of air pollutants [1,41,42]. DME has been used as a fuel additive or alternative fuel in compression ignition engines because of its excellent auto-ignition characteristics [43]. It has a high cetane number (CN=55) and was found to be an excellent ignition improver for HCCI engines [44,45]. The present knowledge on these two isomeric fuels' low-temperature oxidation reactions is more detailed for DME than for ethanol. Experimental investigations, including ignition delay [7,46] and speciation [41,47–54] measurements in JSRs and flow reactors have laid an extensive foundation for DME's reaction kinetics. Quantum chemical calculations

were performed for both the first and second O_2 addition reactions, as well as the further reactions of the $CH_3OCH_2O_2$ (ROO) and CH_2OCH_2OOH (QOOH) intermediates [55]. The pressure-dependent description for these reactions is sensitive to the low-temperature oxidation of DME [56], which was well considered in the recently published DME models of Burke et al. [7] and Rodriguez et al. [57]. Very recently, Jiang et al. [58] determined ignition delay times of *n*-pentane/DME mixtures and their experimental results compared favorably to the pentane isomer model by Bugler et al. [35]. The situation for a detailed study including reactive intermediates of *n*-pentane/DME interactive mixture effects in the LTC regime attempted here should thus be considered favorable.

Ethanol is a commonly used additive to fossil transportation fuels. Different from DME, ethanol has a high research octane number (RON=109 [59]) and displays single-stage ignition. Compared to ample studies on the high-temperature combustion of ethanol, its low-temperature oxidation chemistry has attracted lesser attention [51,60–63]. Haas et al. [61] and Herrmann et al. [51] studied the oxidation of pure ethanol in flow reactor conditions with somewhat different results. Very weak negative temperature coefficient (NTC) behavior might have been observed for the rich ethanol/ O_2 /Ar mixture by Herrmann et al. [51] as evident from their Fig. 3a, but not in the work of Haas et al. [61]. The model of Cancino et al. [60] also showed a slight NTC behavior in the reproduction of Herrmann et al.'s data [51], but no further studies confirmed these results. Recognizing these difficulties, ethanol auto-ignition has been investigated very recently for ST and RCM conditions by adding DME as a radical initiator [64].

Regarding this background, it is to be expected that *n*-pentane will exhibit different global NTC behavior when blended with either isomer of C_2H_6O , namely DME or ethanol. However, there is a lack of prior information on the detailed oxidation reactions and intermediate species mole fractions or on any potential interactions between the two fuels in such mixtures. We therefore provide speciation experiments in a flow reactor for both, the dual-fuel mixtures of *n*-pentane/DME and *n*-pentane/EtOH, at near-atmospheric pressure and in the temperature range of 450–930 K. The species composition along the reaction progress was analyzed using electron ionization molecular-beam mass spectrometry (EI-MBMS). The results for the mixtures were compared to the behavior of each individual fuel component. Temperature-resolved, extensive species information has thus been obtained systematically regarding synergistic or antagonistic effects between these fuels of different reactivity, and combined with an analysis of the detailed chemical oxidation pathways.

Although the main emphasis in the present work is on the experimental results, we have complemented the measured species data with initial simulations by two recent kinetic models. Specifically, we have used the model for pentanes of the Galway group [39] and the recent update of the Polimi mechanism [17]. Discrepancies between experiment and simulation were noted and are discussed in an attempt to improve the understanding of the low-temperature oxidation mechanisms for these mixtures including interactive effects.

2. Experimental and numerical approaches

2.1. Flow reactor experiment

The low-temperature oxidation reactions of *n*-pentane, DME, ethanol, and the respective dual-fuel mixtures were investigated in a flow reactor in the temperature regime of 450–930 K (step size $\Delta T=5$ K), keeping several important parameters constant. The experiments were consistently performed at $\phi=0.7$, 970 mbar, a total cold gas flow rate of 300 sccm (standard cubic centimeters per minute at 1 atm and 273.15 K), and an argon dilution of 90%.

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