

# EXPERIMENTAL INVESTIGATION OF FUEL-SPECIFIC SPECIES FORMATION IN BLENDED PREMIXED FLAMES

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## Abstract

To contribute to the understanding of fuel-structure-dependent influences on chemical pathways and pollutant formation in combustion, low-pressure flames burning hydrocarbon-oxygenated fuel mixtures were investigated with electron-ionization molecular-beam mass spectrometry. The chosen fuel blends – selected combinations of branched and unbranched hydrocarbons and oxygenated fuels – represent a wide span of different chain lengths, branching degree, and structural motives. Two sets of experiments were conducted to investigate the influence of the molecular structure on the species composition in the flames of such mixtures. In one series, *n*-heptane (C<sub>7</sub>H<sub>16</sub>) and iso-octane (C<sub>8</sub>H<sub>18</sub>) were blended with either dimethyl ether, DME, (C<sub>2</sub>H<sub>6</sub>O) or diethyl ether, DEE (C<sub>4</sub>H<sub>10</sub>O) [1]. The second experiment was devoted to mixtures of ethene (C<sub>2</sub>H<sub>4</sub>), 1-butene (1-C<sub>4</sub>H<sub>8</sub>), and isobutene (i-C<sub>4</sub>H<sub>8</sub>) that were blended with esters of different unsaturation degree, namely methyl crotonate, MC (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>) and methyl butanoate, MB, (C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>) [2]. While the respective pool of intermediates in the blends typically consists of species also detected in the pure flames, a strong dependence is noted of the amounts of various intermediates and products – including undesired pollutants – on the individual fuels' decomposition pathways.

## Introduction

The energy demand in transportation is still mainly met by fossil-fuel combustion. To reduce the fossil fuel share, to decrease harmful emissions of carbon dioxide, soot, and unregulated pollutants, and to adjust the fuel characteristics to various operation conditions, blending strategies are being applied. Adding oxygenated compounds to petroleum-based fuels leads to an altered intermediate species pool as well as a different spectrum of exhaust products. While the combustion reactions of many individual fuels in flames have been studied in detail, often providing numerous experimental species profiles in combination with the development and

critical testing of kinetic models, similar work on fuel mixtures has remained scarcer, especially for blends of conventional and biogenic fuels. In the present study, iso-octane and *n*-heptane, representatives of primary reference fuels, as well as three C<sub>2</sub>-C<sub>4</sub> hydrocarbon fuels, namely 1-butene, isobutene, and ethene, were chosen as well-studied base fuels in an investigation of laminar premixed low-pressure flames burning fuel mixtures. The two alkane fuels were blended with DME and DEE, while MC and MB were added to the alkene fuels, resulting in a total of 25 flames of pure fuels and their combinations that permitted to study effects of the specific fuel structure on the combustion chemistry.

### **Experimental Method and Kinetic Modeling**

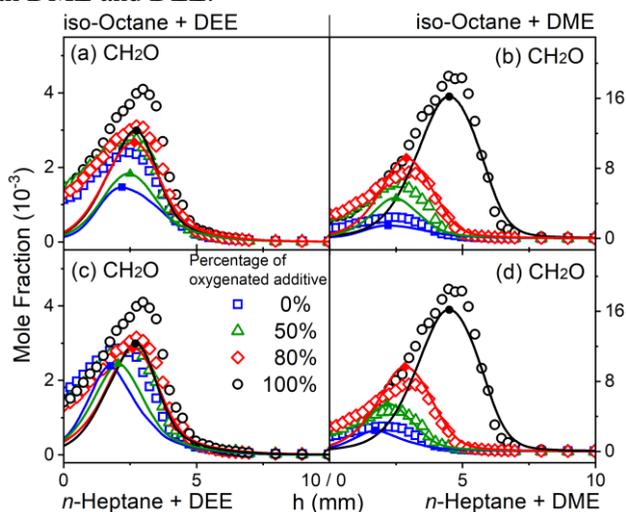
Fuel-rich laminar premixed low-pressure (4 kPa) flames were chosen as a simplified laboratory system and stabilized on a movable, water-cooled (333 K) flat bronze matrix burner. Argon dilution was chosen to provide a good standoff distance of the mixture flames (0.50 for *n*-heptane-, iso-octane-, and ethene-based and 0.25 for butene-based flames). Analyses were performed with a time-of-flight molecular-beam mass spectrometer using electron ionization to enable the simultaneous detection of almost all stable and radical species. The mass resolution ( $m/\Delta m \sim 4000$ ) allowed for the simultaneous separation and detection of all species based on their elemental composition of C/H/O. To support the data interpretation, the experiments were complemented by kinetic modelling. For the simulation of the combustion behavior of the first set of blends, namely iso-octane, *n*-heptane, DME, and DEE, we used the mixture model of [1] that combines the mechanism from Pitsch and collaborators [3] and the sub-mechanisms for DME and DEE from AramcoMech2.0 [4] and Tran et al. [5]. Exploratory modelling of the flames blended with small methyl esters was performed with the model of Yang et al. [6,7] that was chosen because it already includes basic mechanisms of the studied fuels.

### **Experimental Results**

#### ***Small ether addition to *n*-heptane and iso-octane base fuels***

Effects of DME or DEE addition in flames of the linear or branched alkanes *n*-heptane or iso-octane were studied in 8 hydrocarbon/oxygenated fuel mixture flames (in ratios of 1:1 and 1:4 in either fuel combination) and pure flames of each fuel. It was found that the addition of DME and DEE, where species with more than 4 carbon atoms can only be formed from recombination reactions of smaller species, decreases the mole fractions of C<sub>4</sub>-C<sub>9</sub> species compared to mole fractions detected in flames of the pure hydrocarbon fuels. In contrast, the mole fractions of several C<sub>1</sub>-C<sub>3</sub> species were seen to increase. As an example, blending with DME or DEE has a significant effect on the formation of formaldehyde (CH<sub>2</sub>O), known as a typical oxygenated pollutant from fuel combustion. Mole fractions of CH<sub>2</sub>O in all 12 flames are displayed in Fig. 1.

For the two base fuels, the CH<sub>2</sub>O production is, not surprisingly, promoted with increasing DME or DEE fractions, since it is a primary product in the fuel-specific reactions of both DME and DEE.

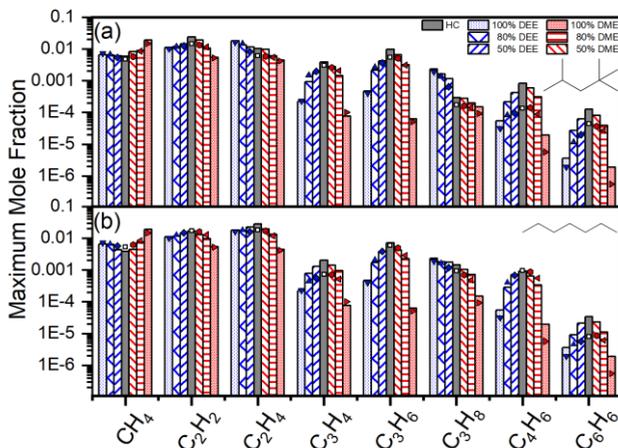


**Figure 1.** CH<sub>2</sub>O mole fractions for the pure fuels and fuel combinations of iso-octane, *n*-heptane, DME and DEE, and model predictions (mixture model [1]). Adapted from [1] with permission from Elsevier/The Combustion Institute.

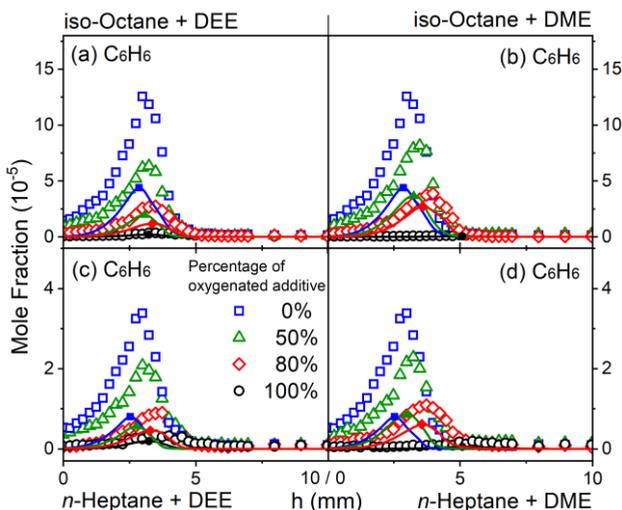
The stronger CH<sub>2</sub>O increase in flames blended with DME can be reasonably explained by the reaction sequence  $\text{DME} \rightarrow \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_2\text{O} + \text{CH}_3$ , which is one of the dominant pathways in DME combustion. The produced CH<sub>3</sub> can then additionally contribute to CH<sub>2</sub>O formation. In DEE decomposition, CH<sub>2</sub>O is mainly a product of a three-step reaction sequence of  $\text{DEE} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{O} \rightarrow \text{CH}_2\text{O}$  involving a less important consumption pathway of DEE [1]. These experimental trends are also satisfactorily captured by the simulation (compare Fig. 1). Further experimental results for hydrocarbon intermediate species are provided in Fig. 2 where their maximum mole fractions are displayed logarithmically; symbols indicate the prediction of the model. Different tendencies can be observed in the mixture flames. For example, methane (CH<sub>4</sub>) mostly increases with DME or DEE blending since it is mainly produced from the CH<sub>3</sub> radical, which is abundantly formed from both additives. Ethene (C<sub>2</sub>H<sub>4</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) mole fractions are higher in the mixture flames with DEE than for the pure iso-octane flame, with an opposite trend observed for the iso-octane/DME mixture flames. C<sub>3</sub>H<sub>8</sub> increases upon blending with DEE, since it is mainly produced from recombination of C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>, both key intermediates from DEE. C<sub>2</sub>H<sub>4</sub> is also a direct decomposition product of *n*-heptane and therefore lower in the *n*-heptane/DEE mixture flame.

Mole fractions of species with higher carbon numbers, here exemplarily shown for C<sub>4</sub>H<sub>6</sub> (calibrated as 1,3-butadiene) and C<sub>6</sub>H<sub>6</sub> (calibrated as benzene), were found to

be lower in the mixture flames than in the pure flames, with a stronger effect on iso-octane blends. For further inspection, experimental and simulated mole fraction profiles of  $C_6H_6$  are displayed in Fig. 3 for all 12 flames.



**Figure 2.** Maximum mole fractions (logarithmic scale) of selected hydrocarbon species for the pure fuels and fuel combinations of iso-octane, *n*-heptane, DME and DEE; experiment: bars, model: symbols (mixture model [1]).



**Figure 3.**  $C_6H_6$  mole fractions for the pure fuels and fuel combinations of iso-octane, *n*-heptane, DME and DEE, and model predictions (mixture model [1]). Adapted from [1] with permission from Elsevier/The Combustion Institute.

Simulations with the mixture model only qualitatively reproduce the experimental trends upon DME and DEE addition, and the benzene mole fractions are typically

under-predicted by at least a factor of two. The mole fractions of  $C_3H_3$  (not shown here), known as a major benzene precursor, are also seen to decrease upon ether addition in both iso-octane and *n*-heptane flames. It is therefore reasonable that  $C_6H_6$  shows the same tendency. It should be noted that the  $C_6H_6$  mole fraction is significantly higher for the branched fuel iso-octane than for *n*-heptane.

### ***Small methyl ester addition to three C<sub>2</sub>-C<sub>4</sub> hydrocarbon base fuels***

To investigate effects of methyl ester addition to alkenes, methyl crotonate (MC) and methyl butanoate (MB) were added to ethene, 1-butene, and isobutene [2]. The base fuels represent differences in chain length or branching degree, and MC and MB exhibit different unsaturation degrees, an important characteristic of biodiesel compounds. A total of 13 premixed hydrocarbon/oxygenated fuel flames were investigated (with mixtures in ratios of 1:1 in either fuel combination) [2]. Generally, the results showed changes in the formation of intermediate species upon ester addition to depend strongly on the molecular fuel and/or additive structure. Overall, partial replacement of all base fuels by either MB or MC leads to higher mole fractions of formaldehyde and methanol. Formaldehyde can easily be formed by a  $\beta$ -scission from both methyl ester fuel radicals. Hence, the effect of the base fuel is more important for  $CH_2O$  formation. Methanol can be formed by MC via  $CH_3O$  radicals by H-abstraction at the weakest C–H bond located at the terminal methyl group of the ester side chain, which is not equally preferred in MB. Therefore, MC addition leads to higher methanol formation. Besides the influence on small oxygenated species, MB and MC addition to the hydrocarbon base fuels significantly affects the pool of  $C_3$ - $C_6$  hydrocarbon species. Not surprisingly, their formation in ethene-based mixture flames is increased. For the butene flames, however, where  $C_3$  species are abundantly present, ester addition decreases the  $C_3$  pool. Highest reduction was found for  $C_3H_6$  in the 1-butene and for  $C_3H_4$  in the isobutene flame. A decrease was noted in  $C_4$ - $C_6$  species for ester addition to the butenes. For example, 1-butene can easily form  $C_4H_6$ , and subsequent dehydrogenation can yield significant amounts of  $C_4H_4$ . Ester addition reduces the contribution of these reactions. Reduction tendencies in  $C_5$  and  $C_6$  species are more prominent for MB addition. Contrarily, addition of the esters to ethene increases  $C_5$  and  $C_6$  species significantly, especially for MC. Most trends are reasonably well captured by the model [6,7], although absolute mole fraction may differ [2].

### **Conclusion**

The influence of small ether and ester additives on alkane and alkene fuels was investigated in two series of premixed low-pressure flames, including those in [1,2]. Species profiles were obtained with molecular-beam mass spectrometry for 25 flames of the pure fuels and their respective combinations. With a set of about 800 mole fraction profiles, the experiments permit reliable inspection of possible differences in the reaction pathways. In general, the respective pool of intermediates in the blends typically consists of species also detected in the pure flames.

Experimentally observed trends could be correlated to the altered species pool induced by the strong dependence on the individual fuels' decomposition pathways. The experimental data were further compared to simulations by kinetic models, mostly revealing reasonable to good agreement of the experimentally obtained trends.

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### Disclaimer

This paper contains work-in-progress and is not intended to be an archival publication.

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