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Influence of the biofuel isomers diethyl ether and *n*-butanol on flame structure and pollutant formation in premixed *n*-butane flames

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ABSTRACT

Diethyl ether (DEE) and its isomer *n*-butanol are both considered as promising fuel additives or neat biofuels. While some effects of their addition to hydrocarbon fuels under engine conditions have been reported, fundamental studies that aim at understanding the joint reaction pathways of such fuel mixtures remain quite scarce. Here, we have chosen *n*-butane as a well-studied hydrocarbon base fuel, and we have added these oxygenated isomers individually under identical conditions in premixed low-pressure flames. Different combustion behavior of the respective alkane-biofuel mixtures must then be related to the fuel structure. Analyses were performed in five fuel-rich flames including flames of *n*-butane, DEE, and *n*-butanol as well as two flames of *n*-butane doped with 50% DEE or 50% *n*-butanol. In this series, the carbon-to-oxygen ratio, argon dilution, pressure, and gas velocity were kept constant. More than 40 species in the range of C₀–C₈ were identified and quantified in each flame by electron ionization (EI) molecular-beam mass spectrometry (MBMS) coupled with gas chromatography (GC). The experiments were partially complemented by tunable synchrotron vacuum ultraviolet (SVUV) photoionization (PI)-MBMS. To assist in the interpretation of the data, a kinetic model was established by combining different sub-mechanisms for these fuels available in the literature. As expected, the formation of toxic carbonyls, such as formaldehyde and acetaldehyde, increased significantly upon addition of both oxygenated fuels to *n*-butane. Blending *n*-butane with DEE noticeably reduces the formation of soot precursors, because primary reactions of DEE mainly release C₁–C₂ hydrocarbon species to the system. *n*-Butanol addition, however, shows no significant reduction effects or even higher formation of soot precursors. These trends were observed both in the experiments and model predictions, and the higher ability of *n*-butanol to form soot precursors compared to DEE indeed results mainly from the differences in the fuel structure.

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1. Introduction

More than 90% of fuels consumed world-wide today are petroleum-based. The demand for transportation energy is rising, and most of this increase comes from heavy-duty-diesel vehicles [1]. As is well known, soot emissions are an important problem of diesel engines. Soot from fuel combustion has been demonstrated to contribute to respiratory dysfunction, heart diseases, and lung cancer [2–4]. Efforts are made to understand the formation process of soot and its precursors and to develop new combustion technologies to reduce soot emissions. At the same time, the need to

reduce greenhouse gas emissions continues to motivate research towards renewable fuels such as alcohols, esters, and ethers [5–7]. It has been shown that the addition of oxygenated compounds represented in biofuels to petroleum fuels is also a promising way to reduce soot emissions [8–10].

Diethyl ether (DEE, C₄H₁₀O) can be produced via dehydration of ethanol over solid acid catalysts and is being proposed as a promising biofuel [11–13]. Because of several favorable properties for diesel engines, including a high cetane number (~125), a more favorable lower heating value (LHV) of 33.9 MJ kg⁻¹ than that of dimethyl ether (28.6 MJ kg⁻¹), broad flammability limits, and high miscibility with diesel fuel, DEE has recently been examined as an additive to diesel fuel [11–13]. Moreover, DEE is being considered as an excellent ignition improver for homogeneous charge compression ignition (HCCI) engines operated with biogas or liquefied petroleum gas (LPG) [14,15]. In view of these interesting properties,

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the combustion chemistry of DEE in fundamental experimental setups has been increasingly investigated, including analysis of ignition delay times [16,17], flames [18,19], and flame speeds [19,20].

n-Butanol, an alcohol and isomer of DEE, can be produced via fermentation processes [21,22] and has been proposed as an alternative to conventional fuels [23], with a high LHV ($\sim 33.1 \text{ MJ kg}^{-1}$) and research octane number (~ 96) [7]. *n*-Butanol was studied as a fuel or as a blending agent for use in spark ignition engines [24,25] as well as in diesel and HCCI engines [26–29]. A large number of fundamental studies on the combustion chemistry of *n*-butanol have reported ignition delay times [30–32], species profiles in premixed [33,34] and non-premixed flames [18,35], and flame speeds [35,36], to name only some. A very detailed compilation of previous studies on this fuel can be found in the review article on alcohol combustion chemistry by Sarathy et al. [37].

Only a few comparative studies have recently become available that evaluated the influence of DEE and *n*-butanol addition on the performance and combustion characteristics of engines [13,38,39]. Rakopoulos [39] pointed out that with increasing percentage (up to 24 vol%) of DEE and *n*-butanol in blends with diesel, smoke opacity, NO_x , and CO were reduced, whereas unburned hydrocarbon emissions increased. Trends regarding DEE and *n*-butanol addition were quite similar, with *n*-butanol showing a slightly better smoke reduction. Opposite effects were noted under the conditions of [38] where DEE showed a more efficient smoke reduction, similar to the results by Imtenan et al. [13] for diesel and jatropha biodiesel upon DEE or *n*-butanol addition, with a reduction of smoke opacity of up to 27% by 10% addition of *n*-butanol and up to 38.5% when adding the same amount of DEE.

To the best of our knowledge, fundamental studies that aim to understand the cooperative combustion pathways in hydrocarbon fuel mixtures blended with these two isomeric oxygenated fuels are not yet available in the literature. We have thus studied the influence of the addition of DEE and *n*-butanol to *n*-butane on the reaction pathways and species pool under premixed low-pressure flame conditions to enhance the understanding of such systems.

2. Experiments

The experiments were performed in laminar premixed flat low-pressure flames using a combination of electron ionization molecular-beam mass spectrometry coupled with a gas chromatograph (EI-MBMS-GC) in Bielefeld as described in [40–42], complemented with synchrotron vacuum ultraviolet photoionization molecular-beam mass spectrometry (SVUV-PI-MBMS) measurements in Hefei following the procedures in [43–46], to provide a detailed chemical analysis of stable and reactive species together with isomer identification. The use of two different analysis techniques is particularly useful since it allows an independent confirmation of the species concentrations quantified in both studies.

2.1. Flame conditions

Five fuel-rich flames, *i.e.* *n*-butane/oxygen/argon ($\phi = 1.7$), *n*-butane/DEE/oxygen/argon ($\phi = 1.75$), *n*-butane/*n*-butanol/oxygen/argon ($\phi = 1.75$), DEE/oxygen/argon ($\phi = 1.8$), and *n*-butanol/oxygen/argon ($\phi = 1.8$) were investigated. Fuel-rich conditions were chosen to obtain quantifiable amounts of higher-mass soot precursor species to analyze potential interaction effects from the species pools generated by the two different fuel classes in flames of fuel mixtures. These flames were stabilized on a home-made flat burner of 64 mm diameter (Bielefeld) at identical pressure (4 kPa), argon dilution (25%), cold gas velocity (73 cm s^{-1} at 333 K and 4 kPa), and C/O ratio (0.52), resulting in slightly different equivalence ratios ϕ . Note that data obtained in the DEE/oxygen/argon flame was partially included in our

previous study to test a newly-developed DEE model [19]. Because experimental data for flames containing DEE is still scarce, the DEE/oxygen/argon and *n*-butane/DEE/oxygen/argon flames were also analyzed under similar conditions at the National Synchrotron Radiation Laboratory in Hefei using SVUV-PI-MBMS to enhance the reliability of the data. There, flames were stabilized on a commercial stainless steel McKenna burner of 60 mm diameter. In both experiments, calibrated mass-flow controllers established the gas flows; liquid fuels were metered by a syringe pump, evaporated at 343–433 K, and added to the gas stream. Flow rates were adapted to obtain near-identical mass flux. Both burners were cooled with water at a constant temperature of 333 K. Table 1 summarizes all flame conditions, and it also introduces abbreviated names for all flames that will be used in the following sections. Centerline species profiles were measured as a function of height above the burner h using the two MBMS setups described in the following section.

2.2. Measurement procedures

2.2.1. EI-MBMS-GC experiment

A detailed description of the EI-MBMS-GC system can be found elsewhere [40–42]. In brief, gas samples were extracted from the flame by a quartz cone (0.3 mm orifice, 25° included angle) which leads to an immediate quenching of the reaction due to the expansion of the sample into the first pumping stage chamber (10^{-5} kPa). This preserves the gas composition of the sample and enables the detection of reactive species such as radicals. The so-formed molecular beam is then skimmed by a home-made copper skimmer and passed into the ionization chamber (10^{-7} kPa). Here the sample is crossed with a pulsed electron beam (10^9 electrons/pulse) emitted by a tungsten filament of a two-stage Wiley-McLaren ion source. The generated ions were extracted into a time-of-flight mass analyzer, energetically focused by a reflectron, then detected with a multichannel plate and counted with a multichannel scaler. This setup (Kaesdorf) enables high mass resolution of $m/\Delta m \sim 4000$ so that the exact elemental composition of C/H/O can be determined for each species. Soft ionization energies (10.0, 11.5, 13.0 eV for intermediates, 16.0 and 18.0 eV for major species) were used to minimize undesired fragmentation. Measured ion signals were integrated by fitting Gaussian-shaped curves to the signal peaks. Integrated signals were corrected for fragment ions originating from the fuel itself and from intermediate species for which a fragmentation pattern was obtained from cold-gas measurements. Isotope corrections of ^{13}C and ^{18}O contributions were also performed when necessary.

The coupled gas chromatograph enabled the identification of stable isomers. To ensure direct compatibility of pure MBMS measurements and GC-MBMS measurements, sampling was performed directly from the flame environment. A low-pressure sampling interface allowed transfer of a gas sample from the first pumping stage into the high-pressure environment of the GC (130 kPa). Here a temporal separation was performed with an Alumina BOND/Na₂SO₄ column (Restek GmbH) and an appropriate temperature program (323 K hold for 2.5 min, heating rate 293 K min^{-1} to 473 K, hold for 10 min), leading to a reasonable separation of hydrocarbons in the C₁–C₆ range. The outlet of the column was connected to the ionization chamber so that full mass spectra could be recorded as a function of the retention time. This simplifies the assignment of occurring signals as chromatograms can be obtained for each specific nominal mass. This procedure therefore presents a significant advantage here over classical FID detection. Spectra were averaged for 3.2 s (0.05 min) to improve the signal-to-noise ratio but keep a maximum of time resolution. A resolving power of 1.00 was achieved for *trans*-2-butene and 1-butene, which corresponds to a FWHM (full width at half maximum) of 0.05 min

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