

# Study of the high-pressure low-oxidation chemistry of *n*-pentane, diethyl ether, and their mixture

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## Introduction

Advanced oxygenated biofuels (second and third generations) are of increasing interest as alternatives to petroleum-based fuels. These biofuels now provide opportunities to extend the petroleum era as complete replacement or as blending agents with petroleum-based fuels. Furthermore, advanced biofuels are well suitable to be used as a component for a dual-fuel “reactivity controlled compression ignition” combustion mode which offers high thermal efficiency and low pollutant emissions [1]. Numerical simulations of dual-fuel combustion require mixture models that must accordingly be developed by grouping individual well-established sub-mechanism of each parent fuel. Therefore, reliable experimental data of pure fuels as well as fuel mixtures are a prerequisite to further develop and test kinetic models. This need is especially acute for high pressure which is relevant to the operation conditions of practical engines.

The purpose of the present study is to identify and quantify species formed during the high-pressure low-temperature (LT) oxidation of diethyl ether (DEE, a promising C<sub>4</sub> oxygenated biofuel), *n*-pentane (an important prototype C<sub>5</sub> hydrocarbon fuel [2]), and their mixture, as well as to characterize the reactivity of these systems.

## Experimental procedure

A dedicated experimental setup was used to perform experiments (Fig. 1). It is composed of a high-pressure jet-stirred reactor [3] coupled to four gas chromatographs with different detectors: i.e. a mass spectrometric detector for the identification of reaction products, and a thermal conductivity detector as well as a flame ionization detector coupled to a methanizer for the quantification of species. Gas chromatographs used of the quantification were fitted with different columns (Carbosphere packed column, PlotQ and HP-5 capillary columns) to separate a wide range of species. The volume of the jet-stirred reactor is 60 cm<sup>3</sup>. Dimensions of this reactor were reduced compared to that of the reactor used for experiments at atmospheric pressure to decrease the consumption of the gases (fuel, helium and oxygen). The reactor is made of fused silica to avoid as much as possible catalytic effects. It is located in a stainless steel vessel to balance the pressure between the inside and the outside (Fig. 1). Helium and oxygen flow rates are controlled using mass flow controllers. Fuel flow rates are controlled using a Coriolis flow controller (in the liquid state) followed by an evaporator in which it is mixed with helium. The pressure is controlled by a pressure controller located downstream of the reactor. The gas phase is directly sampled inside the reactor by the mean of a fused silica capillary tube. The sample is then brought to the sampling valves of the gas chromatographs through a heated transfer line. The capillary tube is requested to maintain the pressure drop between the reactor and the sampling valves (close to the atmospheric pressure).

All studied mixtures were stoichiometric, contained 0.5% fuel, and were highly diluted in helium to avoid a too strong heat release and temperature inhomogeneity. The oxidation of pure DEE and pure *n*-pentane were investigated under identical conditions at 5 bar. A mixture composed of these two fuels was studied at different pressures ranging from 2.5 to 10 bar. The residence time was kept constant at 2 s.

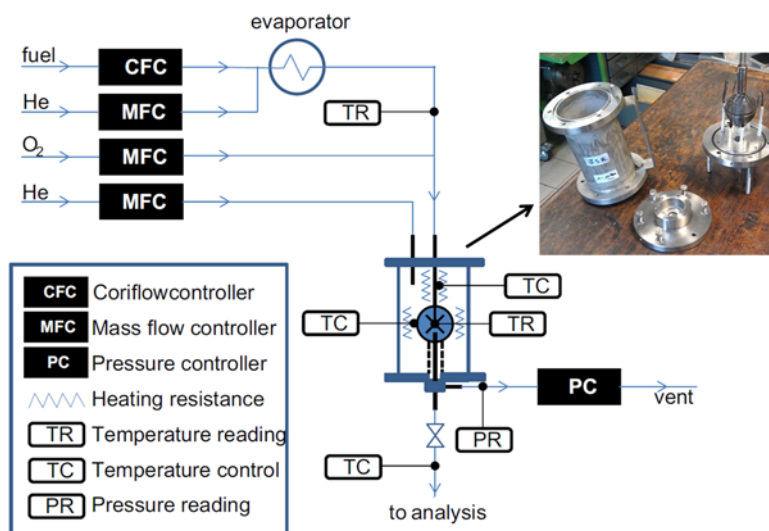


Fig. 1 Scheme of the experimental setup.

## Experimental results

About 30 species were detected with major attention given to fuel-specific low-temperature intermediates and to the influence of pressure on the oxidation behavior. Both fuels are linear, saturated, and they have five atoms in their structure (Fig. 2). However, because of its ether functional group, DEE is found to have a very different oxidation behavior in comparison to *n*-pentane (Fig. 3). For example, DEE starts to react at much lower temperatures, it is more reactive in the low-temperature region and it has a much weaker negative-temperature coefficient than *n*-pentane.

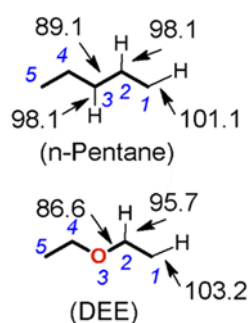


Fig. 2 Structure of the two fuels investigated in the present work.

As far as products are concerned, doubly-oxygenated species are present at high selectivity (Fig. 4). C<sub>1</sub>-C<sub>2</sub> aldehydes, CO, and CO<sub>2</sub> were detected even in higher amounts. At 500 K, CO<sub>2</sub> seems to be not produced via CO routes. At 800 K, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are predominant species. Among doubly-oxygenated species, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-cy and C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> were measured with the highest mole fractions, indicating their importance in the low-temperature oxidation of DEE.

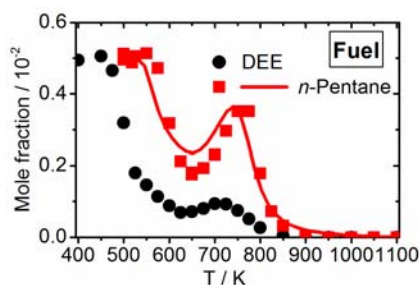


Fig. 3 Comparison of the reactivity of the two fuels investigated in the present work (same operating conditions; computed data calculated with the model of [2]).

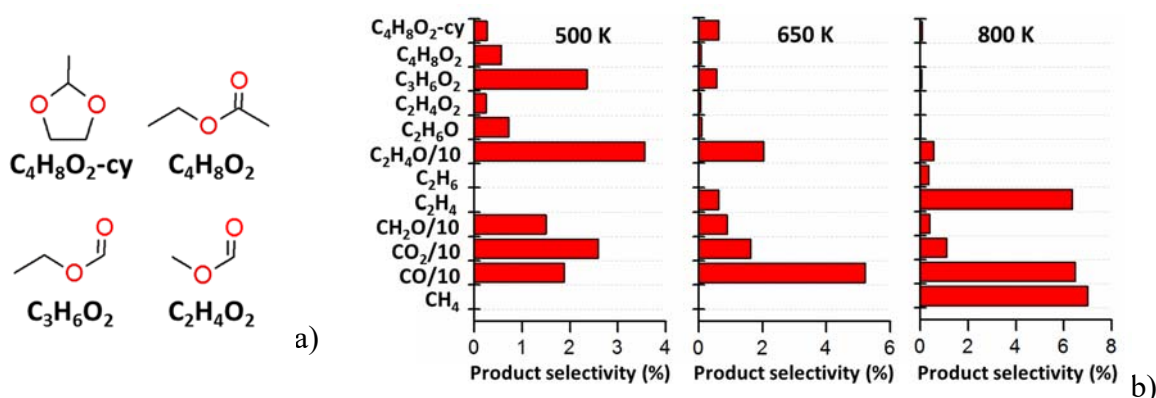


Fig. 4 a) Structure of doubly-oxygenated species detected in the oxidation of DEE. b) Selectivity of reaction products detected in the oxidation of DEE.

Comparisons of CO and selected intermediates provide evidence of differences in species evolution between the two fuels (Fig. 5). While the profiles of CO peak at similar temperatures, those of aldehydes are shifted between two fuels.  $C_2H_4O$  was measured with much higher amount in DEE oxidation.  $C_4H_8O_2$ -cy and MTHF may be produced via a similar principle from DEE and *n*-pentane, respectively, but  $C_4H_8O_2$ -cy shows two peaks and MTHF shows only one peak.

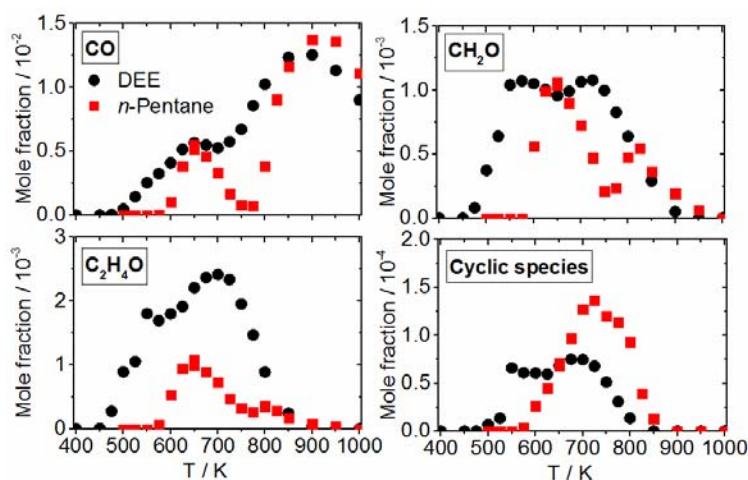


Fig. 5 Comparison of selected intermediates detected in the oxidation of *n*-pentane and DEE (same operating conditions).

As far as the reaction pressure is concerned, it seems to very strongly influence the reactivity of the fuel mixture in the range of 2.5-7 bar, however this influence becomes very weak when the pressure increases from 7 to 10 bar (Fig. 6). These data are being used for testing and improving kinetic models of DEE/*n*-pentane.

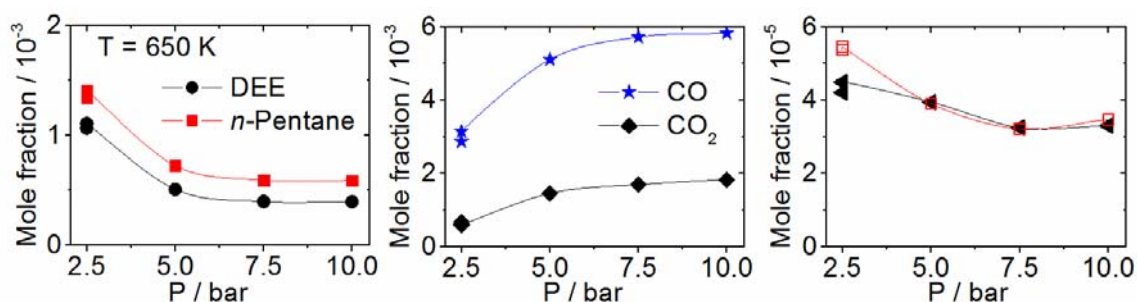


Fig. 6 Evolution of mole fractions as a function of the pressure (same operating conditions).

## Conclusion and perspectives

The first tests with models of the literature have shown that while the model of *n*-pentane can predict the experimental data well, that of DEE needs improvements, especially in the low-temperature range (Fig. 7). Computed data were calculated using the model from Sakai et al. [4].

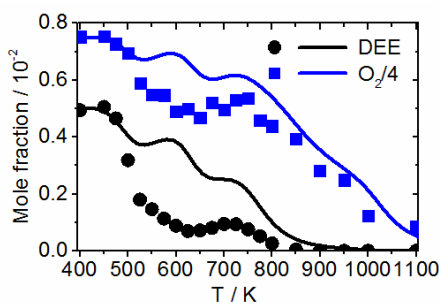


Fig. 7 Comparison of experimental and computed data (the model is from Sakai et al. [4]).

It is planned to investigate the formation of hydroperoxides and ketohydroperoxides using mass spectrometry with ionization using photo-ionization. While the detection of this type of reactive species at 1 bar has been successful for various fuels, measurements at higher pressure are still in progress due to challenges in the high pressure tolerance of the sampling system.

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## References

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