

STSM Report

Details of the STSM:

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1. Purpose of the STSM

One of the advantages of the use of advanced biofuels as blend additives with petroleum fuels is that little or no modifications for existing combustion engines are required. Diethyl ether (DEE, $C_4H_{10}O$) is being proposed as a promising bioadditive to diesel fuel on account of its several favorable properties for diesel engines, including a high cetane number (~ 125), a favorable lower heating value (LHV) of 33.9 MJ kg^{-1} , broad flammability limits, and high miscibility with diesel fuel [1]. 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) [2][3]. With a high cetane number, this biofuel could also be used as a high reactivity fuel for the new combustion mode namely RCCI (reactivity controlled compression ignition) [4]. In view of these interesting properties, the combustion chemistry of DEE has been increasingly investigated. It has been recently shown that the addition of DEE to a hydrocarbon base fuel reduces significantly the formation of soot precursors [5]. However, the data of quantitative species profiles of the low-temperature (LT) oxidation of DEE and its fuel mixtures at high-pressure conditions, more relevant to those of practical engines, are not well established. Such quantitative data is known to be very useful to analyze and understand details of the reaction mechanism in this technically relevant temperature regime. **Therefore, the purpose of this study is to identify and quantify species formed during the oxidation of DEE and of a hydrocarbon base fuel (*n*-pentane) as well as their mixture at LT and high-pressure regime.**

2. Description of the work carried out during the STSM and the major results

A recently developed high-pressure jet-stirred reactor (JSR) at LRGP-CNRS-Nancy [6] was used during this STSM. Figure 1 presents two pictures of this setup. The pressure in this JSR can be increased up to 10 bar. The reactor was preceded by an annular preheating to heat the mixture up to the reaction temperature and to then avoid the formation of important temperature gradients inside the reactor. The reactor was heated by Thermocoax resistances rolled up around it. The reaction temperature was measured by a thermocouple located in the intra-annular part of the preheating with its extremity in a glass finger inside the spherical part.

Reaction products were analyzed using gas chromatographs (GCs) connected to the JSR through a microprobe and a transfer line heated at about 423 K to avoid the condensation of heaviest species. Four GCs coupled to different columns (HP-5, PlotQ, Carbosphere) and different detectors (FID, TCD, MS) were used to quantify and identify chemical species. To obtain the mole fraction profiles, calibrations were carried out by injecting standards and by using the effective carbon number method. The attention was paid at fuel-specific intermediates of the LT oxidation as well as the influence of pressure on the reactivity and the formation of LT species.



Figure 1. Pictures of the high-pressure JSR setup (left) and disassembled reactor's chamber (right)

During this measurement campaign, the LT oxidation of *n*-pentane as a hydrocarbon base fuel and DEE as a biofuel as well as a mixture of these two fuels was investigated as described below. Experimental conditions are summarized in Table 1.

Table 1. Experimental conditions.

Mixture name	T (K)	p (bar)	t (s)	Initial mole fraction			
				<i>n</i> -pentane	DEE	O ₂	He
Pentane-5bar	500-1100	5	2	0.005	0	0.040	0.955
Pentane-10bar	500-800	10	2	0.005	0	0.040	0.955
DEE-5bar	500-1100	5	2	0	0.005	0.030	0.965
Pentane/DEE	650	2.5, 5, 7.5, 10	2	0.0025	0.0025	0.035	0.960

2.1. Measurements of species produced in the high-pressure LT oxidation of *n*-pentane at 5 and 10 bar

In the present study, all the measurements were carried out for a constant residence time of 2s and for a stoichiometric mixture ($\phi=1$). To keep a constant residence time, the total flow was varied, depending to the set temperature of the reactor. The reactor temperature was set in a range of 500-1100K. The mixture composition of *n*-pentane/O₂/He is 0.5%/4.0%/95.5%. A high dilution ratio of He was used to minimize the temperature gradients inside the reactor. Two series of measurements were performed at two pressures (5 and 10 bar).

More than 30 species including reactants, intermediates, and products in the mass range up to $m/z=102$ (C₅H₁₀O₂) were detected. An example of an obtained chromatogram is presented in Figure 2. The obtained data are being evaluated and analyzed.

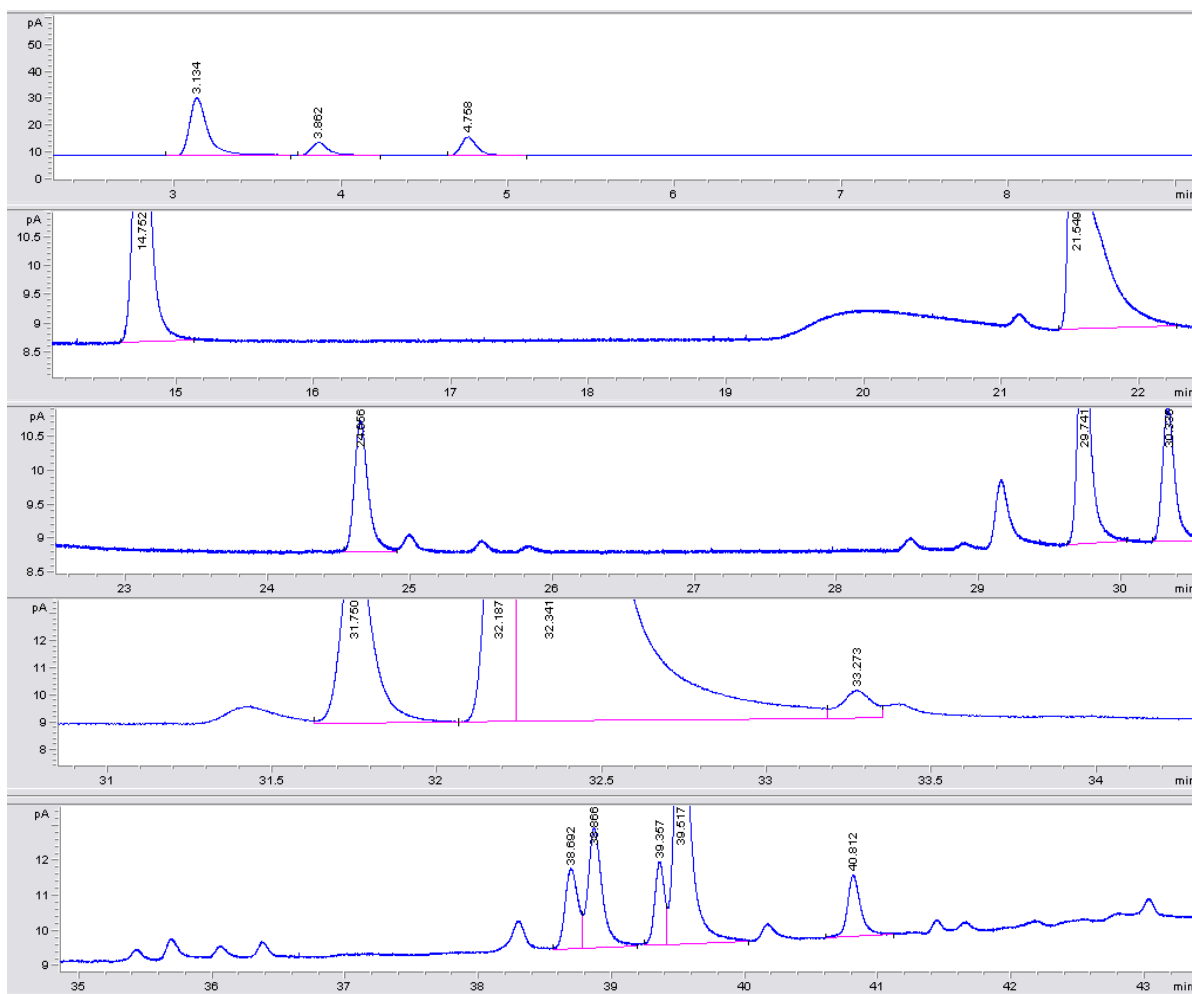


Figure 2. An example of a chromatogram obtained by GC-column PlotQ-FID for the *n*-pentane oxidation at $\phi=1$, 725K, and 5 bar.

2.2. Measurements of species formed in the high-pressure LT oxidation of DEE at 5 bar

Similar to the case of *n*-pentane, here all the measurements were carried out for a constant residence time of 2s, $\phi=1$, and 5 bar. The reactor temperature was set in a range of 500-1100K. The mixture composition is summarized in Table 1. These conditions are identical to those used for *n*-pentane at 5 bar.

About 20 species including reactants, intermediates, and products were detected. These data are being evaluated and analyzed. Figure 3 shows an example of relative raw signals as a function of reaction temperature obtained for DEE at 5 bar as well as for *n*-pentane at 5 and 10. The relative signal is proportional to the species concentration.

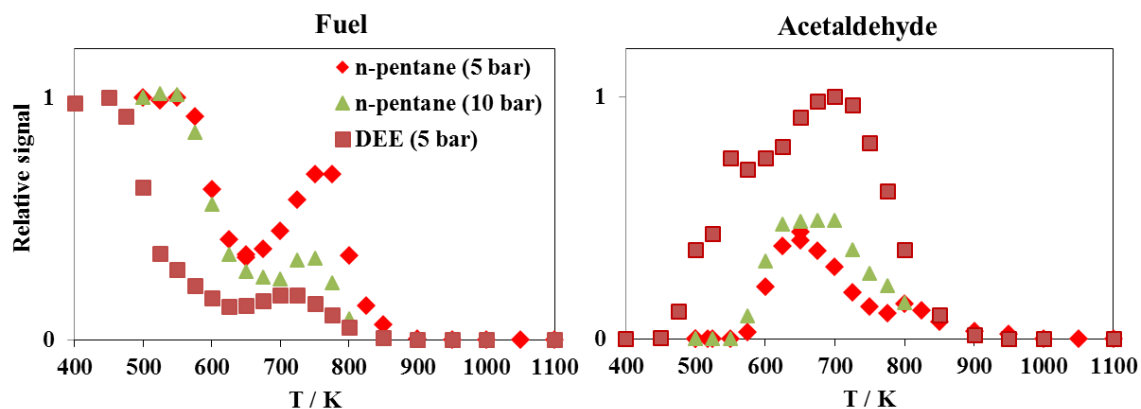


Figure 3. Measured raw signals of fuels and of a selected intermediate species (relative to the highest signal) as a function of reactor temperature

2.3. Measurements of species produced in the high-pressure LT oxidation of a fuel mixture of DEE and *n*-pentane at different pressures

Here the reactor was kept at 650K, and the pressure was varied from 2.5 to 10 bar. The experimental conditions are summarized in Table 1. The residence time was kept constant to 2s, and the mixture is stoichiometric. More than 30 chemical species were measured at different pressures providing data for investigating the effects of pressure on the oxidation behavior of a fuel mixture of DEE and *n*-pentane (50%/50% by mole). These data are being evaluated and analyzed. An example of the raw data on the relative signals obtained for fuels (DEE+*n*-pentane) as a function of the reactor pressure is presented in Figure 4.

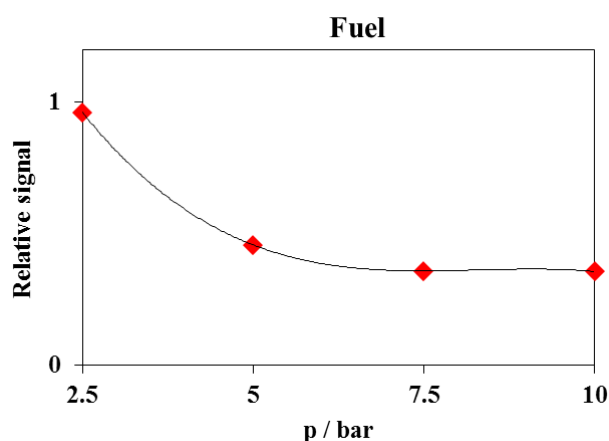


Figure 4. Relative raw signals of fuels (DEE+*n*-pentane) as a function of pressure

3. Contribution of the STSM to the Action's aim

The purpose of the STSM is consistent with that of the SMARTCATS COST Action CM1404, especially with the themes of the Workgroup 1 (Smart Energy Carriers gas phase chemistry: from experiments to kinetic models). The results of this STSM contribute firstly to extending experimental database to high pressures, which are typical of practical combustion

processes, and to improving the understanding of the oxidation chemistry of the important prototype fuels, *i.e.* DEE and *n*-pentane.

4. Future collaboration with the host institution

In collaboration with the host institute, the obtained data have been evaluated, and they will be used for further developments of kinetic models of these fuels. Also, with the host and home institutions, we continue collaborations to gain further insights into the LT oxidation of these fuels using the PI-MBMS technique (in collaboration with the group of Prof. Fei Qi) at the National Synchrotron Radiation Laboratory in Hefei, China.

5. Foreseen publications resulting from the STSM

When the data evaluation as well as further developments on the measurements of very reactive species and on model analyses will be accomplished, the final results will be presented through the publication of a paper in the international scientific journal.

6. Confirmation by the host institution of the successful execution of the STSM

See the attached letter.

7. Acknowledgements

I am grateful to the COST Action CM1404 for financial support for my STSM at the LRGP-CNRS-France. My thanks also go to my host supervisor, Dr. Frédérique Battin-Leclerc, Dr. Olivier Herbinet, and the entire team at LRGP for their support. I am also grateful to my home supervisor, Prof. Dr. Katharina Kohse-Höinghaus, for her support.

8. References:

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