

SMARTCATs STSM final report

Experimental and modeling study of the oxidation of a biofuel nitrogen-containing model compound

1. Details of the STSM

Applicant details

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2. Objective of the STSM

The aim of this Short Term Scientific Mission (STSM) is to extend the collaboration between the *Laboratorium voor Chemische Technologie (LCT)* and the *Laboratoire Réactions et Génie de Procédés (Nancy - France)* within the SMARTCATS COST Action (CM1404). The main purpose of the collaboration is to perform experiments with the jet-stirred reactor, available in Nancy, to investigate the oxidation of a nitrogen-containing model compound present in biofuels. During the stay, experience with experimental apparatus, experience on kinetic model generation and the determination of kinetic and thermodynamic data will be exchanged.

3. Experiments performed during the STSM

During the STSM, experiments are performed on the isothermal quartz jet-stirred reactor. This setup is highly suited for kinetic model development of model compounds, because of its ability to measure detailed effluent concentration profiles. [1-3] The investigated model compound is diethylamine (DEA). In this section, first a short description of the experimental apparatus is given, next the process conditions and main results are summarized.

3.1. Experimental apparatus

Helium (99.99%), used as diluent, is mixed with the liquid fuel and passes through an evaporator. Afterwards, oxygen (99.999%) is added to this gaseous flow. The helium and oxygen flow rates are controlled by gas-mass-flow controllers (Bronkhorst) and the liquid fuel mass flow rate are regulated by liquid-Coriolis-flow controllers (Bronkhorst).

The gaseous mixture passes through an annular preheating zone, where it is heated to the reactor temperature, and enters the jet-stirred reactor through four nozzles. The nozzles and reactor are designed to avoid thermal and concentration gradients. Thermocoax resistance wires provide heating for the annular preheating zone and the reactor. A type K thermocouple measures the temperature in the center of the reactor (measured temperature gradients < 5K). The pressure is set with a needle valve downstream of the reactor.

The reactor outlet is connected to 3 gas chromatographs which enable online quantification of the product species. The transfer lines to the gas chromatographs are heated to avoid condensation. The first gas chromatograph is used to detect CO, CO₂, O₂, N₂ and H₂. This gas chromatograph is equipped with a Carbosphere packed column and a thermal conductivity detector. The detector makes use of helium carrier gas, while argon carrier gas is used in order to enable the detection of H₂. The second gas chromatograph makes use of a PLOT-Q capillary column and a flame ionization detector preceded by a methanizer. The third gas chromatograph has a HP-5ms capillary column and a flame ionization detector. To enable on- or offline product identification, the reactor outlet is connected to a fourth gas chromatograph, which is equipped with either a PLOT-Q or HP-5ms capillary column, and has a quadrupole mass spectrometer. Product quantification for all GC's is done by injecting a known amount of the substance or with the use of the effective carbon number method. The relative experimental error on the compound mole fraction determined by injecting a known amount of the substance is 5% based on experience. In case the effective carbon number method is applied, the relative experimental error equals 10%. In order to quantify the NO_x formation from the oxidation of DEA, an NO_x analyzer is used.

3.2. Experimental results

Oxidation experiments of DEA are performed at fuel-rich, stoichiometric and fuel-lean conditions, corresponding to the equivalence ratios, $\phi=2.0$, 1.0 and 0.5. The temperature is varied from 500 K to 1100 K to cover the complete conversion range, with increments of 25 K. The pressure is kept fixed at 1.07 bar. The residence time is equal to 2 s for a reactor volume of 81.2 cm³, and the DEA inlet mole fraction is equal to 0.01. In contrast to oxygenated species, no low temperature reactivity is observed for DEA. A total of 25 species are detected using the online GC's. For identification of the non-calibrated nitrogen-containing product species, offline samples are submitted to the GC×GC-TOF/MS. In the intermediate temperature range, i.e. from 600 K to 800 K, large nitrogen-containing species are identified, containing five carbon atoms and at least two nitrogen atoms. In addition to CO and CO₂, the main carbon-containing products are methane, ethane and ethylene, while the main nitrogen-containing compounds are hydrogen cyanide, acetonitrile, propanenitrile and acrylonitrile (Figure 1).

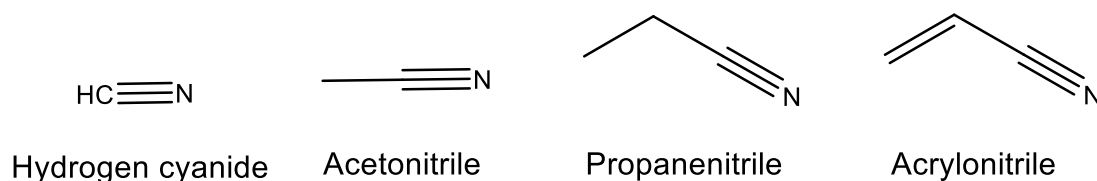


Figure 1: Main nitrogen (and carbon)-containing products resulting from the oxidation of DEA.

Other important products include H_2 , O_2 , N_2 , NO and NO_2 . Preliminary results for the profiles of the main products are depicted in Figure 2. In order to improve the carbon and nitrogen balances, the calibration of all compounds will be revised.

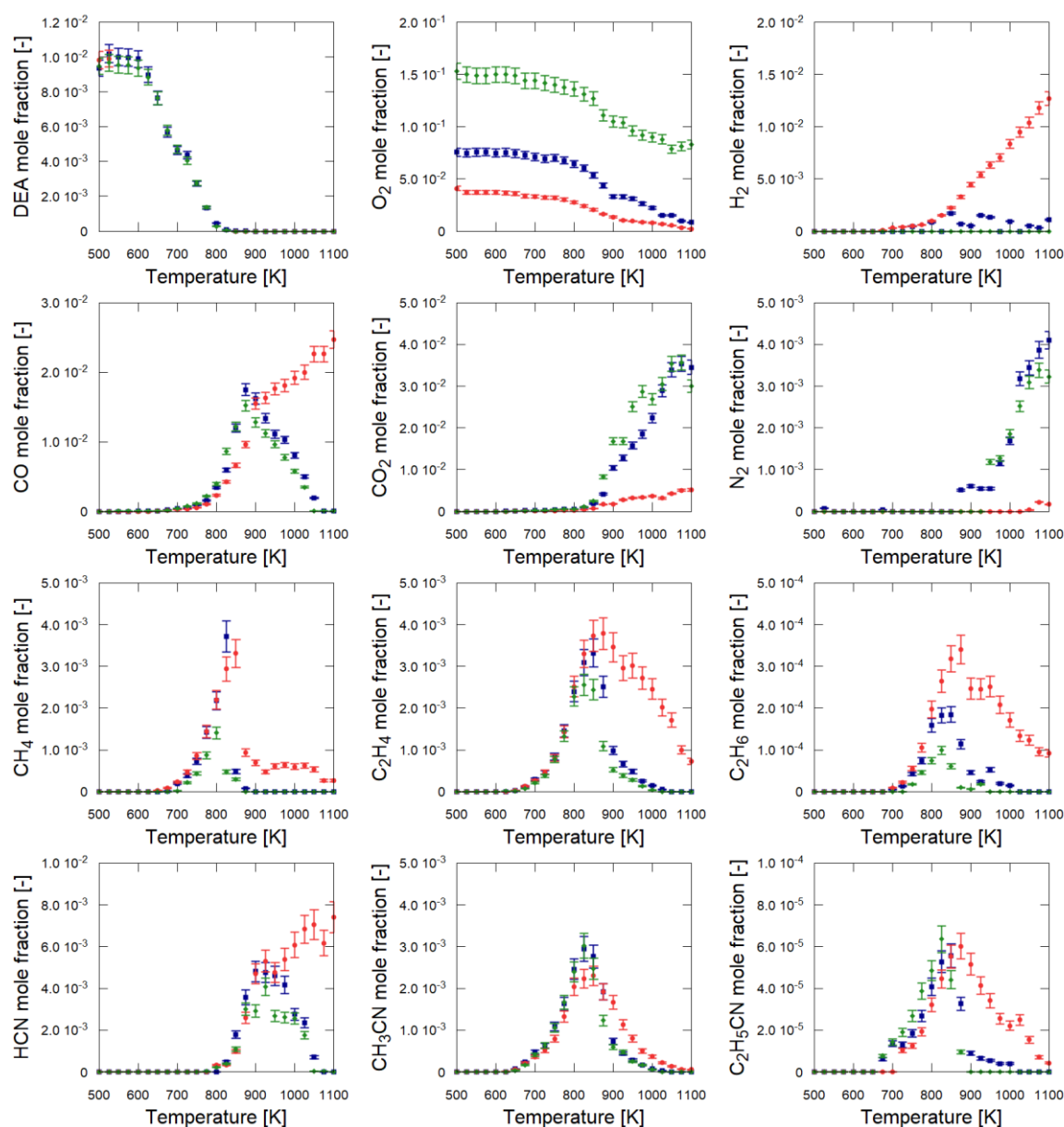


Figure 2. Experimental major product yields of DEA oxidation ($\varphi=1.0$ blue \blacksquare , $\varphi=2.0$ red \bullet , $\varphi=0.5$ green \blacklozenge). Experimental conditions are $P=1.07$ bar, DEA inlet mole fraction 0.01 and residence time 2.0 s for a reactor volume of 81.2 cm³. Experimental relative uncertainties are 5% for species calibrated with a known substance amount and 10% for calibration with the effective carbon number method.

4. Kinetic modeling during and after STSM

A kinetic model for the oxidation of DEA will be developed with the use of an automatic kinetic model generation tool called Genesys, developed at the Laboratory for Chemical Technology.[4] A prerequisite for the generation of detailed kinetic models is the availability

of accurate thermodynamic and kinetic data. Due to the lack of accurate experimental data for nitrogen-containing compounds, computational chemistry is the only viable alternative. Because of the complexity of the generated model, not all parameters can be obtained via computational chemistry and hence approximation methods are required. In Genesys, Benson's group additivity method [5] based on *ab initio* calculations is used to assign rate coefficients to reactions and thermodynamic parameters to species. The implemented group additivity method is extended to enable the approximation of these properties for nitrogen-containing compounds.[6, 7] Both for radical and non-radical nitrogen-containing species as well as for the main reaction families (hydrogen abstraction, β -scission) new group additivity schemes are determined in this work. In Figure 3, the methodology is depicted for determination of both the forward and reverse rate coefficient of the hydrogen abstraction from the N-H bond in DEA by a hydrogen atom making use of the calculated group additivity values.

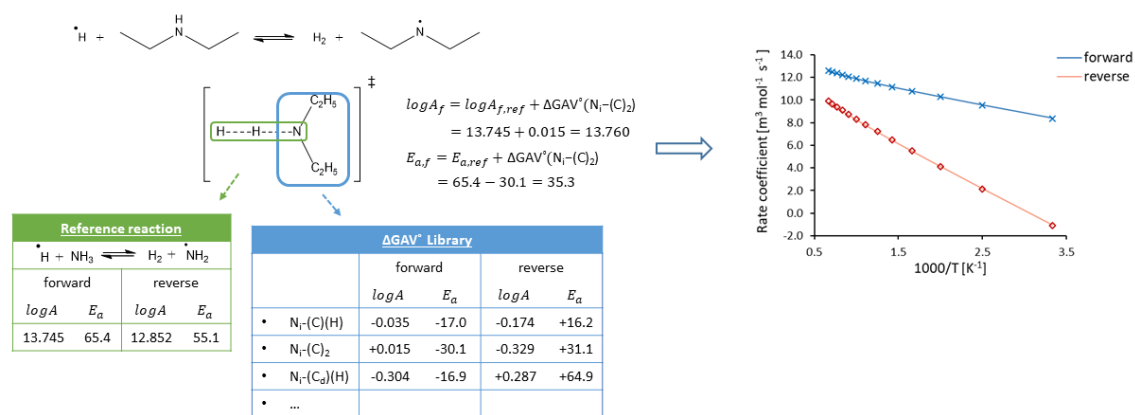


Figure 3: Methodology for determining the Arrhenius parameters of the hydrogen abstraction from the N-H bond in DEA making use of the calculated group additivity values. Arrhenius plot of both the forward (blue) and reverse (red) reaction rate coefficients: full lines indicate the *ab initio* calculated values, data points indicate the group additivity approximated values.

For the determination of both the thermodynamic and kinetic parameters from *ab initio* calculations, the following methodology is used. Electronic structure calculations are performed with Gaussian 09, as implemented on the high-performance supercomputer at Ghent University, at the CBS-QB3 level of theory. The standard enthalpy of formation, the standard entropy and the heat capacity are all calculated from the Gaussian output file. All internal modes are treated as harmonic oscillators except for low frequency hindered rotors with a hindrance potential exceeding a certain threshold value (12 kcal/mol). These are approximated by one-dimensional hindered internal rotations. The hindrance potentials are calculated at the B3LYP/6-31G(d) level of theory with relaxed surface scans in which all coordinates, except for the considered dihedral angle, are re-optimized at each scan angle. The Fourier series expression of the hindrance potential together with reduced moment of inertia calculated at the $I^{(2,3)}$ level, are used to construct the Schrödinger equation for 1-dimensional internal rotation. The eigenvalues of the solution are used to determine the partition function as a function of temperature. The thermodynamic data is calculated from the total partition function after performing a correction for the symmetry and the number of optical isomers. Conventional transition state theory is used to calculate the rate coefficients over a temperature range 300 K – 1500 K with 50 K increment. Tunneling is accounted for using the asymmetric Eckart potential. The resulting rate coefficients are regressed to a simple Arrhenius expression. The

kinetic parameters for the key reactions during DEA oxidation are calculated using this methodology, while the kinetic parameters for the other reactions are approximated with the group additivity method.

5. Contribution to Action's aim

The core of the Action is the development of oxidation and pyrolysis kinetic models for fuels that have a potential to become new smart energy carriers. During the STSM, experiments for the oxidation of a nitrogen-containing model compound for smart energy carriers were performed. [8] The conversion of nitrogen-containing compounds can lead to the formation of NO_x species. [9, 10] By studying the combustion of the secondary amine DEA, which can be considered as one of the most simple nitrogen-containing model compounds present in biofuels, insight can be gained in the conversion of this fuel-bound nitrogen. In order to address the lack of accurate data for nitrogen-containing compounds, new kinetic and thermodynamic data have been determined starting from quantum chemical calculations. Using these data, a model will be developed for the oxidation of DEA in order to study the decomposition pathways of DEA leading to the formation of the main carbon- and nitrogen containing products, among which NO_x species.

6. Future collaboration

During future collaboration, a detailed kinetic model for DEA pyrolysis and oxidation will be developed. The kinetic model development will be in collaboration with the group of Frédérique Battin-Leclerc (host institute). Further details about the collaboration will be discussed over a Skype meeting.

7. Confirmation by host institute of successful execution

The confirmation by the host institute is attached to the mail.

8. Resulting publications

An abstract and manuscript, concerning the pyrolysis and oxidation of DEA, will be submitted for the 9th European Combustion Meeting (ECM2019) in April 2019.

9. References

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