

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 (18th – 22nd of February 2019) is the continuation of the STSM 41397 (3rd – 28th of September 2018), which is a 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 is to perform experiments with the jet-stirred reactor, available in Nancy, to investigate the pyrolysis 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. The helium flow rate is controlled by a gas-mass-flow controllers (Bronkhorst), while the liquid fuel mass flow rate is regulated by a liquid-Coriolis-flow controller (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 two gas chromatographs which enable online quantification of the product species. The first gas chromatograph makes use of a PLOT-Q capillary column and a flame ionization detector preceded by a methanizer. The second 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 third 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%.

3.2. Experimental results

Experiments are performed to study the pyrolysis of DEA in the JSR reactor. The temperature is varied from 750 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. A total of 27 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. The main carbon-containing products are methane, ethane and ethylene, while the main nitrogen-containing compounds are hydrogen cyanide, acetonitrile, propane nitrile and acrylonitrile (Figure 1).

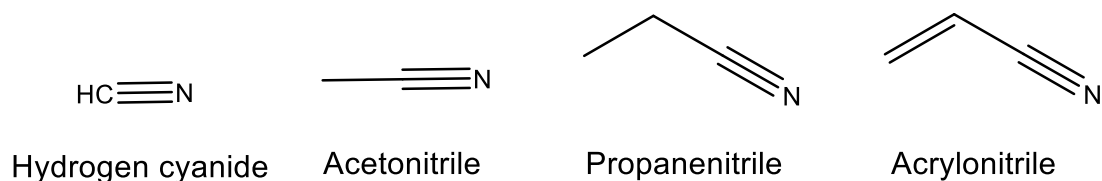


Figure 1: Main nitrogen (and carbon)-containing products resulting from the pyrolysis of DEA.

In the intermediate temperature range, i.e. from 800 K to 1000 K, large nitrogen-containing recombination products are formed, containing five carbon atoms and at least two nitrogen atoms.

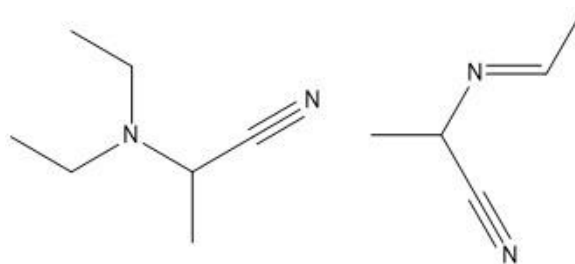


Figure 2: Large nitrogen-containing recombination production formed during the pyrolysis of DEA.

4. Kinetic modeling during and after STSM

A kinetic model for the oxidation of DEA is 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.

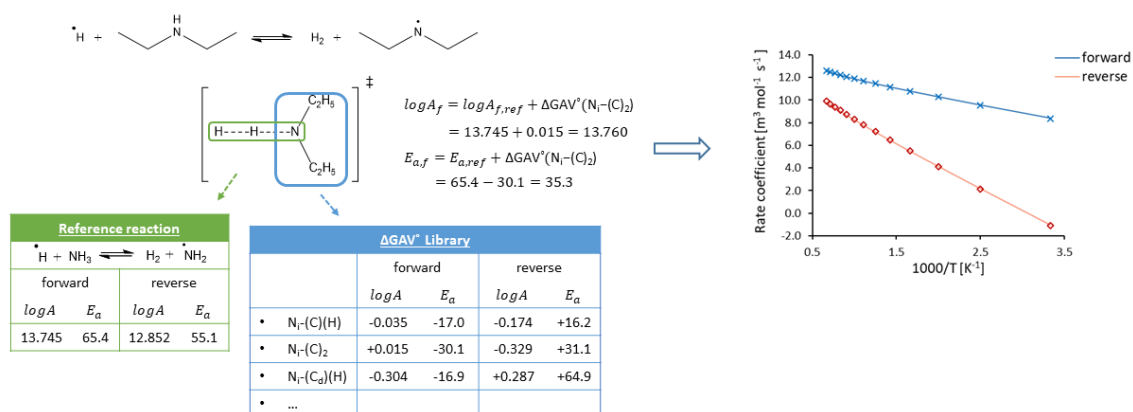


Figure 3: Methodology for determining the Arrhenius parameters of the hydrogen abstraction from the N-H bond in DEA making use of the calculated group additivity values. Arrhenius plot of both the forward (blue) and reverse (red) reaction rate coefficients: full lines indicate the *ab initio* calculated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

The mole fractions of the major products for both oxidation ($\phi=1$) and pyrolysis of DEA are presented in Figure 4. Overall, a good agreement is obtained between the experimental data and the predictions obtained with the microkinetic model.

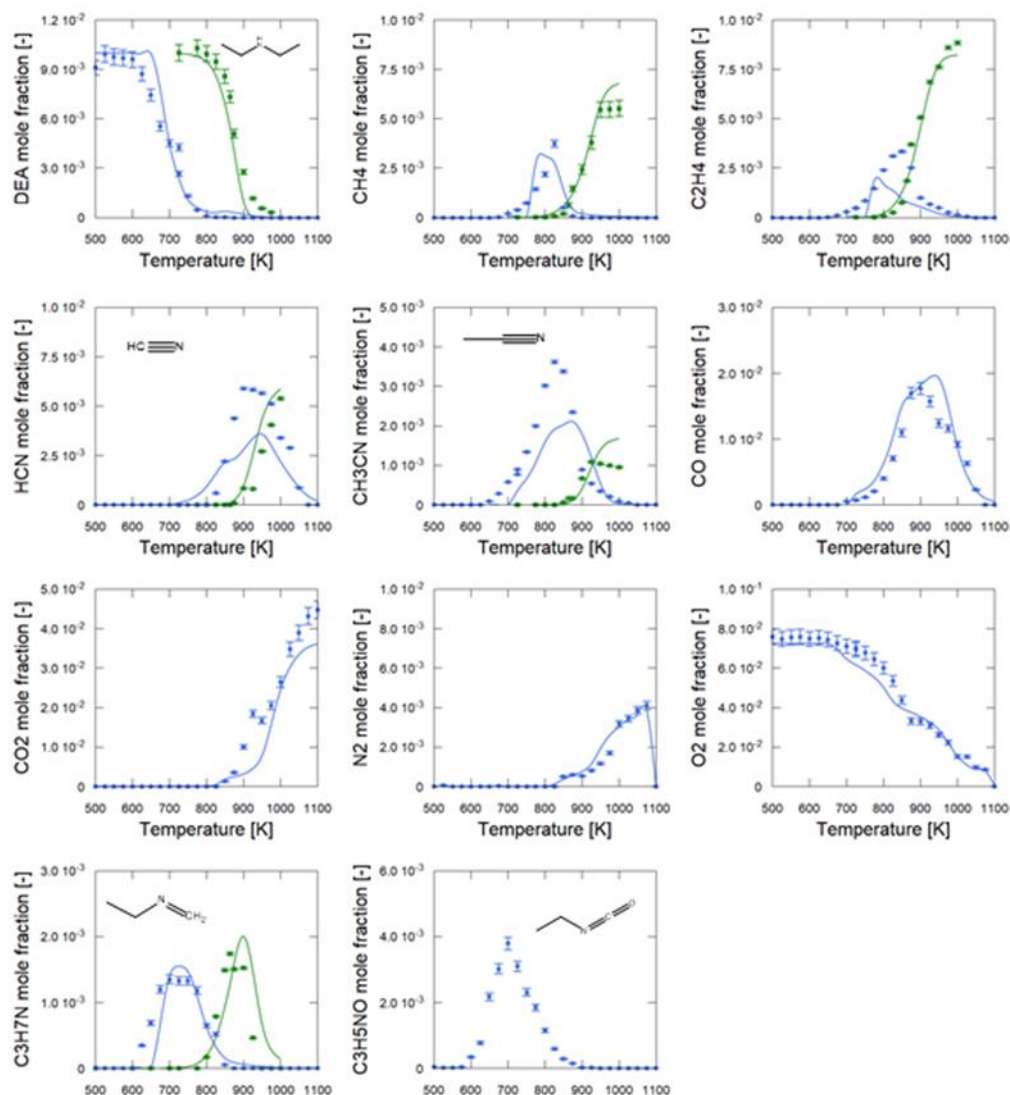


Figure 4. Experimental major product yields for the pyrolysis (green) and oxidation (blue) of DEA. Experiments (symbols) and simulations (lines) are compared. Experimental conditions are 1.07 bar, DEA inlet mole fraction 0.01 and space time 2.0 s for a reactor volume of 81.2 cm³. Experimental relative uncertainties are 5% for species calibrated with a known substance amount and 10% for calibration with the effective carbon number method.

When comparing pyrolysis and oxidation, the reactivity of DEA starts at respectively 775 K and 625 K, while complete conversion is reached at respectively 925 K and 800 K. During oxidation, the same nitrogen-containing products are formed as during pyrolysis, except from one specific nitrogen- and oxygen-containing intermediate species.

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 pyrolysis of a nitrogen-containing model compound for smart energy carriers were performed. [8] This was done in order to complement the oxidation experimental data acquired during the previous STSM. 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 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 the newly acquired pyrolysis data in addition to the oxidation experimental data acquired in the previous STSM, a model has been developed for the combustion of DEA.

6. Future collaboration

The development of the first-principles-based kinetic model for DEA pyrolysis and oxidation will be continued, 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

The performed work concerning the pyrolysis and oxidation of DEA will be presented at the 9th European Combustion Meeting (ECM2019) in April 2019.

(<https://ecm2019lisbon.wixsite.com/ecm2019>)

9. References

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