Investigations on the Deposit Formation and Decomposition from Urea in SCR Systems

AUTHORS

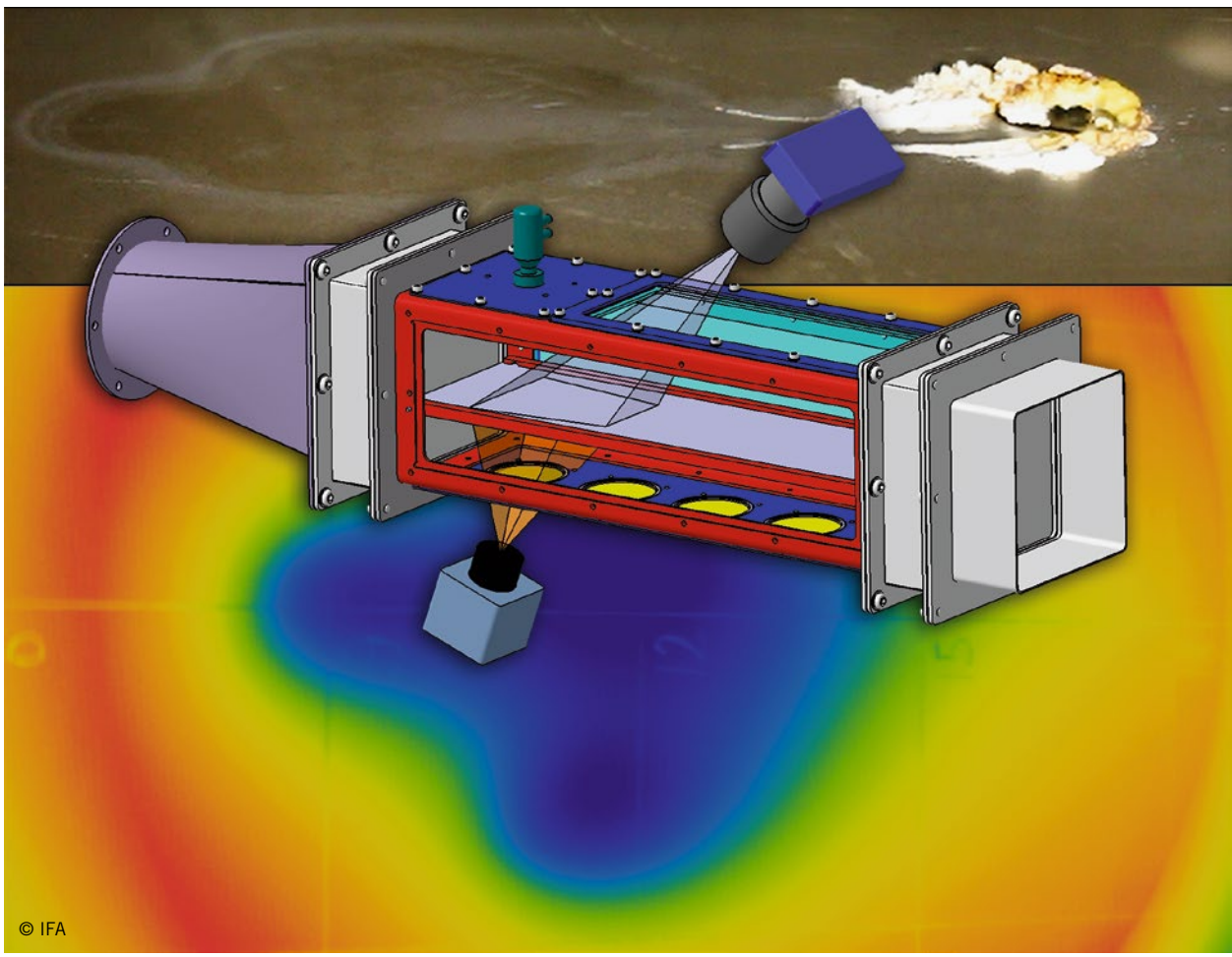
Dipl.-Ing. Uladzimir Budziankou is Project Assistant in the area of SCR Modeling at the Institute for Powertrains and Automotive Technology (IFA) of the Vienna University of Technology (TUW) (Austria).

Christian Kuntz, M. Sc. is Research Associate in the group "Multiphase Processes and Reactors" at the Institute of Chemical Technology and Polymer Chemistry (ITCP) of the Karlsruhe Institute of Technology (KIT) (Germany).

Dr. Marion Börnhorst is Head of the group "Multiphase Processes and Reactors" at the Institute of Chemical Technology and Polymer Chemistry (ITCP) of the Karlsruhe Institute of Technology (KIT) (Germany).

Prof. Dr. Thomas Lauer is Associate Professor at the Institute of Powertrains and Automotive Technology (IFA) of the Vienna University of Technology (TUW) (Austria).

Long-term reliability and high conversion rates are major criteria for engine exhaust aftertreatment with selective catalytic reduction by a Urea-water Solution. Unfavorable operating conditions may lead to the formation of solid deposits which degrade the system efficiency. Within the framework of the FVV project no. 1262, at the Karlsruhe Institute of Technology (KIT) and the Vienna University of Technology (TUW), fundamental experimental and numerical investigations on deposit formation and decomposition were carried out.



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1 MOTIVATION

Selective Catalytic Reduction (SCR) is a widely used aftertreatment solution to remove nitric oxides (NO_x) from the exhaust gas of diesel-fueled vehicles. The reducing agent ammonia, which is added to the exhaust gas by injecting a Urea-water Solution (UWS) as carrier fluid, reduces the nitric oxides to nitrogen and carbon dioxide in a downstream SCR catalyst.

Due to space restrictions as well as low-load or highly transient operating conditions, the dosing of the carrier fluid may result in liquid film formation on mixer blades or pipe walls and a slow or even incomplete evaporation. As a result, urea reactions induce the formation of solid by-products like biuret, cyanuric acid or ammelide [1, 2]. Solid deposits affect the system efficiency in a negative way, as they increase back pressure and decrease the formation of ammonia and its uniformity over the catalyst cross-section. Therefore, a numerical approach is desirable in order to predict deposit formation and thus contribute to a cost-effective development of SCR systems. The necessary research was carried out in the framework of this FVV project at the Institute of Chemical Technology and Polymer Chemistry (ITCP) of the Karlsruhe Institute of Technology (KIT) and at the Institute for Powertrains and Automotive Technology (IFA) of the Vienna University of Technology (TUW).

2 EXPERIMENTAL SETUPS

Detailed experimental observations are necessary to understand the underlying processes of deposit formation and to develop and validate the numerical models. The test bench setup at the Vienna University of Technology, **FIGURE 1**, is designed to produce solid deposits under conditions, which are similar to those within a mixing section of a mobile SCR system [3]. To measure the propagation of the liquid film due to shear forces and gravity, an optically accessible box was integrated in which the UWS injection is carried out on a 2 mm thick impingement plate. The spray deflection, film propagation, deposit formation and cooling of the impingement plate were documented with laser diffraction, video and infrared imaging. Exhaust-typical temperatures and mass flows of a turbocharged diesel engine can be adjusted by selecting the operating point. Steady-state and transient experiments are used to investigate the mechanism of deposit formation under various operating conditions, such as the influence of changes in temperature, mass flow and injection strategy.

Deposits that were generated and sampled at the test bench were subsequently examined with respect to their chemical composition by Thermogravimetric Analyses (TGA) and High-performance Liquid Chromatography (HPLC). TGA was performed in a Netzsch STA 409 C instrument to reveal the sample mass loss due to evaporation and chemical reactions over temperature. For quantitative analysis of the deposit composition, HPLC measurements were performed with a Hitachi VW12 HPLC instrument

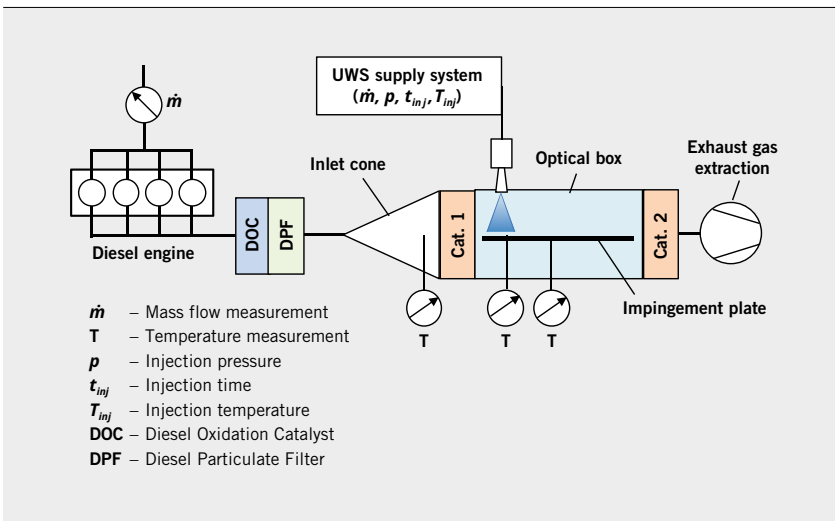

FIGURE 1 Layout of the engine test bench setup for investigating deposit formation (© IFA)

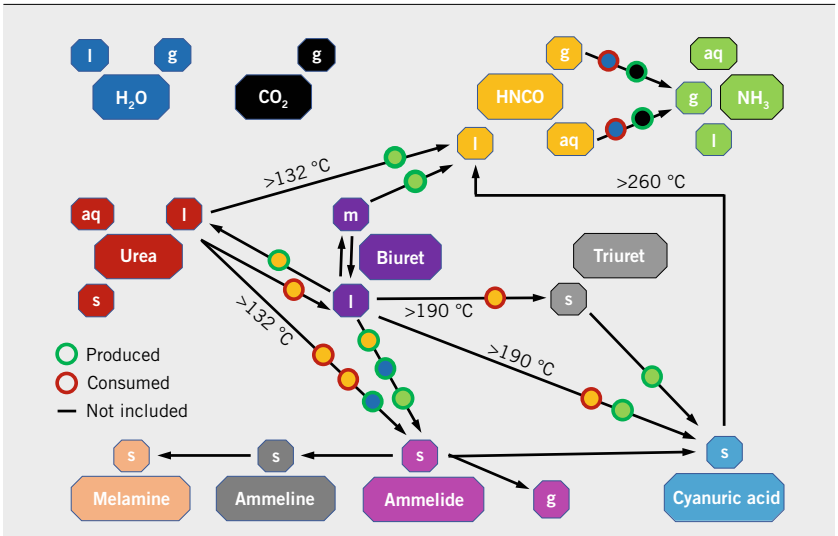

FIGURE 2 Urea decomposition mechanism (© ITCP)

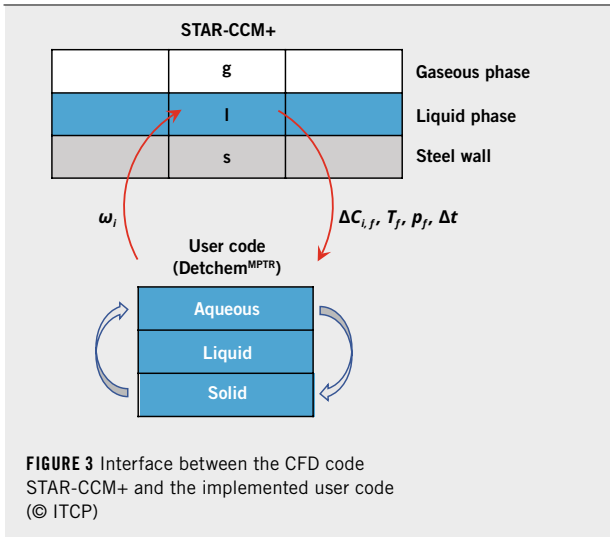

FIGURE 3 Interface between the CFD code STAR-CCM+ and the implemented user code (© ITCP)

employed with a L-2200 sampler. Deposits were dissolved in a N_2HPO_4 buffer solution at a constant pH of 10.4 [4].

Based on several TGA and Differential Scanning Calorimetry (DSC) experiments of pure urea and its by-products a kinetic model by Brack et al. [5] was extended with thermodynamic equilibria between the different states of aggregation (gaseous, liquid, solid) and adapted for the implementation into the Computational Fluid Dynamics (CFD) simulation [6], **FIGURE 2**.

3 MODELING APPROACH

The two main challenges of modeling deposit formation are, on the one hand, the considerable number of physical and chemical processes involved, like spray impingement, liquid film formation and propagation as well as the complex chemical schemes in the liquid film. On the other hand, a huge variety of time scales from microseconds of droplet impingement events up to several minutes of deposit formation must be covered by one numerical method. The software Star-CCM+ v13.06 enables simulations with the necessary temporal and local resolution. To adapt this CFD program, modifications to the spray and film model [7] as well as a coupling with detailed chemistry and an implementation of a source term approach were carried out.

In a first step, the chemical reactions in the liquid film, that were solved with the software package Detchem [8], were implemented through a user coded interface, **FIGURE 3**. Each cell that contains liquid film represents a 0-D batch reactor model containing one gaseous (g), one liquid (l), one aqueous (aq) and multiple solid (s) phases. The data of concentrations $c_{i,f}$, temperature T_f and pressure p are transferred from the CFD code to the user code for each liquid film cell in each time step Δt where reaction rates ω_i are calculated by the user coded algorithm. All physical processes, such as gas-liquid equilibria, are calculated in the CFD code. In a second step, the modeling of large time scales was investigated. In order to speed-up the CFD simulation, the numerical parcels that represent the spray were substituted by source terms of mass, momentum and energy. These source terms were calculated simultaneously during a single injection event, stored and applied to the film and gaseous phase in the following transient simulation with long time durations [4].

With this procedure, physical times of 45 s/day could be simulated using one computer core per 30,000 cells. In spite of the additional preparation work of pre-calculating the source terms for the specific operating conditions this is a substantial improvement compared to conventional CFD techniques.

4 MODEL VALIDATION WITH EXPERIMENTS

An extensive number of experiments and simulations were compared to determine the potential and validate the modeling approach. As an example, a comparison between simulated and observed deposit formation after 5 min, **FIGURE 4** (top), and after 20 min experiment time, **FIGURE 4** (bottom), is shown, for which the operating conditions are shown in **TABLE 1**. The first column depicts the simulated thickness of the liquid film, the middle one the thickness of solid deposits and the right one the corresponding experiment. After 5 min injection time, the simulated spreading area of the film is in good agreement with the observation, most deposits are predicted on the left side of the liquid film, which also correlates well with the experimental data. After end-of-injection the film temperature starts to rise and a rapid film evaporation can be observed. Further propagation of the film is inhibited due to its higher viscosity and adherence of solid deposits to the steel surface, which can be seen after 20 min experiment time. The simulation is qualitatively in good agreement, but overpredicts the final position of the solid deposits by approximately 40 mm. The main reason for this deviation is that the current 2-D liquid film model cannot simulate the adherence of solid deposits to a surface. This will be a topic for future work.

The main component of the simulated deposits at the end of the first part of the experiment is biuret. After end-of-injection the film temperature starts to rise which causes the decomposition of biuret to ammelide (60 %), biuret matrix (28 %) and cyanuric acid (12 %). In contrast, the solid deposits from the experiment mainly consisted of cyanuric acid (81 %) and ammelide (12 %). Deviations between experiment and simulation

may be caused by to a low concentration of isocyanic acid in the simulated liquid film, which is necessary for the reaction of biuret to cyanuric acid. Due to the high saturation pressure of isocyanic acid, it evaporates quickly from the liquid film and, hence, is not available for its reaction with biuret. The revision of the thermodynamic properties and the use of an updated kinetic model by Tischer et al. [8] may further improve the simulation results in terms of the deposit composition.

Operating condition	Values
Exhaust gas mass flow [kg/h]	1000
Exhaust gas temperature [°C]	275
Duration of experiment [min]	20
Duration of injection [min]	5
Injection rate [mg/s]	35

TABLE 1 Operating conditions of the experiments on the test bench setup (© IFA)

5 SUMMARY

Within the research project, detailed experimental and numerical investigations on multiphasereacting flows in SCR systems were carried out, thus creating a comprehensive modeling approach for deposit formation from the UWS. The relevant physical and chemical processes were studied with advanced measuring techniques at realistic operating conditions. The obtained deposits were analyzed using TGA and HPLC measurements. Based on analysis data and thermodynamic considerations, the urea decomposition model was extended and kinetically adapted.

For the modeling of the deposit formation, turbulent flows, heat transfer, UWS injection, formation and propagation of the film were considered. The resulting simulation model was combined with a new source term approach in order to substantially speed up the calculations. This made it possible to represent several minutes of an experiment in one simulation. The results are in a reasonable agreement with the experimental results from the test bed regarding the position and composition of the deposits. Further improvement and adaptation of the model and the kinetics is necessary and already in progress.

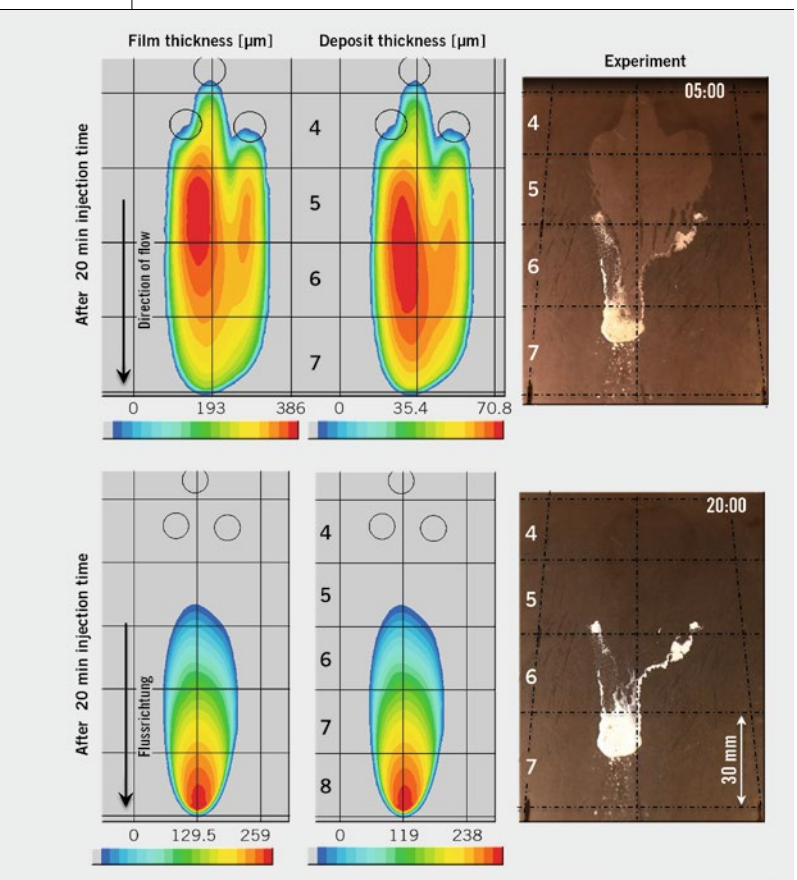

FIGURE 4 Film and deposit formation on the impingement plate: simulated film thickness (left), simulated thickness of solid deposits (center) and experimentally generated deposits after 5 min experiment time (top) and after 20 min experiment time, respectively (© IFA)

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