

Optical and Numerical Investigations on the Mechanisms of Deposit Formation in SCR Systems

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ABSTRACT

Long-term reliability is one of the major requirements for the operation of automotive exhaust aftertreatment systems based on selective catalytic reduction (SCR). For an efficient reduction of nitrogen oxides in the SCR catalyst it is desirable that the thermolysis of the injected urea water solution (UWS) is completed within the mixing section of the exhaust system. Urea might undergo a number of secondary reactions leading to the formation of solid deposits on system walls. A deeper understanding of the mechanisms and influence factors is a basic requirement to prevent and predict undesired decomposition products.

This paper outlines the mechanisms of UWS transport and deposition on a typical mixing element geometry. The conditions leading to deposit formation were investigated based on optical and temperature measurements in a box with optical access. A good correlation with the deposit location observed at the close-to-series exhaust system was found. A chemical analysis complemented the investigations. Wall film formation and propagation within the SCR system were simulated with a validated CFD model. Numerous influence parameters were studied and integrated into a predictive post-processing routine.

The observations show that deposits can be formed up to Leidenfrost temperature. The liquid film pathways did not change significantly depending on the operating conditions. An increase of the UWS injection rate solely shifted the deposit location.

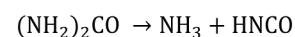
Further work is necessary to enhance and verify the modelling approach with respect to wall film and deposit chemistry. It will also focus on decreasing simulation wall time.

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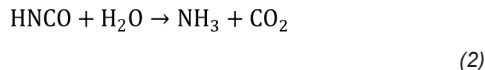
INTRODUCTION

Stringent legislative emission standards for diesel engines have forced car manufacturers to develop exhaust aftertreatment technologies for the further reduction of nitrogen oxides. Among the available systems, the selective catalytic reduction (SCR) has proven to be one of the most promising techniques that has been successfully introduced in series production for both light [1] and heavy duty vehicles [2]. Automotive SCR systems are subject to ongoing development and will increasingly be used with the introduction of future emission limits such as Euro 6 and the American Tier 2 BIN 2 standards [3].

Mobile SCR systems typically use a 32.5 wt % urea water solution, also known as AdBlue or Diesel Exhaust Fluid (DEF), which is injected into the hot exhaust gas in the mixing section upstream of the SCR catalyst. The ammonia that is necessary for the reduction of nitrogen oxides is then generated from the UWS in a decomposition process that follows the evaporation of the water content. It is generally understood that urea melts and decomposes into equal amounts of gaseous ammonia (NH₃) and isocyanic acid (HNCO) at temperatures above 133 °C through the following thermolysis reaction [5, 6, 7, 8, 9]:



In the subsequent hydrolysis reaction the isocyanic acid is then converted into ammonia and carbon dioxide (CO₂):



In order to enhance the UWS preparation process, mixing elements are used to decompose the liquid more rapidly. On the one hand this is achieved through the break-up of impinging droplets into smaller droplets. On the other hand this is realised through the formation of a liquid film on the blades of the mixing element. The direct contact between the UWS and the hot components of the exhaust system significantly increases the heat input into the fluid, thus accelerating the evaporation and decomposition process [21, 22].

The thermolysis reaction has been observed to take place instantaneously when urea has reached its melting point. By contrast the hydrolysis reaction occurs only to a very little extent and at elevated reaction temperatures ($\geq 400^\circ\text{C}$) unless further measures, such as the use of an adequate catalyst, are taken [6]. Since the SCR catalyst handles this task, it is desirable that the thermolysis reaction is completed within the mixing section of the exhaust system. However, during this process urea might undergo several undesirable secondary reactions that can lead to the formation of solid deposits on the walls of the exhaust system. As a result of the availability of gaseous HNCO in the vicinity of melted urea the formation of biuret is a possibility and also a starting point for consecutive reactions including the formation of cyanuric acid, ammeline, ammelide and melamine. Furthermore, HNCO may react with itself in a trimerisation reaction to form cyanuric acid which is also known to be subject to consecutive reactions.

A detailed literature review will be given in the following section. A parameter study on a close-to-series exhaust system is presented and the mechanisms of deposit formation such as liquid film formation and transport as well as deposit formation and growth are depicted on a typical mixing element geometry. A correlation between the numerical results and the measurements is presented and a study of a multitude of influence parameters affecting the risk of deposit formation is conducted. Finally, a post-processing method is derived to estimate the deposit formation risk.

LITERATURE REVIEW

The relevant deposit formation chemistry is complex and has been addressed by a couple of authors, such as Dong et al. [7] and Fang and DaCosta [8]. Schaber et al. [5] present the most elaborate description. A validated kinetic model is discussed by Ebrahimian et al. [9].

However, whether deposits are formed also depends on the flow field and thermodynamic as well as geometrical boundary conditions. Great efforts have been made to study the influence of various process parameters on the decomposition efficiency of urea under laboratory conditions [6, 10]. Model-

based studies on the influence of process parameters provide a more detailed and theoretic insight into the mechanisms underlying deposit formation and decomposition [9, 11]. Theoretical considerations about the various sub-processes complement numerical and experimental results [11, 18]. Furthermore, alternatives to the classic SCR technology are discussed based on thermodynamic considerations [19]. Simplified setups were used to provoke and analyse deposits generated under defined conditions [16]. Geometries with optical access have been used to study various impact plate setups and injection strategies [17]. In a similar manner the extent of wall wetting has been investigated [13, 17]. The authors conclude that deposit formation can be impeded if wall wetting is prevented. Zheng et al. [13] consider permanent wall wetting as the critical boundary, whereas Nishioka et al. [17] assume that deceeding Leidenfrost temperature will lead to deposit formation. The evaluations do not take into account further wall film properties. Parameter studies on (close-to-) series exhaust systems have aimed at improving performance and reducing deposition risk. Numerous boundary conditions facilitating deposit formation have been identified and recommendations for improved setups have been made [7, 11, 12, 13, 14, 15, 16]. Dong et al. [7] observed that improvements in spray quality impeded deposit formation. The experimental studies of Strots et al. [14] revealed that deposits could be found everywhere within the aftertreatment system from the injector to the SCR catalyst face. Numerous studies showed that increased exhaust and ambient temperatures reduced the risk of deposit formation and recommended the usage of thermal insulation [11, 13, 14]. The investigations of Zheng et al. [13] showed that the usage of S-bend injector mountings and mixing elements was beneficial for both ammonia uniformity and deposit formation risk. The combined application of numerical and experimental techniques has become a common practice [11, 12, 13, 15, 17, 20]. Especially the use of CFD simulations has proven to be capable to substantially support the development process of SCR systems. It is frequently used to evaluate the ammonia uniformity upstream the SCR catalyst [21, 22, 23, 24], but can also help to identify situations facilitating urea deposition. In the area of the injector dome, recirculation zones and welding gaps were correlated to deposit formation and geometry optimisations suggested based on CFD results [11, 12, 15]. In general, droplet impingement and liquid film are seen as a precursor for deposit formation [11, 13, 17, 22]. However, there is great insecurity about the temperatures at which deposit formation is possible. Often the Leidenfrost temperature was given as a critical wall temperature above which deposit formation is expected to be negligible. Values ranging from $T_{\text{wall}} = 190\text{...}210^\circ\text{C}$ [13] up to $T_{\text{wall}} = 265\text{...}280^\circ\text{C}$ [25] have been reported. Further results confirm the dependency of the critical temperature on the actual experimental setup [22].

Most works focused on the identification of basic correlations. Considering the complex flow field and spray dynamics it is questionable if the prediction of deposit formation is possible without taking into account the complex interaction of the multitude of influence factors. More recently, Munn and Strots [26] have

[11] investigated on spray distribution and wall wetting using CFD simulations. Based on the locations and amounts of generated wall film a mixing section geometry could be optimised. However, the formation of a wall film does not necessarily result in deposit formation since the latter is highly dependent on the liquid film pathways and properties as well as their evolution during longer timescales. It is the aim of the presented work to investigate on the relevant influence factors.

CHEMISTRY OF DEPOSIT FORMATION

Figure 27 (appendix) depicts three major temperature regimes. For low UWS temperatures ($T \leq 133^\circ\text{C}$, “a”) urea remains in solution and is not subject to noticeable decomposition. It may however partly recrystallise if the temperature-dependent crystallisation limit is exceeded. The corresponding urea mass fractions can be found in Figure 1.

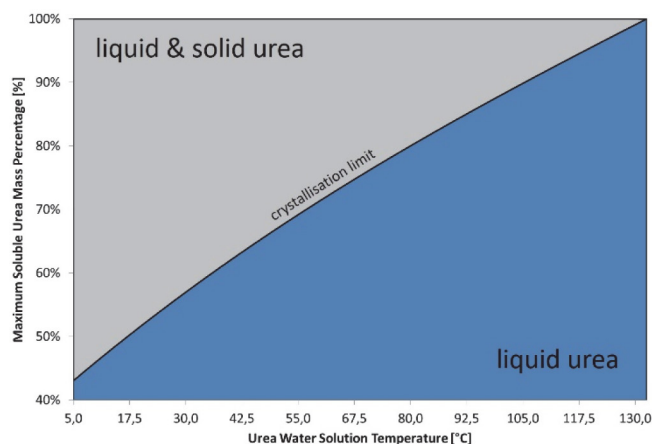


Figure 1. Urea crystallisation limit as a function of the temperature according to Kontin et al. [26]

In the second temperature regime ($133^\circ\text{C} < T < 160^\circ\text{C}$, “b”) urea starts to decompose slowly. Yet, secondary reactions cannot be observed prior to the third temperature regime ($T \geq 160^\circ\text{C}$, “c”), which is characterised by significant urea decomposition rates. However, secondary reactions are bound to the availability of gaseous HNCO . Due to the complexity of the urea thermolysis kinetics it is obvious that universally valid reaction rates cannot be given in a form as simple as depicted in Figure 27 (appendix). Still, the chart gives a good overview about the approximate temperature ranges at which single components are produced or decomposed and relates the corresponding rates to each other. It shall be used as a rough guideline.

INVESTIGATIONS ON A SERIES EXHAUST SYSTEM

Test Bench Setup and Operating Conditions

The investigations were carried out on a state-of-the-art passenger car underbody SCR system. The setup included a turbocharged 4 cylinder 2.1 l series diesel engine equipped

with a DOC, DPF, an S-bend pipe injector mounting and an SCR catalyst, see Figure 2. The mixing section was equipped with a static mixing element and a 16° 3-hole injector.

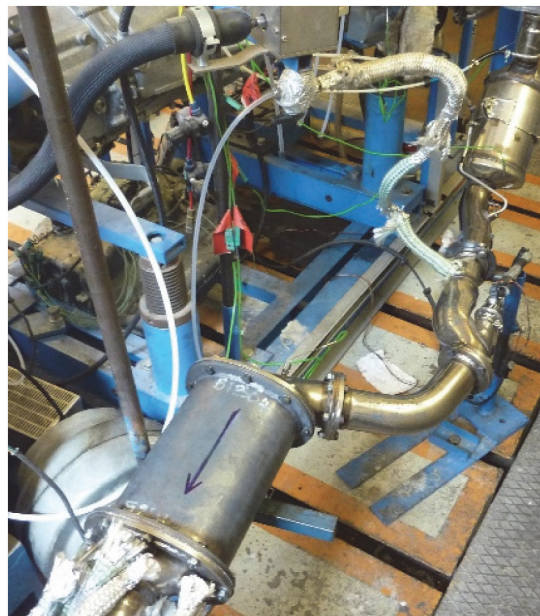


Figure 2. Test bench setup of the series exhaust system

Both SCR catalyst light-off and significant urea decomposition rates are reached at temperatures above 180°C [5, 19]. The latter is therefore a typical temperature for the onset of UWS injection. Moreover, especially low-temperature operating points have been found to be related to deposit formation [13] and occur frequently during typical test cycles [22]. Therefore, the selected operating points (OPs) are considered as representative for typical conditions with a high risk of deposit formation. A stoichiometric injection rate $\dot{m}_{\text{UWS}} = 13 \text{ mg/s}$ ($\alpha = 1$) has been chosen for the lowest temperature operating point. Since overstoichiometric injection is a common practice at low temperature OPs to fill up the catalyst NH_3 storage [4], an increased injection rate $\dot{m}_{\text{UWS}} = 35 \text{ mg/s}$ ($\alpha = 2.9$) has been added and kept constant during exhaust temperature variation, see Table 1. The injection frequency is set to 3 Hz for all OPs.

Table 1. Operating conditions for the experiments on the series exhaust system

Operating Point	Unit	OP 180/13	OP 180/35	OP 200/35	OP 220/35
Exhaust temperature	[°C]	180	180	200	220
Exhaust mass flow	[kg/h]	100	100	100	100
UWS injection rate	[mg/s]	13	35	35	35
UWS injection freq.	[Hz]	3	3	3	3
Experiment duration	[hrs]	2	4	4	4

Study of Deposit Formation in a Series Exhaust System

All experiments were started from a clean, deposit-free system. UWS injection was initiated when steady state operating conditions had been reached. When the predefined injection duration had been completed, the system was shut down immediately and the mixing pipe was dismantled for documentation. When required, injector and mixing pipe were weighed separately. The deposit weight was obtained by comparing the difference in weight of the system before and after the experiments. Measurement accuracy was ± 0.01 g.

Initial investigations on deposit formation were carried out for OP 180/13. Four separate experiments were conducted, each starting from a clean, deposit-free system with durations of 15, 30, 60 and 120 min, see [Figure 3](#) (30 and 60 min not shown). Deposits appear to grow linearly with time and the locations of the main deposits remain identical in each experiment. The respective deposit nuclei are clearly visible after 15 min. It becomes obvious that deposit accumulation is slow at the investigated OP, i.e. at stoichiometric injection rate the exhaust system shows a good performance with respect to deposition.

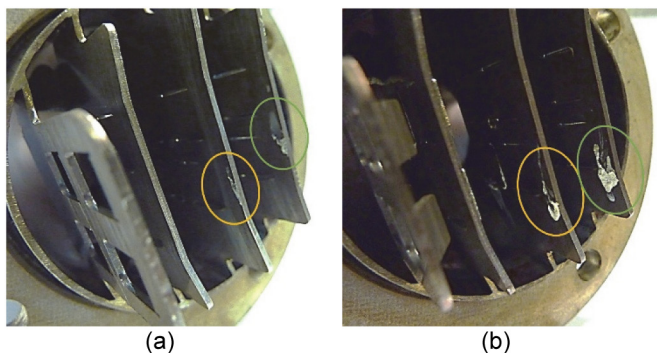


Figure 3. Deposit growth on the mixing element as a function of time at OP 180/13: 15 min (a) and 120 min (b)

A parameter study was carried out to investigate on the locations of deposit formation. Temperature was varied from 180 °C to 220 °C, maintaining a constant injection rate of 35 mg/s and an experiment duration of 4 h. [Table 2](#) depicts that the amount of deposits reduces significantly with increasing exhaust temperature. While at OP 180/35 14.5 % of the injected urea is converted into deposits, the amount is reduced by approximately one order of magnitude at OP 220/35.

Table 2. Deposit amount as a function of the exhaust temperature

Operating Point	Unit	OP 180/35	OP 200/35	OP 220/35
Injected urea mass	[g]	163.8	163.8	163.8
Deposit mass mixing pipe	[g]	23.79	7.21	2.41
Deposit mass injector	[g]	0.17	0.12	0.12
Deposit yield	[%]	14.5	4.4	1.5

The analysis shows that the amount of deposits adhering to the injector varies to a much lesser extent than the overall mass. The thin but closed deposition layer that has spread over the injector cone substantially contributes to the increased deposit weight at OP 180/35 in contrast to the higher-temperature OPs, see [Figure 4](#). It is worthwhile mentioning that despite the deposits that have formed around the injector holes, no blockage has been observed. The distinct temperature-dependency of the deposit weight is not reflected in the optical impression of the deposits that have been formed on the mixing element, compare [Figure 4](#) and [Figure 28](#) (appendix). Since the mixing element is the primary impingement target, it is also the key location for deposition. However, especially at low temperature OPs the enthalpy flux is often not sufficient to guarantee complete preparation of the impinging UWS. Excess UWS strips from the mixer rear edges. Thus, secondary impingement and deposition are shifted to the downstream piping of the exhaust system. The latter accounts for a major fraction of the deposit weight for low-temperature OPs, compare [Figure 28](#) (appendix). Only minor deposits were found on the catalyst inlet.

Deposits on the mixing element can always be found in similar places. Differences can only be identified with respect to the exact location and amount. While the pathways of liquid film trickling alongside the mixing element blades remain similar regardless of the operating point, the different exhaust temperatures result in differing solidification timescales, i.e. at lower temperatures the UWS will cover a larger trickling distance until the entire water content is evaporated and the remaining urea has been converted to deposits.

The comparison between the deposits observed at the injector and the mixing element ([Figure 4](#)) reveals further details. Both areas are exposed to deposit formation. Yet, the underlying mechanisms are of entirely different nature. At the mixing element droplet impingement is the primary cause, since it leads to liquid film generation and trickling, as well as to droplets stripping from its rear edges. The latter effects will be discussed in detail in the work at hand. At the injector, deposit formation is mainly triggered by injector leakage, i.e. liquid film release and droplet ejection after the completion of the actual injection event. Both effects have been observed during experiments at the institute by Mayer [27] and have also been discussed in literature [28]. Numerous parameters have an impact on deposit formation at the injector, such as the open/close characteristics as well as injection velocity and droplet spectrum. Further, the gas exchange and thus the species concentrations within the injector dome are driven mainly by the exhaust flow field. The latter is characterised by low velocity magnitudes and a recirculation zone, see [Figure 5](#), similar to findings in literature, compare [12, 15].

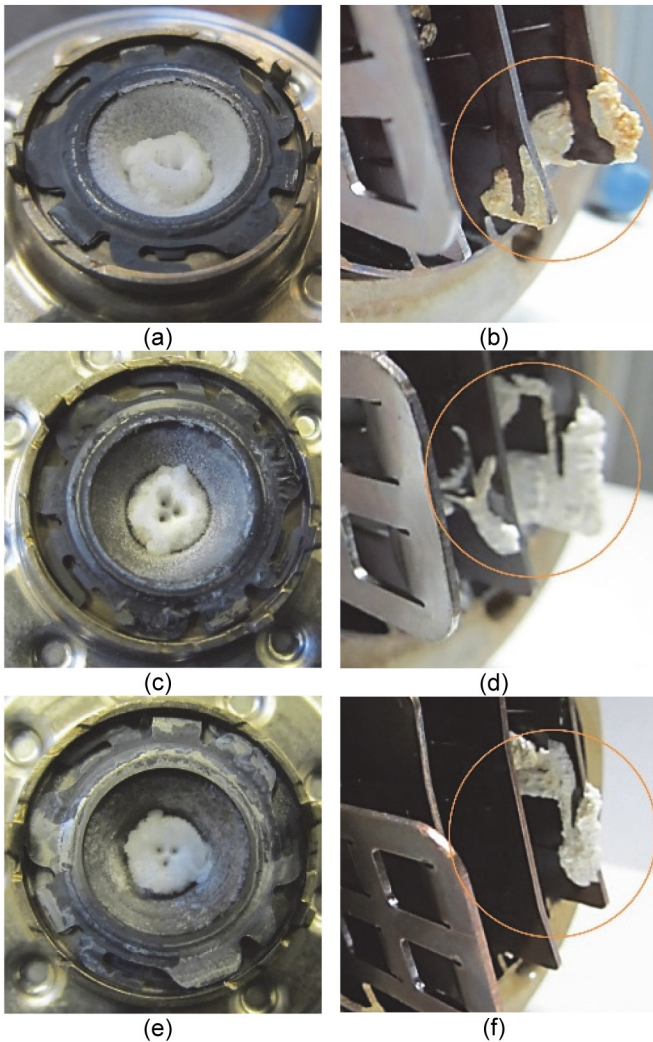


Figure 4. Deposit formation on the injector (left) and on the mixing element (right) as a function of the operating conditions: OP 180/35 (a, b), OP 200/100 (c, d) and OP 220/35 (e, f)

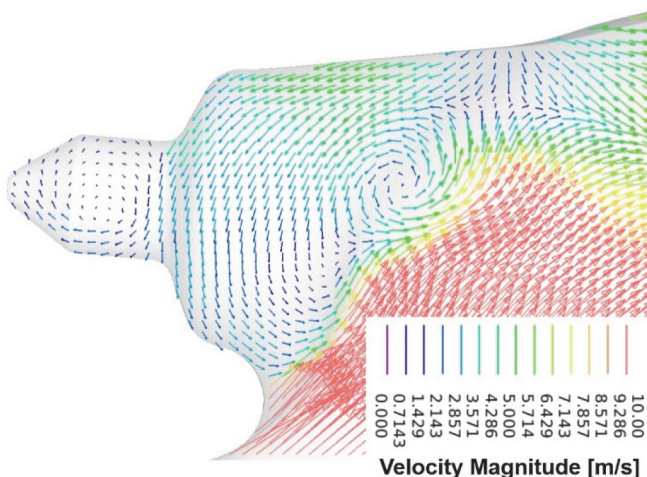


Figure 5. Recirculation zone in the area of the injector dome: OP 180

While increased HNCO concentrations in the vicinity of liquid film do increase the risk for secondary reactions, injector leakage is expected to play the dominant role triggering deposit

formation in the area of the injector. The recirculation of trapped droplets is not inevitably bound to wall film formation in the injection dome. It further applies mainly to small droplets and therefore to a minor fraction of the injected UWS mass, as discussed by Munnannur et al. [11]. Injector leakage on the other hand inevitably leads to liquid film formation in the area of the injection holes. However, a detailed description goes beyond the scope of the simulation method that will be discussed in the following. Due to the differences with respect to the mechanisms of deposit formation the separate consideration of mixing element and injector is an imperative.

DEPOSIT FORMATION ON A MIXING ELEMENT GEOMETRY

In order to gain a deeper understanding of the mechanisms underlying deposit formation, a volume with optical access was built up in order to observe impingement, wall film formation and deposition. It shall allow the identification of liquid film pathways and the localisation of deposit nuclei as well as the investigation of deposition growth, timescales and the influence of further boundary conditions that affect them, such as temperature and injection rate.

Test Bench Setup and Operating Conditions

The investigations were carried out on the test bench described in a previous section. In order to provide substantial optical access to the areas exposed to deposit formation the mixing pipe, including the mixing element and the attached SCR catalyst, were replaced by a box with optical access, see Figure 6(a). Single blade elements were manufactured imitating the geometric features of the original mixing element geometry in terms of characteristic lengths, bend angles and radii as well as edge characteristics, see Figure 7. The elements can be combined and variably mounted within the optical box, allowing to model a large variety of surrogate mixing elements and therefore well-defined impingement conditions, see Figure 6(b). The injector has been mounted on the optical box instead of the S-bend in order to ensure a distance between mixing element and point of injection that is identical to the original setup of the series-exhaust system. The rotational orientation of the injector is also variable.

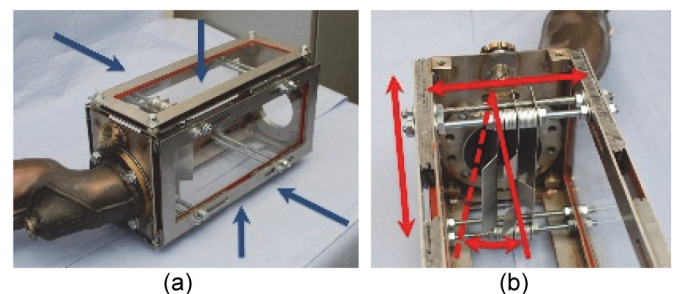


Figure 6. Optical accessibility of the box (a) and setup variability of the blade elements (b)

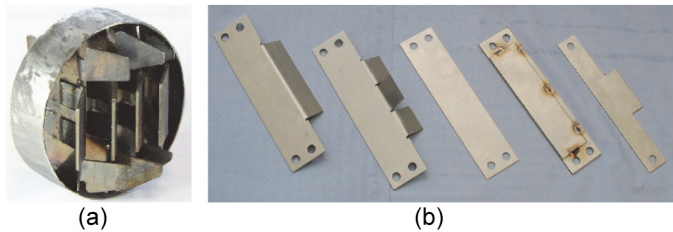


Figure 7. Original mixing element (rear perspective, a) and typical blade elements (b)

A planar light source was used to illuminate the mixing element. A customary Canon 650D DSLR equipped with a Tamron 28...300 mm zoom lens was applied to provide video recordings of the experiments under various perspectives. The test bench setup is shown in Figure 8.

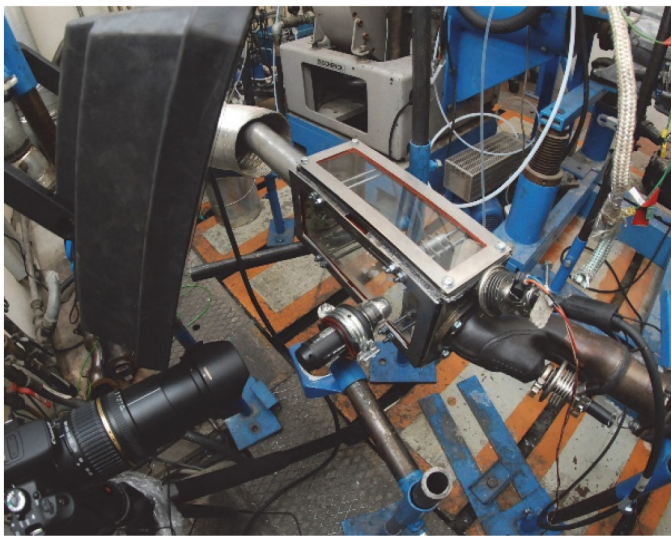


Figure 8. Test bench setup of the optical box

Two operating points have been defined for the parameter study on the optical box, see Table 3. The low-temperature OP is identical to the one that has previously been used, compare Table 1. For the second OP the exhaust temperature has been chosen right below Leidenfrost providing conditions that guarantee both wall wetting and a temperature variation significant enough to allow a clear identification of its influence. The injection rate was varied over a wide range while the exhaust mass flow and the injection frequency have been kept constant.

Table 3. Operating conditions for the experiments with the optical box

Operating point	Unit	OP 180/ $\dot{m}$	OP 250/ $\dot{m}$
Exhaust temperature	[°C]	180	250
Exhaust mass flow	[kg/h]	100	100
UWS injection rate $\dot{m}$	[mg/s]	3.3 ... 35	
UWS injection frequency	[Hz]	3	
Experiment duration	[min]	30, 60	

Mechanisms of Wall Film Transport

A mixing element plate exposed to two injector beams was used to visualise wall film generation and transport. A steady state had been achieved for each operating point considering wall temperature, UWS evaporation, liquid film spreading and transport. It can clearly be observed that the area exposed to wall wetting increases with the injection rate and decreases for rising temperatures. For an exhaust temperature of 180 °C a complete wall film evaporation is unachievable even for lowest injection rates, such as 3.3 mg/s. In contrast, at 250 °C this can be achieved for injection rates as high as 6.5 mg/s, compare Figure 29 (appendix). Excess wall film is transported off the primary impingement zones into adjacent areas. It will be shown that in this case deposition has to be expected.

Wall film that trickles off the primary impingement areas often reaches blade edges. Typically wall film accumulation occurs on the blade side exposed to direct incident flow, see Figure 9(a). Accumulated wall film may then flip onto the reverse side of the blade, see Figure 9(b), where it can also be transported upstream. Edges with intense liquid film accumulation are typically subject to droplet stripping that impinge on subjacent blades, see Figure 9(c), or downstream piping. Blade joints have been identified to distribute wall film onto all adjacent blade faces, see Figure 9(d). The observations indicate that wall film that is not evaporated instantly is extensively distributed on the mixing element. In areas with a distinct flow field, shear stress is the primary driving force for thin liquid films. Gravity plays an increasing role for thick films and in wake regions.

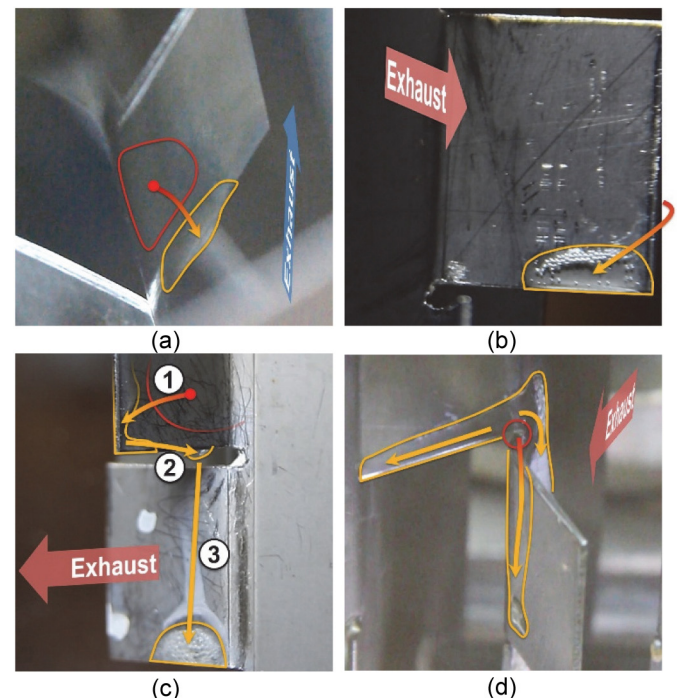


Figure 9. Wall film pathways and accumulation at edges exposed to direct incident flow (a), droplet flipping around edges and accumulation on reverse blade sides (b), droplet stripping from edge and accumulation on subjacent blades (c), wall film distribution at blade joints (d). Primary impingement areas are marked in red, areas with wall film accumulation are marked in yellow.