

The Benefits of Diesel Exhaust Fluid (DEF) Additivation on Urea-Derived Deposits Formation in a Close-Coupled Diesel SCR on Filter Exhaust Line

Matthieu Lecompte
IFP Energies nouvelles, Institut Carnot IFPEN TE

Jerome Obiols
TOTAL Marketing and Services

Jerome Cherel and Stephane Raux
IFP Energies nouvelles, Institut Carnot IFPEN TE

ABSTRACT

Diesel Exhaust Fluid (DEF) like Adblue® is a urea/water solution injected upstream from the SCR catalyst. Urea decomposes into ammonia (NH₃) which acts as reducing agent in the de-NO_x reaction process. However, incomplete decomposition of urea can lead to unwanted deposits formation, thereby resulting into backpressure increase, loss of NO_x reduction efficiency, and durability issues. The phenomenon is aggravated at low temperatures and can lead to restriction or stop of DEF injection below certain exhaust temperatures.

This paper focuses on the influence of the additivation of DEF on deposits formation in a passenger car close-coupled SCR on filter Diesel exhaust line installed in a laboratory flow bench test. The behavior of two different additivated DEF was compared to Adblue® in terms of deposits formation on the mixer and SCRF canning at different temperatures comprised between 240°C and 165°C, and different air flows. The influence of the DEF additivation on the cooling effect of the fluid and the surface temperature of the exhaust line downstream from the injector were also investigated.

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INTRODUCTION

Background

With more and more stringent emission standards for nitrogen oxides (NO_x) worldwide, for both heavy-duty, off-road applications and more recently passenger cars, most Original Equipment Manufacturers (OEMs) have chosen Selective Catalytic Reduction (SCR) technology to reduce NO_x emissions in Diesel engines.

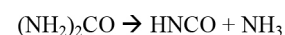
SCR technology requires the injection of a reducing agent upstream from the SCR catalyst to reduce NO_x emissions. The most common reducing agent selected by OEMs for SCR systems is a liquid composed of 32.5% wt. urea and 67.5% wt. deionized water and referenced as AUS 32 (aqueous urea solution) according to the standard ISO 22241 [1]. The German Association of the Automotive Industry (VDA) has registered the trademark AdBlue® for AUS 32 which is the common commercial name used in Europe. It is also referred to as Diesel Exhaust Fluid (DEF) in the US and other countries. For simplification purposes it will be referred to as DEF in this paper.

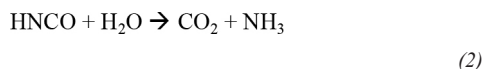
Literature Review on Urea Related Deposits Formation in SCR Exhaust Lines

When DEF is injected as a spray in a hot Diesel exhaust stream, water will evaporated and urea will undergo a decomposition process producing ammonia (NH₃), which is then adsorbed in the washcoat of the downstream SCR catalyst and used to reduce NO_x into nitrogen and water.

The decomposition of urea into ammonia is a complex multi-step process that can lead to undesired side-products. This process has been widely studied in the literature [2, 3, 4, 5, 6, 7] and can be summarized as follows:

The first step consists of the thermolysis of urea into isocyanic acid and ammonia due to the heat (Eq. 1). The second step is the hydrolysis of isocyanic acid which reacts with water to form carbon dioxide and ammonia (Eq. 2)





However, this decomposition of urea can be incomplete due to space limitations on the exhaust line leading to poor mixing and vaporization of the water solution, low exhaust gas temperatures and wall impingement by the DEF. The consecutive steps of deposit formation are impingement, liquid film accumulation, deposit nucleus formation and deposit accumulation [8]. It results in the formation of white solid crystal like substances usually referred to as urea deposits. A schematic example of this process is proposed in Figure 1. These deposits are formed between 150°C and 250°C, are water soluble, mainly composed of urea and biuret and decompose above 250°C [9].

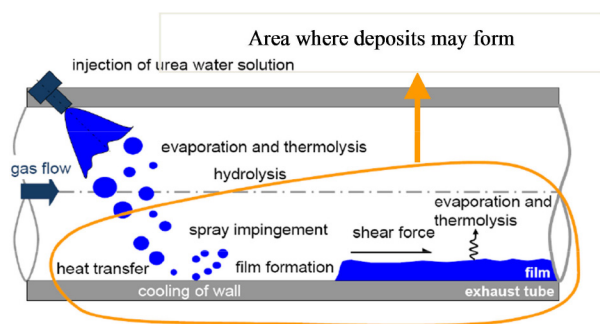


Figure 1. Schematic example of urea related deposits formation process in SCR exhaust line

Also, side reactions can occur during this decomposition process. The isocyanic acid produced during the thermolysis of urea can react with unreacted urea to form biuret and triuret, or other high molecular weight heterocyclic compounds, which are known to form another type of deposits in the exhaust. These high molecular weight compounds are formed at higher temperature in the range of 250°C to 350°C are insoluble and are mainly composed of cyanuric acid, ammeline, melamine and higher molecular weight oligomers such as melam, melem and melon. They start to decompose above 350°C but Weeks et al. [6] observed the presence of deposits between 335°C to 425°C in a Diesel engine exhaust line. The analysis showed that these deposits were mainly composed of cyanuric acid that was not completely reacted even though the exhaust temperature exceeded the temperature at which this compound would thermally decompose, indicating that other factors than temperature could limit the decomposition of cyanuric acid and its derivatives.

At temperatures above 550-600°C, which are typical of Diesel Particulate Filter (DPF) active regeneration events, all deposits can be removed [10-11]. However, on deposits formed in engine exhaust line with low quality DEF spray, some authors observed the presence of polymeric compounds that could not decompose during TGA analysis despite temperature exceeding 1000°C [3].

Urea-derived deposits in SCR exhaust lines are highly undesirable. Indeed, once initiated and formed even in very small quantity, deposits will act as preferential sites for the accumulation of additional deposits [8]. Deposits formation will result in inefficient use of urea, and their decomposition caused by a sudden temperature increase like a DPF regeneration event, can lead to the formation of considerable amounts

of NH_3 , leading to massive NH_3 -slip. Deposits formation is aggravated at low exhaust gas temperature and low ambient temperature and can impose OEMs to restrict or even stop DEF injection below certain exhaust temperatures. For example, Jain et al. [12] mentioned an increase in the threshold temperature of DEF dosing from 190°C to 210°C as a way to minimize deposits formation in city laden cycles. Smith et al. [8] also mentioned the value of 180°C as a typical temperature for the onset of DEF injection for passenger car application, since both SCR catalyst light-off and significant urea decomposition rates are reached above this temperature.

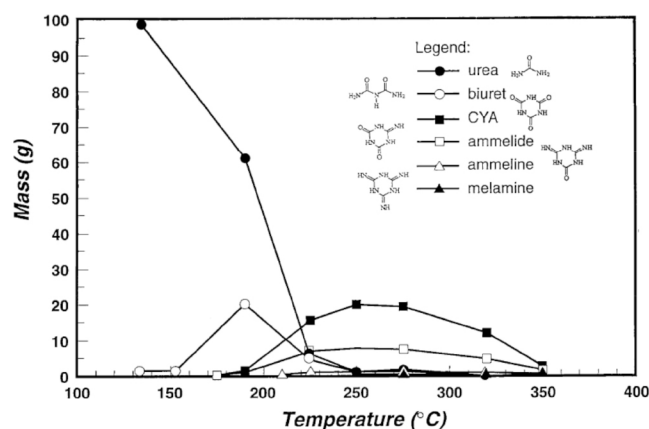


Figure 2. HPLC Mass Plot : urea pyrolysis reaction (assume 100.0 g of urea initially)

Moreover, beyond a certain level of accumulation, which can depend on the exhaust hardware, the presence of deposits can result into significant backpressure increase leading to power losses, increased fuel consumption, loss of NOx reduction efficiency, and potentially triggering a service event. Similarly, Eakle et al. [5] observed stainless steel corrosion initiated by high molecular weight compounds derived from urea decomposition at gas temperatures of 340-360°C. Furthermore deposits formation on the SCR catalyst surface can also block the pores and the active sites of the catalyst, reducing its NH_3 storage capacity and thus its efficiency.

For all of the above reasons, OEMs need to optimize SCR after-treatment systems in order to minimize deposits formation. The main factors increasing the formation of urea derived deposits are well known [5, 11, 12, 13]: low exhaust gas and ambient temperatures, low exhaust flow, high DEF flow, non optimized injector/mixer characteristics and implementation leading to high wall wetting. Improving the DEF spray and its vaporization thanks to optimized injection and mixing process is considered as very important to mitigate urea related deposits formation. Numerous studies, often based on Computational Fluid Dynamics [14, 15, 16], have been conducted to address this problem. Additionally, Larsson et al. [17] evaluated the benefits of a flash-boiling DEF injector allowing small pre-heated droplets to evaporate faster and achieving better mixing with the surrounding exhaust gases.

By optimizing all of these factors, reduction of deposits formation can be achieved up to a level where they can be considered as acceptable on most operating conditions. However, these optimizations are often the result of compromises affecting either

total cost of the system or its performances. Also, in some cases like urban driving under cold ambient temperatures, deposits formation is still an issue.

Another option to reduce urea related deposits formation in SCR systems, which can be combined with the above suggestions, is the use of additivated DEF. Dumas et al. [18] studied the effects organic surfactants blended in DEF and demonstrated that well-selected additivated DEF could significantly reduce the amount of urea related deposits in heavy-duty SCR exhaust lines, both on engine test bench and on field tests. The engine bench tests were carried out on Heavy Duty Euro 4 engine during 8 hours on a steady-state point with and air flow of 360 kg/h, DEF flow of 0.3 g/s and gas temperature upstream of DEF injector of 320°C. Figure 3 shows the influence of surface tension on deposits formation for several urea solutions additivated with different surfactants, with additive treat rates ranging between 10 and 5000 ppm, and compared to non additivated DEF (AUS32). A relationship between deposits formation and surface tension was observed, indicating that a reduction of surface tension of DEF would lead to a reduction of deposits formation. Commercial additivated DEF can be found on the market under the names DIAXOL (Total), CleanR MAX® (Renault Trucks Oils) or Air1® OptiSpray™ (Yara) and claim benefits in terms of deposits reduction in SCR exhaust lines, especially for vehicles with frequents stops, cold weather conditions or low load operation.

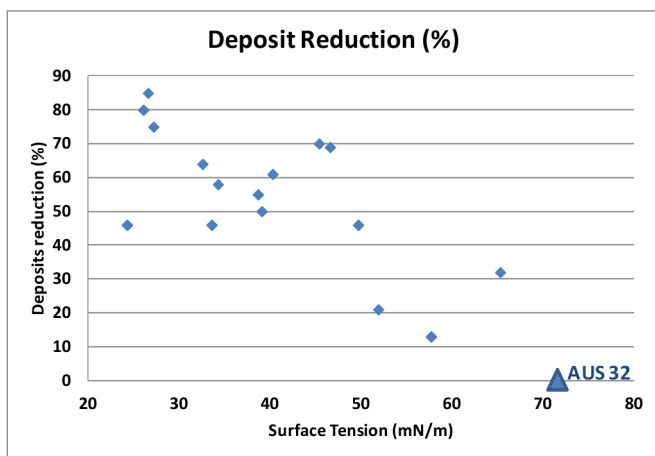


Figure 3. Influence of surface tension on deposits formation for different additivated urea solutions compared to AUS32. Tests carried out on HD Euro 4 engine test bench.

If deposits formation in SCR exhaust lines of large, heavy-duty Diesel engines is well documented in the literature as was summarized above, it is not the case for passenger car and light-duty Diesel vehicles, for which the use of the SCR technology is more recent with the introduction of Euro 6 regulation in September 2014 for European passenger cars.

Different SCR exhaust configurations can be found on passenger car applications. In the first configuration, referred to as underfloor configuration [19], the SCR is installed under the floor of the vehicle (generally after a minimum distance of 0.5 to 1m from the combustion chamber). In this configuration the SCR system is placed in a zone without significant space limitations, allowing the use of

exhaust geometries prone to create good mixing and vaporization conditions of the DEF with exhaust gas. Another type of configuration consists in placing the SCR system very close to the engine in order to benefit from higher temperature exhaust gas, thus improving SCR efficiency [20, 21, 22]. This « close-coupled » configuration is becoming standard for SCR on filter exhaust systems, where the SCR catalyst and the particulate filter are combined into a single element. However, the drawback of this configuration is that it requires very compact injector/mixer packaging in order to minimize distances, which could lead to less ideal mixing/vaporization conditions than with underfloor configurations. Smith et al. [8] have conducted optical and numerical investigations of deposits formation at low temperatures (180°C to 250°C) in a 2.1L Diesel engine using an underfloor SCR system equipped with a Diesel Oxidation Catalyst (DOC), DPF, S-bend pipe injector mounting, mixer and SCR catalyst. They observed deposits formation mainly in the mixing pipe and at injector tip, the latter being attributed to injector leakage.

In [15] the authors developed a deposits formation risk model and highlighted the importance of the mixer geometry of close-coupled passenger car production-like exhaust system setups.

Objectives

In this paper, the influence of the additivated DEF on deposits formation was investigated in a production passenger car close-coupled SCR on filter (SCRoF) Diesel exhaust line installed in a laboratory flow bench test. Indeed, urea related deposits formation in SCRoF is of particular concern since it can lead to significant deposits inside the filter, thereby increasing exhaust back-pressures more significantly than in the case of an open SCR catalyst. The behavior of two different additivated DEF was compared to non-additivated DEF (Adblue®) in terms of deposits formation on the mixer and SCRoF canning at different temperatures comprised between 240°C and 165°C, and different air flows. The influence of the additivated DEF on the cooling effect of the fluid and the surface temperature of the exhaust line downstream of the injector was also investigated.

DEPOSITS FORMATION IN A SCROF CLOSE-COUPLED EXHAUST LINE

Experimental Set-Up

Flow Test Bench

DEF spray evolution along the exhaust line is very complex. Indeed, a lot of parameters impact the conversion of DEF to gaseous ammonia: spray dynamics, interaction between spray and walls, droplet vaporization followed by complex urea decomposition to NH_3 consisting in urea thermolysis into ammonia and isocyanic acid (HNCO) and finally HNCO hydrolysis into ammonia [3]. There are two possible approaches to experimentally characterize the flow pattern of the injected fluid. The easiest solution is to simulate the exhaust gas in a flow bench including a temperature-controlled air flow device, an air heater, a tunable blower and thermo-couple sensors [25]. The second possibility is to work directly on an engine bench test [23][24]. This second solution allows a better representativeness of the vehicle

application conditions, but induces a more complex access to the exhaust line and higher difficulties to control external factors (engine vibration, pulsating flow, repeatability).

The first solution was chosen for this study. The experimental bench test is presented in Figure 4.

The exhaust gas is simulated by a pre-heated air blower to reach conditions representative of a Diesel exhaust in terms of flow rate and temperature.

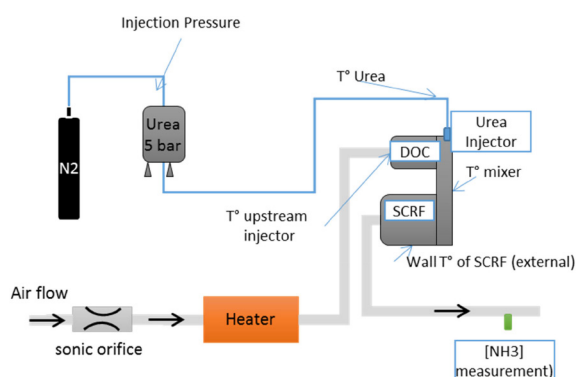


Figure 4. Flow test bench

The DEF injection system is composed of a tank pressurized at 5 bar using compressed nitrogen and a production injector originating from the same car as the catalyst housing. The flow bench test is instrumented with thermocouples, pressure sensors and ammonia probe.

Exhaust Line Geometry and Adaptation on Flow Test Bench

The aftertreatment module used in this study comes from a Volkswagen (VW) Diesel passenger car [26]. This Tier 3 exhaust system is composed of a DOC and a SCRoF in a close-coupled configuration. The DEF injector is located between the DOC and the SCRoF, just upstream of the mixer and the distance between the injector nozzle and the SCR catalyst is around 30 cm. The geometry of this system is presented on Figure 5.

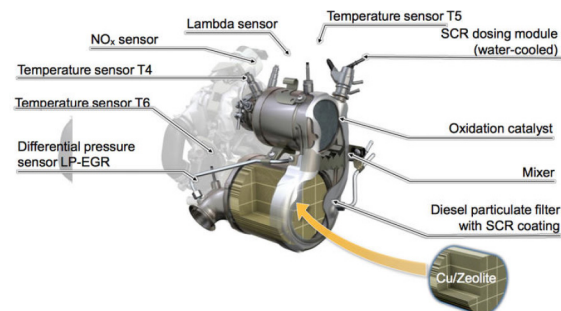


Figure 5. Schematic layout of the aftertreatment module [26]

To analyze urea deposit in the exhaust line, some adaptations are necessary. Firstly, the exhaust line was divided in three parts, in order to separately weigh the deposits formed in the vicinity of the injector, on the mixer and after the mixer. The injector itself was weighed dismantled. The overall deposit mass results from the weighing of

four parts (Figure 6) as summarized in Table 1. Secondly, in order to maximize the mass ratio between deposits and canning and hence ensure a sufficient accuracy of the measurements, the SCRoF was removed from the exhaust line. This approach also prohibits the adsorption of ammonia and water in the zeolites composing the SCR catalyst which would bias the weighing of the deposits.

Since ammonia measurements were planned, in order to avoid ammonia storage in the SCR catalyst, the SCR on filter was removed from the exhaust line.

Table 1. Interesting parts of the exhaust line

Part A	Injector nozzle
Part B	Upstream of the mixer
Part C	Mixer
Part D	Downstream of the mixer

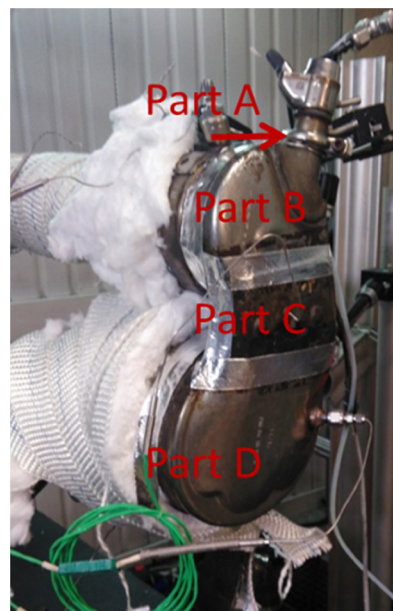


Figure 6. Exhaust line divided on four parts

Test Fluids

Three different fluids were evaluated in this study:

- Standard, commercial grade DEF (AdBlue®), manufactured from pure urea - with no addition of any other substances - and pure water. The urea concentration is 32.5% m/m, as specified in ISO 22241. It will be referred to as “Non Additivated DEF” in this paper.
- A commercial additivated DEF. It will be referred to as “Additivated DEF n°1”. The additive used is a low molecular weight organic surfactant molecule, intended to reduce the surface tension of the fluid, thereby enhancing the spray properties through reduction of the droplets size, leading to a better atomization of the DEF in the exhaust. Indeed, as shown by Dumas et al. (cf. reference [18] and Figure 3), reducing surface tension has a positive effect on urea-related deposit formation.