

Development of a 3rd Generation SCR NH₃-Direct Dosing System for Highly Efficient DeNO_x

Christian Gerhart, Hans-Peter Krimmer and Benedikt Hammer
AlzChem Trostberg GmbH

Bernd Schulz
NIGU Chemie Waldkraiburg

Oliver Kröcher and Daniel Peitz
Paul Scherrer Institut

Thomas Sattelmayer, Plamen Toshev, Georg Wachtmeister and Alexander Heubuch
Technical University Munich

Eberhard Jacob
Emissionskonzepte

ABSTRACT

In this project funded by the Bayerische Forschungsförderung two fundamental investigations had been carried out: first a new N-rich liquid ammonia precursor solution based on guanidine salts had been completely characterized and secondly a new type of side-flow reactor for the controlled catalytic decomposition of aqueous NH₃ precursor to ammonia gas has been designed, applied and tested in a 3 liter passenger car diesel engine.

Guanidine salts came into the focus due to the fact of a high nitrogen-content derivate of urea ([figure 1](#)). Specially guanidinium formate has shown extraordinary solubility in water (more than 6 kg per 1 liter water at room temperature) and therefore a possible high ammonia potential per liter solution compared to the classical 32.5% aqueous urea solution (AUS32) standardized in ISO 22241 and known as DEF (diesel emission fluid), ARLA32 or AdBlue®. Additionally a guanidine based formulation could be realized with high freezing stability down to almost -30 °C (-11 °C for AUS32). The decomposition of this new precursor to ammonia NH₃ could be realized on a gold doped TiO₂ catalyst completely without any critical side products at temperatures above 240 °C.

Due to the fact of temperatures above 240 °C required for the complete residue-free decomposition to ammonia gas, a side flow reactor concept has been developed for controlled decomposition of the precursor solution. In addition, this reactor concept could be operated with various liquid ammonia precursor such as AUS32 or aqueous guanidinium formate. In this heated catalytic reactor the decomposition is realized under controlled conditions independent of the main exhaust flow and operation conditions of the engine. NH₃-gas is produced in real-time and directly dosed to the main exhaust flow without any buffer. With a venturi nozzle setup the homogeneous mixing of the NH₃-gas into the exhaust flow is realized. Measurements in steady state and transient cycles show an up to 60 % more efficient NO_x reduction (DeNO_x) on a standard SCR catalyst in comparison to a classical urea to exhaust dosing system. Specially for exhaust conditions below 200 °C much higher efficiencies could be achieved by direct NH₃-gas dosing than with liquid AUS32 dosing.

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INTRODUCTION

New world wide regulations for diesel engine emissions will increase the demand on operation stability for exhaust cleaning systems under all climatic and constructive conditions. Even very exotic applications (low quantities) in on and non-road will force to integrate ambitious exhaust aftertreatment systems.

For passenger cars and trucks, large volume production of first and second generation SCR NO_x reduction (DeNO_x) systems (with and without air support dosing) are already available. For each application a lot of energy had been put into the adaption, design and integration of the complete systems, specially for the NH₃-precursor (aqueous urea solution 32 % - AUS32) storage and supply [1]. Urea tank and dosing systems are critical in relation to climatic, operation or driving conditions. Since AUS32 is only the liquid ammonia precursor required for the operation of SCR DeNO_x, it has to fulfill a long list of requirements: high NH₃-release potential, stability at all climatic conditions (winter, summer), long term stability during storage and distribution, nontoxic, low-cost and least but not last a reliable, complete and easy decomposition to NH₃ upstream of the SCR catalyst in the tailpipe.

Many of these requirements, specially concerning technical integration, are still not satisfactorily solved and hinder a proper integration in exotic and low volume engine applications with minor budget for engineering effort. In the project "NORA", funded by the Bayerische Forschungsförderung, some of the mentioned challenges have been investigated and new ideas could now be presented. Therefore two major aspects had been taken into focus: the basic chemistry for an alternative NH₃-precursor based on guanidinium salts and the side flow generation of ammonia gas from liquid precursors in a separate hydrolysis reactor.

This combination of chemistry and engineering led to an alternative new generation of SCR-systems presented in the following.

NH₃-PRECURSOR CHEMISTRY

Direct use of pressurized ammonia gas for the selective catalytic reduction of NO_x in the exhaust gas flow had been banned due to safety issues of the very toxic NH₃. Instead, safe ammonia precursor are currently used such as aqueous urea solution 32.5 % (AUS32). Under exhaust gas conditions this liquid precursor should completely decompose upstream of the SCR-catalyst to the reduction agent ammonia. No other side products which would cause residues at the catalyst or tailpipewalls should occur. During handling, storage and distribution of this liquid precursor at normal climatic conditions it shouldn't do anything: no decomposition, no other reactions and no phase change (e.g. freezing). AUS32 as an accepted liquid precursor is limited to -11 °C, carries 67.5 % of water and is becoming instable in time (critical for storage and distribution) at elevated ambient temperatures

(remarkable above 40 °C). Even the decomposition in the exhaust tailpipe becomes critical for operation conditions with temperatures below 200 °C upstream of the SCR catalyst.

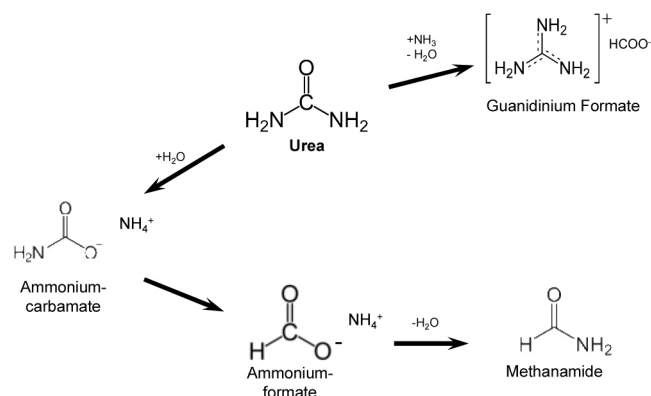


Figure 1. Urea derivatives - possible Ammonia precursor for SCR DeNO_x applications with various molecular structure and N-content - from 1 N in Methanamide to 3 N in guanidinium formate (GuFo).

With guanidinium formate (GuFo, produced by AlzChem) (figure 1) an alternative N-rich molecule has been taken into further investigations [2,3]. First of all it has remarkable solubility of about 6.2 kg per 1 liter water (86 %) at room temperature. Even the preparation of dry GuFo powder is hard to achieve due to its high hygroscopicity (figure 2). Dry material at ambient conditions would uptake humidity from the air and would become fluid again. Dry crystal residues from spilled solution will not occur under normal conditions.

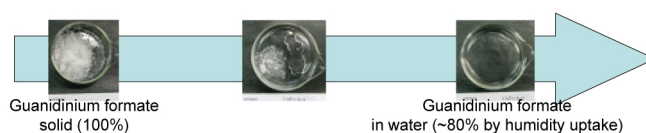


Figure 2. Humidity uptake of guanidinium formate (from left to right) - dry material gets again a liquid solution after 3 hours only by ambient humidity (rel. humidity in the air of ~55 %)

Guanidinium formate could also be mixed with urea and combined to a freezing (crystallization free) formulation (table 1). For example, the aqueous solutions of 37 % GuFo with 18 % Urea (GuFo37/18) is completely crystal-free down to -28 °C and could be supercooled far below -35 °C. Still this solution has more than 1.5 factor higher NH₃ release potential per liter compared to AUS32. A formulation with similar crystal free properties as AUS32 would be GuFo43/19 but almost double NH₃ release potential per liter.

Table 1. Comparison of NH_3 -precursor urea and guanidinium formate (GuFo) solutions

Ammonia precursor solution	Composition [%]			Temp. stability		NH ₃ capac.	
	Urea	GuFo	H ₂ O	Melting point [°C]	Boiling point [°C]	kg/kg	kg/L
AdBlue®	32.5		67.5	-11.5	decomp	0.18	0.20
GuFo60	-	60	40	-5	~100	0.29	0.34
GuFo 37/18	18	37	45	-28		0.28	0.33
GuFo 43/19	19	43	38	-11		0.32	0.38

Some other physical properties of guanidinium formate compared with AUS32 are listed in table 2. Specific differences in the species could be found concerning volume dilation factor during phase change (freezing) with lower expansion for GuFo solutions and also for electrical conductivity. Aqueous guanidinium formate (salt) is dissociated in ions and therefore has a much higher electrical conductivity than aqueous urea.

Table 2. Physical properties of guanidinium formate and urea (aqueous solutions of: GuFo60 = guanidinium formate 60 %, GuFo38/15 = guanidinium formate 38 % with urea 15 %, AUS32 = urea 32.5%).

Parameter	GuFo60	GuFo38/15	AUS32
volume dilation factor 30 °C, [10^{-4} 1/K]	4.73079	4.788	4.705
volume dilation factor phase change	-2%	+2%	+7%
Viscosity [cP] (20 °C)	5	4	1.4
surface tension [10^{-3} N/m] (20 °C)	64.7	61.7	65
electrical conductivity [mS/cm]	117	105	1.97
spec. heat capacity liquid, $C_p(T)$ (20 °C)[J/g K]	2.7	2.87	3.5
melting enthalpy [J/g]	210.7	203.5	270
vapour pressure [hPa] (40 °C)	40	47	70

A formulation of pure aqueous GuFo60 (60 % guanidinium formate) has a reduced crystal free temperature range, still strong supercooling effects down to around -30 °C (melting point is -5 °C) and obvious good stability at elevated temperatures (figure 3). In the diagram the pressure above AUS32, a mixture from urea and GuFo and pure GuFo60 solution is shown over a period of several days at a high temperature of 80 °C. Pure aqueous GuFo solution has an excellent long term stability without changing the concentration or releasing of ammonia compared to urea even at very high temperatures. The high stability of GuFo is a result of the ionic structure of the molecule but also in the fact that decomposition of this salt is harder than that of urea. The behavior of a GuFo / urea mixture is mainly influenced

by the decomposition of urea and therefore the curve is almost similar to the pure urea solution.

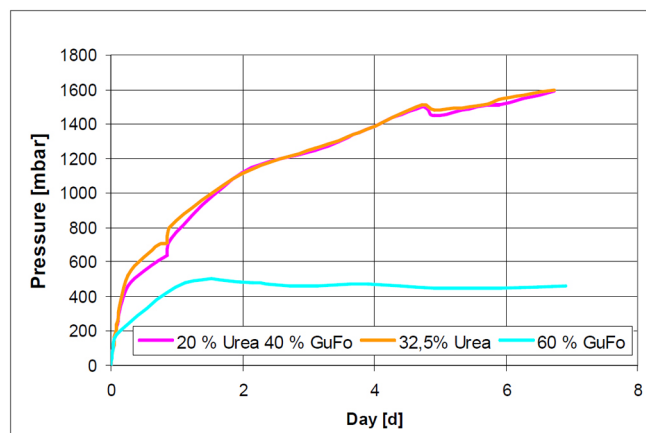
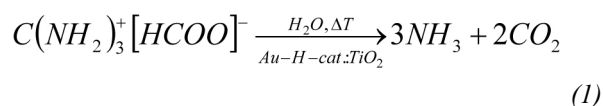


Figure 3. Stability of aqueous urea and guanidinium formate at elevated temperatures (80°C) within several days detected by the pressure over the liquid

The good stability at elevated temperatures for GuFo could be an advantage in some applications. On the other hand, GuFo like urea, is just a precursor for ammonia, and has to decompose at typical exhaust temperatures completely to ammonia by equation (1). Exhaust gas temperatures at the SCR section required for decomposition of liquid ammonia precursor seems to become a problem in modern diesel engines. During emission test cycles, temperatures are even below 200 °C (see also figure 16) and are already quite low for efficient water evaporation and urea decomposition. This results in incomplete decomposition, and side reaction products such as cyanuric acid are found in solid residues downstream of the precursor injection.



Therefore the decomposition process has been studied in a newly designed lab-emission test setup [4] (figure 4). With this setup it is possible to change the key parameters of main gas flow and simulate the gas fractions of an exhaust flow at various temperatures and humidity. Control of humidity in this case is realized directly by $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ reaction on a Pt-catalyst to ensure a fluctuation-free water dosing to the gas flow. Liquid precursor could be sprayed through a capillary nozzle on exchangeable hydrolysis catalysts into the model exhaust gas atmosphere under controlled and steady state reaction conditions. The precursor spray is positioned to cover the complete front surface area of the heated hydrolysis catalyst avoiding contact with the reactor wall. With an elaborate analytical setup, gaseous (FTIR-spectrometer) and aerosol (HPLC absorbent solution) components could be