

Formation of Engine Internal NO₂: Measures to Control the NO₂/NO_x Ratio for Enhanced Exhaust After Treatment

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ABSTRACT

The proportion of nitrogen dioxide in the engine-out emissions of a Diesel engine is of great importance for the conversion of the total oxides of nitrogen (NO_x) emissions in SCR catalysts. Particularly at lower engine loads and lower exhaust temperatures an increase of the already low NO₂/NO_x fraction will enhance the SCR operation significantly. For this purpose, the understanding of the NO₂ formation during the Diesel combustion and expansion stroke is as substantial as being aware of the different thermodynamic impacts and engine operating parameters that affect the formation process.

To determine the influences on the NO₂ emission level several variation series were performed on a single-cylinder research engine. Especially the charge dilution parameters like the air-fuel ratio and the EGR rate as well as the injection parameters could be identified to be decisive for the NO₂ formation.

Empirical models were generated for different operating points by the use of statistical test plans in order to predict the impacts of those parameters on the NO₂ emissions. The model behavior could be validated with test data and with results from the chemical kinetic modeling of the NO₂ and NO_x formation.

In general, it turned out that the NO₂ concentration always increases with the total NO_x concentration, so the formation of NO also affects the formation of NO₂. While nearly every measure that leads to an increase of NO_x emissions, like earlier injection timings, higher rail pressures or lower EGR rates, leads to a disproportionately lower increase of the NO₂ emissions, only the dilution with additional air has a greater influence on NO₂ than on NO. This effect enables to adapt the NO₂/NO_x ratio without changing the total NO_x emissions by simultaneous varying the air-fuel ratio against other parameters. The different application measures for this were mapped out and analyzed in the current work.

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INTRODUCTION

Among the pollutant emissions of Diesel engines, the oxides of nitrogen (NO_x) are considered the most critical. Particularly nitrogen dioxide (NO₂) is known for its harmful impacts on human health and environment. While nitrogen monoxide (NO) is usually considered to be a product of the combustion process that is formed within the combustion chamber, the formation of nitrogen dioxide occurs at several locations. Of course, NO₂ can also be formed during the combustion, for example by the conversion reaction of already existing nitrogen monoxide with reactive oxidants or intermediates [1]. But the different formation pathways for this are not fully understood yet and so they are also a subject of current research.

In addition, particularly high NO₂ is produced at Diesel oxidation catalysts (DOC) by the oxidation of nitric oxide with excess oxygen [1] [2]. Considering the chemical equilibrium of NO and NO₂ in an oxygenated environment suggests that NO₂ can also be formed more

intensively in colder areas of the exhaust tract or at the latest in the atmosphere. This makes it necessary to minimize the emission of both components, NO and NO₂, as completely as possible.

In order to ensure this, modern Diesel engines rely on the selective catalytic reaction (SCR) of oxides of nitrogen with ammonia, which is provided by the hydrolysis and thermolysis of a urea-based solution that is injected into the exhaust tract. Both species, NO and NO₂, can be reduced with ammonia in the SCR-catalyst. The velocity and the demand for oxygen for this reaction significantly depend on the ratio of NO₂/NO_x [3].

For this reason, the efficiency of the exhaust after-treatment systems can be decisively influenced by the proportion of the NO₂ emissions. In the current work, methods have been developed that can be used to directly influence the NO₂ emissions without affecting the level of the total NO_x concentration. In order to achieve this, the influence on

the formation processes were identified and evaluated. Subsequently, the possibilities for changing the ratio of NO_2/NO_x were derived from those results and then rated.

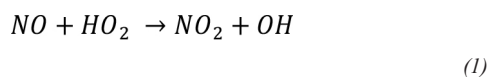
Formation of NO_x in Diesel Engines

The collective term NO_x summarizes various nitrogen compounds. In the context of engine exhaust gas, those are usually limited to the two species of nitric oxide and nitrogen dioxide. NO is the dominant component, whereas NO_2 is usually only about a few percent of the total NO_x emissions in the raw exhaust gas. Maximum ratios of NO_2/NO_x may be up to 30 percent [4] but under usual operating conditions the proportion of NO_2 lies between 5 and 10 percent of the total NO_x [5].

The formation mechanisms of nitrogen monoxide are well known. Above all the formation of thermal NO and the formation via N_2O are considered to be most important for Diesel engines [6]. The extended Zeldovich mechanism [7] that describes the formation of nitric oxides with excess oxygen at high local peak temperatures above 2000 K is considered to be the most relevant formation path for compression ignition combustion engines. Along with the N_2O mechanism, the formation of NO_x in Diesel combustion processes may be described quite completely. The N_2O mechanism relies on the reaction of $\text{N}_2 + \text{O}$ with a third-body molecule to form N_2O , which is able to react with oxygen atoms to 2NO under lean conditions [6]. Further formation mechanisms like the prompt NO mechanism or fuel-derived NO are considered to be less important for the formation of nitrogen oxides in Diesel engines.

It is noticeable that the entire NO_x emissions can usually be described with adequate accuracy without explicitly taking nitrogen dioxide into account. The formation of internal engine NO_2 has not been considered that detailed as the formation of NO. Previous studies show that NO_2 forms from already existing NO. This is one reason that the NO_x emissions can be described with good accuracy only considering the approaches for the formation of NO.

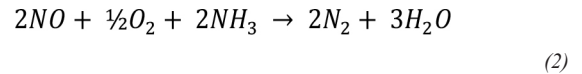
Reaction with HO_2 is assumed to be the most dominant path for the conversion of nitric oxide to nitrogen dioxide [1].



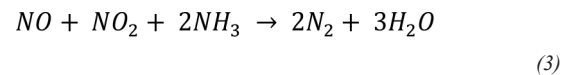
It is assumed that HO_2 is produced in relatively cold regions of unburnt gas, close to the flame front [8] and that it then reacts with the thermal NO that is formed in the hot flame front. The most important factors that influence the conversion of NO to NO_2 are temperature, reaction time, fuel type and the initial concentration of fuel (λ), NO and O_2 [1] [9]. It is further assumed that NO_2 is only exhausted at lower temperatures because above 1200K NO_2 reverts back again to NO [10].

The Role of NO_2 in Exhaust after Treatment

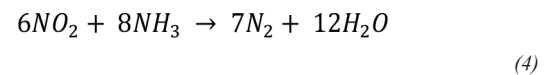
The ratio of the NO_2/NO_x concentrations in the exhaust gas is of great importance for the exhaust after treatment of Diesel engines. Particularly the conversion rates of urea-based SCR catalysts significantly vary with this. The conventional SCR reaction describes the conversion of NO to N_2 and water by ammonia (NH_3).



The presence of NO_2 enables the so-called “fast SCR reaction”, converting an equimolar amount of NO and NO_2 . This reaction is favorable due to the enhanced reaction rate especially at lower temperatures (below 300°C) [11]:



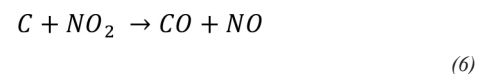
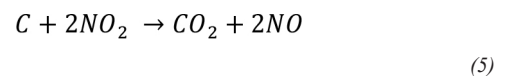
If solely NO_2 is present in the exhaust gas the conversion reaction is slowed down. The “slow SCR reaction” describes the conversion of NO_2 and NH_3 without any NO:



For the most efficient conversion of NO_x , it is desirable that the decomposition completely runs on the fast SCR reaction. For this purpose, an NO_2/NO_x ratio of 50% is necessary [3]. For Diesel engines, NO_2/NO_x in the raw emissions is usually within the range of 5-30%, with the largest ratio at lowest loads [4].

Usually, Diesel oxidation catalysts, applied upstream, are in the first instance in exhaust after-treatment systems. Here, first of all, residual carbon monoxide CO, but also NO, are oxidized [2]. The NO_2/NO_x ratio increases significantly, depending on the geometry, position, and coating of the catalyst as well as on engine load and speed. However, the specific adjustment of the NO_2 rate is very difficult. Therefore, the efficiency of SCR catalysts is hard to predict so that the catalyst has to be dimensioned larger to ensure a sufficient conversion even at lowest NO_2 rates.

In addition, NO_2 is also very useful for the passive regeneration of Diesel particulate filters. This is done by the continuous conversion of soot according to the following reactions:



The continuous soot regeneration in the DPF contributes to prolong the intervals between the active regenerations or even to promote a purely passive regeneration [12].

The current work at the Karlsruhe Institute of Technology deals with the engine internal formation of NO_2 in Diesel engines. The first part of the investigations considers the different impacts on the formation

of NO_x , respective NO_2 . Therefore various engine operating parameters, like injection parameters and the composition of charge air have been varied to identify and to analyze those influences. The conclusions and the resulting options to affect the NO_2 fraction in the exhaust gas are also a part of this publication. Application measures to adjust the NO_2/NO_x fraction in order to enhance and optimize strategies and components of the after treatment will be reviewed and discussed.

Already existing model approaches, e.g. Finesso et al. [13], work on the prediction of the NO_2 emissions or the NO_2/NO_x ratio for the entire engine map, considering various input parameters. In this work, however, only individual operating points are considered. The objective is to provide insights into the engine-internal formation of NO_2 by performing detailed parameter variations. In combination with the chemical-kinetic modeling, carried out parallel to the experimental investigations, a basis for the extended understanding of the NO_2 formation in the combustion chamber is created. The current work focuses on experimental investigations and statistical modeling. Chemical modeling will be discussed in future publications.

EXPERIMENTAL

For the investigation of the thermodynamic influences and the impacts of the operating conditions on the formation of NO_2 , an engine test bench was set up at the *Institute of Internal Combustion Engines* at the *Karlsruhe Institute of Technology (KIT)*.

Here, various input values were selectively varied in order to ascertain the impacts on the internal engine pollutant formation. The most important engine data and an overview of the relevant test bench features and measurement systems are given in the next section.

Experimental Setup

A single cylinder research engine, based on a modern EU6 commercial vehicle Diesel engine was used. The essential engine data are shown in [table 1](#).

Table 1. Engine specifications

Parameter	Value	
Bore / Stroke	110 / 135	mm
Displacement	1283	cc
Compression Ratio	17,4: 1	
Max. Charge Pressure	0,45	MPa
Max. Torque (@1400 rpm)	220	Nm
Max. Speed	2200	rpm

The engine is equipped with a common rail direct injection system. An external fuel conditioning unit, featuring a *Bosch CP4.2* high-pressure pump, delivers fuel pressures up to 240 Mpa. The fuel consumption is continuously measured by an *AVL KMA* fuel measuring system. Separate conditioning circuits enable the precise setting of the pressures and temperatures of coolant and lubricant, independent of engine speed and load. The fresh charge, delivered by

an air compressor system, is cooled and dehumidified before it is passed to the inlet. The temperature can be set by a separate heater and the humidity can be set by enriching the charge air with water vapor.

Additionally, the engine features a high-pressure EGR system. The recirculated exhaust gas is cooled down to the coolant temperature and precisely adjusted by an EGR valve. For the continuous measurement of the EGR ratio a non-dispersive infrared analyzer (NDIR), type *ABB AO2020 URAS EGR*, is used. The exhaust backpressure was controlled with an additional flap in the exhaust tract.

A *DEWetron 800 Combustion Analyzer* is used for the dynamic acquisition of the combustion pressure, charge pressure, exhaust pressure, common rail pressure and the injector signal. The data are recorded with a precision of 0.1 crank angle degrees.

Various gas analyzers are used to measure the different components in the exhaust gas. The system *AVL AMA4000* measures the following species: carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HC), nitric oxide (NO) and oxides of nitrogen (NO_x). For measuring the nitrogen compounds a 2-channel chemiluminescence detector (CLD) with an NO_2 -converter is used. Thus, NO_2 is determined as the difference between the two values of NO_x and NO and is not measured directly. Additionally, a Fourier transform infrared spectrometer (FTIR), type *MGs MG2030*, is applied to enable the measurement of various species in the engine-out emissions, also including NO_2 . In order to compare the different measurement technologies, especially for the determination of nitrogen dioxide, a highly dynamic mid-infrared analyzer, the *DEGAS REFAM* [15] is used. But the evaluation and rating of the different measurement systems is not a part of this publication. The results shown in the subsequent analysis were recorded with the *AMA4000* which was recalibrated periodically to minimize possible measurement errors. However, it has to be stated, that the accuracy of the NO_2 measurement depends on the performance of two separate analyzers as well as on the efficiency of the NO_2 -NO converter. This efficiency was between 97% and 99% in all studies, which is why the measured NO_2 concentration was always about 1 to 3% lower than the actual value. The relevant technical specifications of the *AMA4000 CLD* device are given in [Table 2](#). FTIR and the *DEGAS* were always used for monitoring the measured values.

Table 2. Specifications of the chemiluminescence detector (CLD)

Parameter	Value	
Type	AVL CLD4000hhd	
Measurement Ranges	0 - 10 / 100 / 1.000 / 10.000 ppm	
Detection Limit	35 ppb	
Linearity Error	$\leq 1,0 \%$	
Noise	$\leq 1,0 \%$	
Cross Interference	$\leq$	0,15 ppm / %CO
	$\leq$	1ppm / 1.000 ppm NH_3
	$\leq$	3 ppb / ppm C_3H_6
Converter Efficiency	$\geq 95 \%$	

The control of the various measurement systems, the conditioning circuits, and the entire data acquisition is managed by the test bench automation system *D2T Morphée*.

Identification and Analysis of Impacts on NO_2 and NO_x

For the analysis of the different impacts on the formation of NO_2 preliminary experiments have been performed. Besides load and speed particularly the charge condition, as well as the injection parameters revealed great influences on the NO_2 emissions. The following results show various parameter variations, which were performed at an engine load of 25% (IMEP 0,65 MPa) and an engine speed of 1400 rpm. The basic settings of the operating point are given in Table 3. The fuel was injected by a single injection. Neither pilot-injections nor post-injections were used.

Table 3. Initial point for parameter variations

Engine Settings:		
EGR ratio	18,0	%
rel. A/F ratio (λ)	2.05	-
rail pressure	135	MPa
Start of injection	7,9	CA BTDC

For all variations only one of the shown parameters was varied at a time. This means, for example, that the rail pressure remained unchanged during a variation of the SOI and, of course, vice versa.

Injection Parameters

Changing any parameters of the Diesel injection, e.g. the injection pressure or the injection timing directly influences the combustion process without changing further operating parameters, particularly the condition and the composition of the cylinder charge remain unaffected.

Although the impact of the two measures on the combustion process may be different, the effects on nitrogen oxides show to be very similar. The SOI directly affects the start of the combustion while the rail pressure affects the rate of the combustion. Since both, earlier SOI and higher rail pressure, lead to an earlier combustion phasing and thus to higher rates of heat release during the combustion process, the NO_x emissions increase significantly. Figure 1 illustrates the impacts on the nitric oxide components.

It revealed that any variation of the injection parameters could not affect the nitrogen dioxide emissions separately. All changes of the emitted NO_2 were driven by a more significant change of NO , respectively of total NO_x .

Even if the increase of NO_2 is almost proportional to the increase in NO emissions, it is always accompanied with a slight decrease of the NO_2/NO_x ratio.

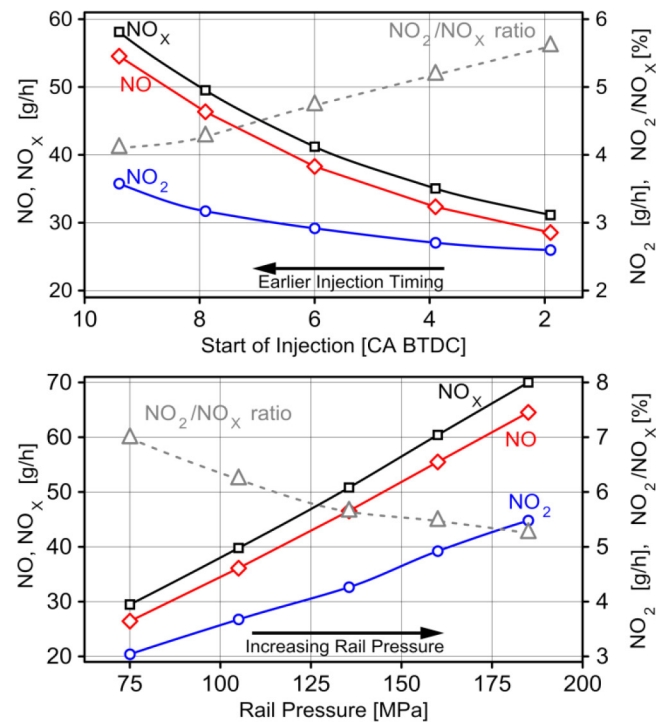


Figure 1. Influence of injection timing and rail pressure on nitrogen oxide emissions

Cylinder Charge

The condition of the cylinder charge is influenced by various operating parameters, thermodynamic impacts and application measures. Several variables are necessary for its characterization. For example, those implement the pressure and the temperature of the charge. Further, the charge composition can be described by the humidity and the rate of EGR. Alternatively, the concentrations of water, oxygen or carbon dioxide may also be used.

In the following, the effects of the charge dilution on the NO_x formation will be described. The cylinder charge can either be diluted with fresh air, with recirculated exhaust gas or with both. The dilution with air may be quantified by the relative air-fuel ratio λ , while the mass or the ratio of EGR describes the dilution with exhaust gas.

The amount of charge is usually only minor changed and any changes in the EGR rate are achieved by substituting fresh charge. This makes it very difficult to separate the effects of the dilution with EGR and fresh charge. Hereinafter, the effects are separated by varying only one dilution parameter while the other one is kept constant. This could be achieved by adjusting the charge pressure.

It revealed that the EGR has an immense impact on the NO emissions and thus also on the total NO_x emissions. But the nitrogen dioxide emissions were only slightly affected, even when NO_x gets to a minimum. This leads to very high NO_2/NO_x fractions for high EGR rates and lowest NO_x concentrations like shown in Figure 2.

Similar to the effects of the injection parameters this also shows a disproportionately lower impact on NO_2 than on NO_x .

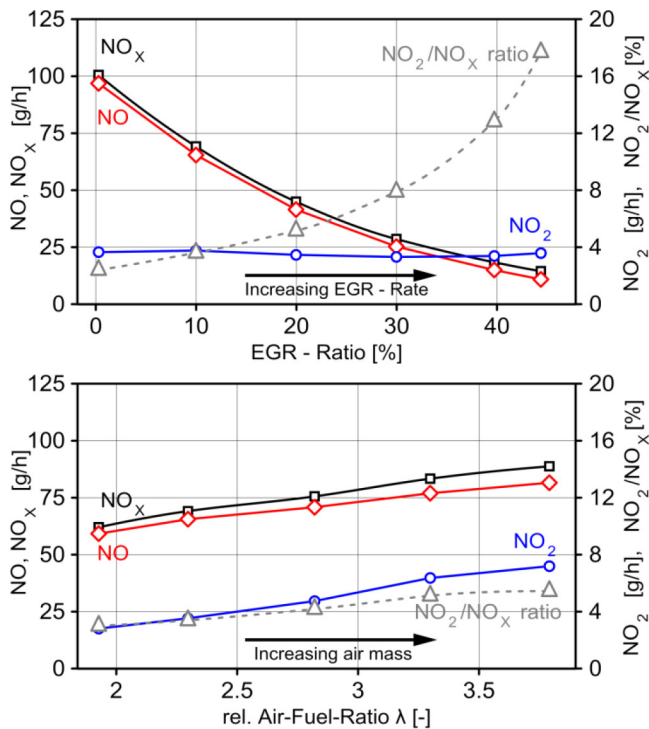


Figure 2. Influence of charge dilution with EGR and fresh air on nitrogen oxide emissions

The influence of the dilution with fresh air on the total NO_x emissions is only minor, compared to the influence of additional EGR. But particularly NO₂ is affected by changes in the air mass and thus by the additional oxygen. The nitrogen dioxide emission also increases together with the NO emissions, but in this case even disproportionately higher. As shown in Figure 2, the NO₂/NO_x fraction increases with higher λ values and higher NO_x emissions. The increase in the EGR rate drastically reduces the NO_x emissions without significantly affecting the NO₂ emissions. This leads to an enormous increase of NO₂/NO_x towards the lowest NO_x emissions.

Comparing different variants of the charge dilution underlined that the EGR rate primarily affects the NO, and thus, the NO_x emissions, but only minor influences the NO₂ concentration. Contrary to that, additional air has a major influence on the NO₂ emissions. It is reasonable to presume that nitrogen dioxide is mainly influenced by the concentration of oxygen, and thus by λ. Figure 3 shows the dependence of the NO₂ emissions on the relative air-fuel ratio λ for the different variants: additional air, additional EGR, substitutional EGR. In this case, the dependency of NO₂ and lambda is approximately linear.

Besides the dilution parameters also the humidity and the temperature of the charge influences the NO_x emissions. The humidity has a very considerable influence on the NO_x emissions. As the water content increases, NO and NO₂ decrease drastically. But the change of NO₂ concentration is also disproportionately low. A slight influence is also given by the temperature of the charge. An increase leads to the increase of NO and NO₂, while the NO₂/NO_x fraction drops. As the focus of this work lies on the modeling of the NO_x emissions and the influences of those parameters are well known so far, those impacts

will not be further discussed here. Accordingly, the impacts of humidity and charge temperature will be evaluated in the modeling section.

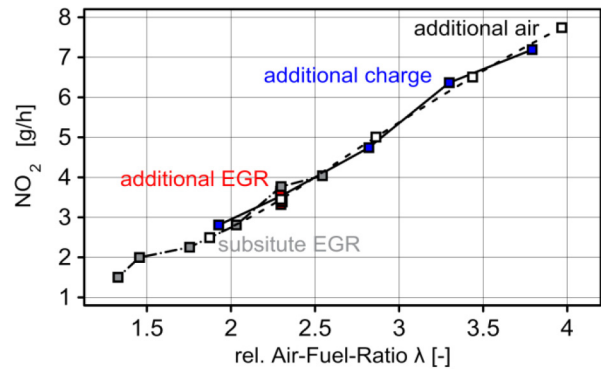


Figure 3. Influence of air-fuel ratio on NO₂ emissions

However, the influences of the different parameters are difficult to separate, since many effects can only be detected in interaction with each other during engine operation. Thus, for example, an increase of the EGR rate simultaneously causes a lowering of the air-fuel ratio, while the charge temperature and the humidity increase.

Generally, any increase of the nitrogen dioxide emission always comes along with a simultaneous increase of the nitrogen monoxide emissions, respective with NO_x, also independent from engine speed and load. This statement is in agreement with the assumption, that existing NO is converted to NO₂ [1] [9] [11]. A change in the NO emissions usually goes along with a disproportionately lower impact on NO₂. This results in lowest NO₂/NO_x fractions for the highest NO_x concentrations. The presence of oxygen enhances the formation process, which can be demonstrated by the influence of λ.

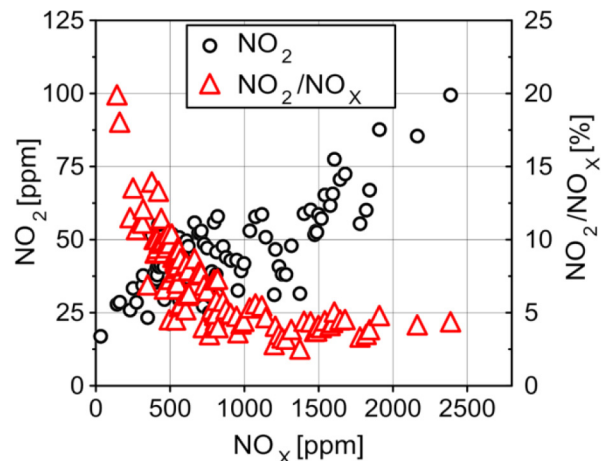


Figure 4. Experimental results: NO₂ concentration and ratio NO₂/NO_x

Figure 4 shows the NO₂ over NO_x concentrations for a variety of parameter variations at different engine speed and loads. The black markers illustrate the dependency of the NO₂ concentration on the NO_x concentration.