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Methanol combustion engine exhaust gas aftertreatment

Exhaust Gas Aftertreatment Solutions & CCS

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ABSTRACT

Methanol as a combustion fuel is considered to be a promising option for reducing greenhouse gas emissions – provided the alcohol is produced with a low carbon footprint. Combustion in dual-fuel engines may be achieved via different pathways, either in a diffusive or premix principle. Both routes come with specific challenges and opportunities, due to the different combustion modes different exhaust conditions and pollutant concentrations are observed, while emission targets and ambitions remain identical. This contribution focuses on the impacts for the exhaust gas aftertreatment system.

In comparison with combustion of diesel or natural gas, the different emissions require aftertreatment system adaptations, depending on the specific deviations in terms of compounds, concentrations, or conditions. Particularly in case of port fuel injection concepts with potentially higher concentrations of unburnt (CH3OH) or partially burnt (e.g., HCHO) fuel components, side reactions on the SCR catalyst used for NOx reduction become significant. These side reactions not only impact the NOx removal performance but also give rise to undesired secondary emissions e.g., highly poisonous HCN. The relevant reactions are briefly introduced, pointing out at which exhaust conditions they may detrimentally impact current SCR system designs. Furthermore, guidance is provided how combustion concepts could be optimized to reduce requirements for additional aftertreatment. Exhaust gas aftertreatment system architectures appropriate for the various engine concepts are presented allowing a comparison of different engine combustion concepts regarding their emissions.

Laboratory experiments with synthetic exhaust gas are presented, the composition and concentrations of exhaust compounds are set to mimic specific methanol combustion engine setups. Individual catalysts specifically designed to target for instance concerning secondary emissions, but also different combinations of catalysts are tested under these conditions, highlighting the evolution and removal of concerning intermediate side reaction products.

The systematic studies in the laboratory are complemented by providing results from methanol combustion engine aftertreatment systems commissioned on medium- and high-speed engines.

Overall, achieving lower greenhouse impact by switching to alternative fuels such as methanol also requires careful consideration of the associated changes for exhaust gas aftertreatment. Close collaboration between engine development and exhaust gas aftertreatment ensures meeting legal pollutant requirements while maintaining low emissions of undesired non-regulated substances.

1 INTRODUCTION

In order to reduce the greenhouse gas impact of the large engine industry, alternatives to fossil fuels are sought after. Due to the convenience of stable and safe storage at ambient conditions, methanol, the simplest alcohol possible, is increasingly introduced as a liquid fuel for combustion engines. Methanol is a globally traded chemical base commodity handled at large scales, not only in chemical facilities but also in ports and as a cargo on vessels. Most of it is produced from fossil resources, but biomass is becoming a more relevant feedstock. The common large scale production route is via syngas, both for fossil and biomass-based methanol. [1] The syngas route enables the use of various sources, ultimately even captured CO_2 and low CO_2 footprint H_2 can be utilized using the reverse water gas shift reaction for syngas production. Thus, the production facility capacity, just like the methanol fuel consumers can be prepared for methanol and the shift to lower CO_2 footprint raw materials can be achieved separately according to the availability of feedstock and desired level of green methanol proportion.

There are two fundamental engine technology approaches for methanol combustion. One is high pressure direct injection with a diffusive combustion regime, the other uses typically lower pressure fuel injection systems and combustion of a fuel-air premix . Both routes come with specific advantages and shortcomings, in the end there are good reasons to see both in the market for specific applications considering also first-fit and retrofit situations. As the presented contribution is focusing on exhaust gas aftertreatment aspects, only the differences of the combustion concepts yielding different exhaust composition are highlighted: While the type of exhaust components, including the chemical compounds which may be considered to be pollutants, are generally the same in both routes, the concentrations are not. In comparison to premix combustion, diffusive combustion typically yields a higher level of complete combustion of injected methanol, achieving lower amounts of unburnt or only partially burnt fuel components. However, in comparison, NO_X emissions will tend to be higher from diffusive combustion due to higher temperatures. Exhaust temperatures may also vary between the two combustion concepts, but due to the many other factors which impact this parameter, it should not be discussed at this point but covered by presenting our catalyst test results over a wide temperature window. The ignition architecture considered in this contribution is limited to Diesel pilot ignited dual fuel concepts, compression ignition of methanol as also investigated [2], is not considered, neither is spark ignition. [3] However, the general observations of exhaust gas reactions in the catalyst system could also be transferred to these latter two methanol ignition methods.

Hug Engineering has demonstrated to be a reliable partner for exhaust gas aftertreatment systems in demanding applications of stationary [4] and mobile [5] engines in commercial applications as well as to serve customers with special emission control systems for engine test benches or engine production end testing facilities. [6] This contribution focusses to support the transition towards low CO_2 footprint fuels by supplying methanol combustion engines with dedicated aftertreatment systems.

2 MAIN SECTION

2.1 Emission challenges of standard aftertreatment systems in methanol operation

Long-chain alkanes, alkenes and aromatic compounds as typical hydrocarbon emissions from Diesel combustion do not significantly impact the SCR (selective catalytic reduction) reaction on common VWT (vanadia-tungsten-titania) based SCR catalysts. However, in methanol operation with high shares of methanol substituting Diesel fuel, the hydrocarbon (HC) composition is dominated by unburnt methanol (CH_3OH or MeOH) and formaldehyde (HCHO) the latter as an incomplete combustion product from methanol.

Depending on the combustion concept, the absolute amount of incompletely and unburnt compounds in the exhaust varies, also engine designs affect the concentrations. As a general indication, air-fuel premix concepts in small bore engines running at higher rpm are prone to produce higher amounts of emissions potentially reaching up to 1’000’s of ppm. Direct injection concepts tend to emit below 1’000 ppm of HC emissions. Regardless of the injection concept, the impact on the SCR performance is clearly visible in Figure 1. An addition of 500 ppm methanol is supposed to represent diffusive methanol combustion in a high-pressure direct injection (HPDI) concept, 3’000 ppm methanol are representing lower pressure fuel injection concepts with premix methanol dual fuel combustion. The experiments are performed with synthetic exhaust gas (700 ppm NO_X, 5 vol.% H_2O, air balance) in a catalyst test bench, the temperature is varied over a wide range representing expected dual fuel engine exhaust gas temperatures. Depending on the engine configuration, combustion principle, methanol fuel share, air-fuel-ratio and other parameters, the water and oxygen content may differ strongly from the assumed concentration of 5 vol.%.

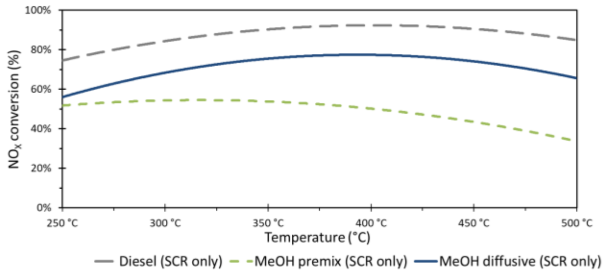

Figure 1. NO_X conversion over “SCR only” exhaust gas aftertreatment system for different fuels and combustion concepts.

Utilizing a typical “SCR only” exhaust gas aftertreatment system designed for a Diesel fuel combustion engine also in methanol operation on dual fuel engines reveals several shortcomings as mentioned in the following paragraphs.

Significant impact on the NO_X conversion compared to standard diesel operation at otherwise identical conditions (NH_3 to NO_X ratio, /alpha = 0.9) can be observed. The impact on NO_X conversion depends on the exhaust gas temperature, for the methanol premix combustion case, in the temperature range of 250 – 400°C a decrease of approximately 20% is measured, at 500°C the impact is even a halving of the observed NO_X conversion.

The reason for the reduced NO_X conversion on the SCR catalyst in methanol operation are side reactions of methanol with the dosed NH_3. In consequence, NH_3 concentrations are lowered and no longer available for the intended NO_X reduction. In detail, the chemical reactions are the decomposition of methanol (Eq. 1) and the consecutive reaction with NH_3 (Eq. 2) to form HCN.

$$2\,CH_3OH + O_2 \rightarrow 2\,HCHO + 2\,H_2O \qquad (\mathbf{1})$$

$$2\,NH_3 + 2\,HCHO + O_2 \rightarrow 2\,HCN + 4\,H_2O \qquad (\mathbf{2})$$

Thus, not only NO_X conversion is impacted, but also toxic HCN (prussic acid) is formed. Under the assumed conditions containing 3’000 ppm of methanol, HCN concentrations above 350 ppm were detected (see Figure 2) which is more than 100 times above the occupational threshold limit of 0.8 ppm according to EU REACH regulation.

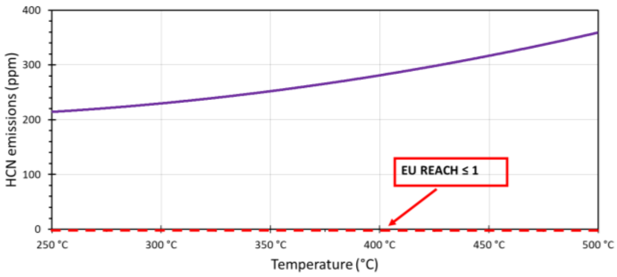

Figure 2. Formation of HCN emissions by “SCR only” exhaust gas aftertreatment system for MeOH premix concept.

Besides the increased HCN formation, formaldehyde is formed from partial methanol oxidation on the SCR catalyst reaching a concentration of 700 ppm at 250°C (see Figure 3), clearly exceeding existing formaldehyde emission limits such as the 44. BImSchV for lean burn engines, which would typically be around or below 10 ppm (defined in regulation as 20 mg/Nm^3 at 5% Oxygen reference).

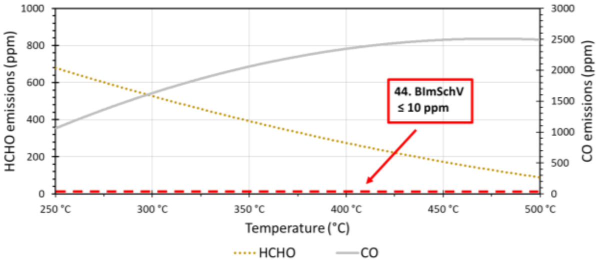

Figure 3. Formation of formaldehyde (HCHO) and CO emissions by “SCR only” exhaust gas aftertreatment system for MeOH premix concept.

The emitted HCHO levels decrease strongly with increasing temperature, reaching less than 100 ppm at 500°C, however, even such a concentration is high in comparison to the abovementioned emission regulation. The reaction product is mainly CO in accordance with (Eq. 3) which in turn is confirmed by increasingly high CO levels reaching 2’500 ppm at 500°C.

$$2\,HCHO + O_2 \rightarrow 2\,H_2O + 2\,CO \qquad (\mathbf{3})$$

In case the aftertreatment system also includes a platinum group metal (PGM)-based oxidation (Oxi) catalyst after the SCR stage, the emissions are different than in the previously described case (see Figure 4).

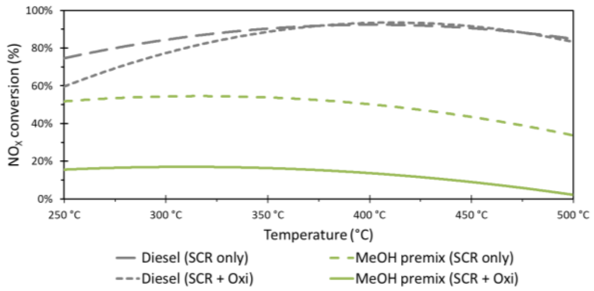

Figure 4. Comparison of NO_X conversion over “SCR only” and “SCR + Oxi” exhaust gas aftertreatment systems for different fuels and combustion concepts.

As intended, CO and HCHO emissions are avoided by oxidizing both to CO_2 (Eq. 4 & Eq. 5).

$$HCHO + O_2 \rightarrow H_2O + CO_2 \qquad \textbf{(4)}$$

$$2\,CO + O_2 \rightarrow 2\,CO_2 \qquad \textbf{(5)}$$

When operating on Diesel fuel the impact of the downstream oxidation stage on NO_X conversion is limited to temperatures below 350°C, when oxidation of unreacted NH_3 slip to NO_X becomes relevant (Eq. 6).

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \qquad \textbf{(6)}$$

However, in methanol operation, for the premix combustion concept, when assuming 3’000 ppm methanol in the exhaust gas, the impact is significant. The overall NO_X conversion is limited to less than 20% at 350°C while under the same reaction conditions a NO_X conversion of ca. 90% can be achieved in Diesel fuel operation. In methanol operation, NH_3 is almost completely consumed by the formation of HCN (Eq. 2), thus, the impact of NH_3 oxidation to NO_X on the PGM catalyst is of minor importance. However, the HCN produced as a side product on the SCR catalyst is oxidized by the downstream oxidation catalyst with a high selectivity to NO_X (Eq. 7), thereby strongly impacting the possible overall NO_X conversion.

$$4\,HCN + 7\,O_2 \rightarrow 4\,NO + 4\,CO_2 + 2\,H_2O \qquad \textbf{(7)}$$

Even though after the oxidation catalyst HCN levels are well below acceptable levels, the NO_X conversion is strongly diminished, thus, rendering existing SCR systems as non-compliant under current IMO Tier III or similar legislation.

2.2 Two-reactor concept for all methanol combustion concepts

To counter the challenges in methanol operation posed by increased hydrocarbon contents, especially methanol (CH_3OH or MeOH) and formaldehyde (HCHO), in the exhaust gas, several approaches are possible. For newbuild projects with some design flexibility, a dedicated methanol oxidation stage prior to the reducing agent dosing is a robust concept. In this case, the pilot Diesel fuel quality determines the chemical composition of the methanol oxidation catalysts, as it may also serve as backup fuel. While for EN 590 and ASTM D975 grade Diesel fuel a PGM-oxidation catalyst is feasible, lower fuel qualities require a PGM-free oxidation catalyst for extended endurance. For this reason, the performance of a robust and proven PGM-free catalyst in methanol oxidation is also presented in this paper, as this type of catalyst has a high resistance against sulphur as a catalyst poison. As the supply of methanol is currently difficult to be ensured on a global scale also in remote ports, many marine methanol dual fuel engines and their respective exhaust gas aftertreatment systems are expected to also deal with traditional marine distillate fuels which can have a sulphur content of 0.5% internationally and up to 0.1% in ECA zones. A general concept of the setup described is shown in Figure 5.

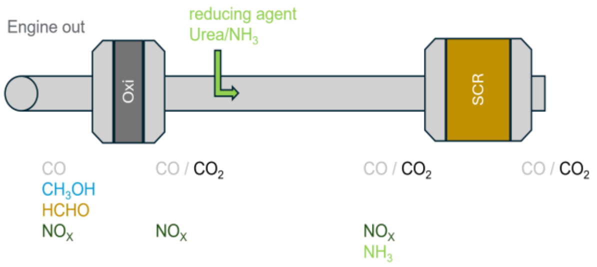

Figure 5. Scheme for upstream oxidation catalyst exhaust gas aftertreatment concept to ensure SCR catalyst NO_X conversion and suppress side product formation.

The performance of a PGM catalyst and a non-PGM oxidation catalyst is shown in Figure 6. In this diagram both catalysts are equally sized to enable a comparison under identical conditions. While for the PGM catalyst full conversion is achievable at all relevant temperatures, the non-PGM catalyst requires temperatures above 300°C to oxidize more than 80% of the incoming methanol. However, at temperatures above 400°C the PGM-free catalyst exhibits methanol conversion rates close to those of a PGM oxidation catalyst making it a realistic and cost-effective alternative. For temperatures below 300°C, a sizing factor between the PGM and non-PGM catalysts must be applied (depending on exact exhaust gas conditions and targeted downstream oxidation catalyst concentration) to achieve comparable conversions.

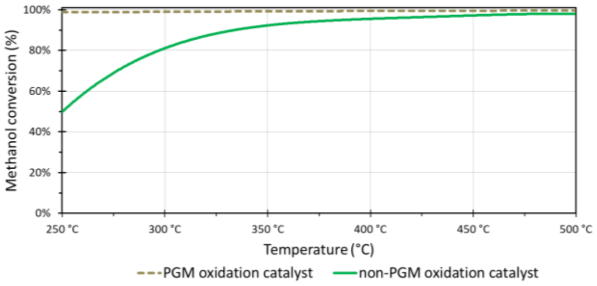

Figure 6. Comparison of methanol conversion for different oxidation catalysts at identical size and space velocities.

The two catalysts have different selectivity for methanol oxidation. While the PGM catalyst forms mostly CO_2 (Eq. 8), the non-PGM oxidation catalyst produces mostly CO (Eq. 9).

$$2\,CH_3OH + 3\,O_2 \rightarrow 4\,H_2O + 2\,CO_2 \tag{8}$$

$$CH_3OH + O_2 \rightarrow 2\,H_2O + CO \tag{9}$$

Both compounds are chemically inert in a downstream SCR stage, so there is no impact on the NO_X reduction. However, as the formation of CO_2 is strongly exothermic and releases approximately twice as much energy as the formation of CO, the respective temperature increase must be considered for the downstream SCR stage. The amount of unburnt methanol and HCHO contained in the engine raw exhaust gas is essential in assessing the maximum expected temperature increase due to the exothermic oxidation reactions which can increase exhaust gas temperatures significantly. Generally, the specific temperature increase due to the exothermic oxidation reaction on the catalyst depends on several factors, in particular the concentration of unburnt (= methanol) and partially burnt (=HCHO, CO) fuel as well as the specific heat capacity of the exhaust (in particular water and CO_2 content, so a function of lambda). For the test conditions chosen to represent a premix combustion concept, an adiabatic temperature increase of approx. 60 K would result at full conversion by the oxidation catalyst.

2.3 Single-reactor concept for premix methanol combustion concepts

While the concept with upstream methanol oxidation (see Figure 5) is feasible for any methanol combustion concepts but focusing on new systems, even more challenging space restrictions in retrofit methanol conversion projects are often limiting to fit a dedicated upstream reactor. These conversion projects also are typically more likely to be using port fuel injection equipment, leading to higher methanol shares in the exhaust gas due to the premix combustion concept. For such applications, a single-reactor concept as depicted in Figure 7 is preferable. Here, a secondary catalyst is placed inside an existing SCR reactor after the standard SCR catalyst by partially replacing it.

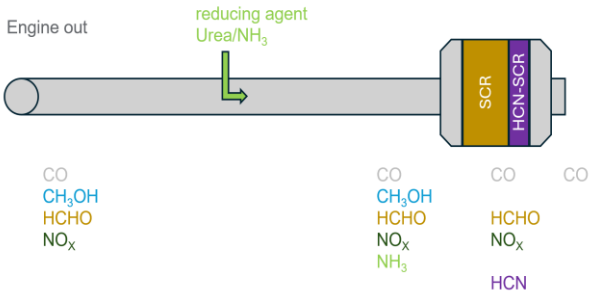

Figure 7. Scheme for HCN-SCR catalyst exhaust gas aftertreatment concept to remove SCR catalyst side products and ensure NO_X conversion.

This new catalyst acts as an HCN-SCR catalyst using the HCN side product formed on the SCR catalyst to reduce NO_X. The relevant reaction is a two-step process of HCN hydrolysis forming NH_3 (Eq. 10) which in turn reacts with NO_X present in the exhaust gas according to the standard SCR reaction (Eq. 11).

$$HCN + H_2O \rightarrow NH_3 + CO \tag{10}$$

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \tag{11}$$

In consequence, both undesired pollutants, HCN and NO_X, are mutually eliminated forming CO and harmless N_2.

When testing the described setup consisting of a common SCR and consecutive HCN-SCR catalysts under conditions previously used for “SCR-only” and “SCR + Oxi” catalyst, no penalty in NO_X conversion due to methanol operation in comparison to the Diesel fuel operation mode is visible even in case of the premix combustion concept with assumed 3’000 ppm of methanol in the engine exhaust (see Figure 8).

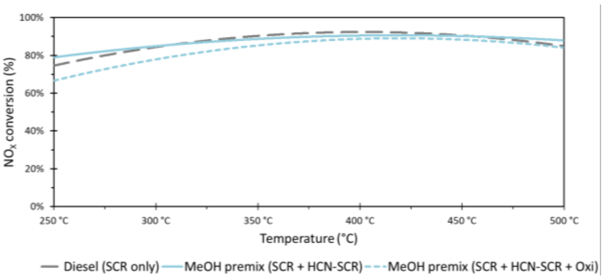

Figure 8. Comparison of NO_X conversion over “SCR + HCN-SCR” and “SCR + HCN-SCR + Oxi” exhaust gas aftertreatment systems for MeOH

premix combustion concept in comparison to a reference “SCR only” exhaust gas aftertreatment systems for Diesel fuel combustion.

In case an additional oxidation catalyst is added downstream of the SCR + HCN-SCR combination to ensure compliance with e.g. CO and HCHO limits, a slight decrease in NO_X conversion at temperatures below 400°C due to the oxidation of residual HCN to NO_X (Eq. 7) becomes visible.

2.4 Single-reactor concept for direct injection diffusive methanol combustion concepts

Alternatively, to comply with CO and HCHO limits and using only one reactor, a dedicated methanol oxidation catalyst (MeOH-Oxi) is an option for direct injection combustion concepts with methanol slip limited to < 1000 ppm conditions. This catalyst can be placed also after NH_3 injection inside the SCR reactor as depicted in Figure 9.

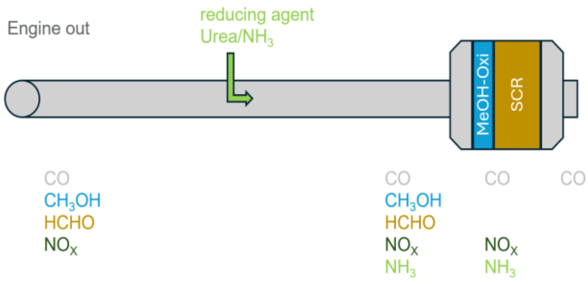

Figure 9. Scheme for MeOH oxidation catalyst exhaust gas aftertreatment concept to ensure SCR catalyst NO_X conversion and suppress side product formation.

This catalyst is tuned to selectively oxidize methanol to CO_2 (Eq. 8) while having only minor activity for NH_3 oxidation at temperatures relevant for exhaust gas as visible in Figure 10.

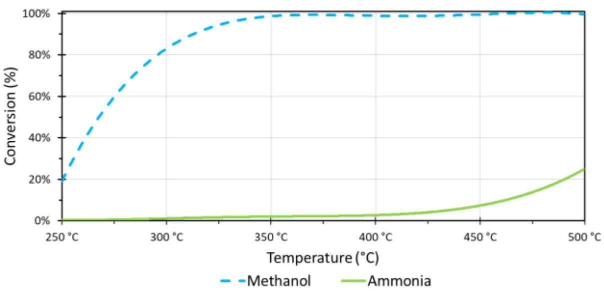

Figure 10. Oxidation selectivity of dedicated methanol oxidation catalyst for MeOH dual fuel diffusive combustion concepts.

This functionalization enables a methanol-free, diesel-like performance of the standard SCR stage following the selective methanol oxidation catalyst as shown for Diesel operation in Figure 4.

The temperature window in which the catalyst exhibits high methanol but no to low ammonia conversion ranges from approx. 300 to 450°C with CO_2 being the predominant oxidation product (see Figure 11).

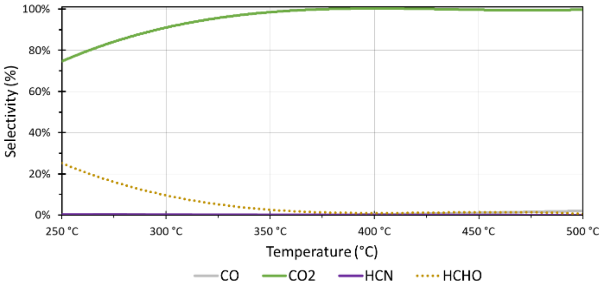

Figure 11. Product selectivity of dedicated methanol oxidation catalyst for MeOH dual fuel diffusive combustion concepts.

Only minor fractions of HCHO are formed at T<350°C with no CO or HCN formed over the entire temperature range thus eliminating a potential safety risk.

3 SUMMARY AND OUTLOOK

Methanol is considered a promising pathway for internal combustion engines to achieve low net CO_2 emissions in shipping – several combustion concepts are developed for various engine platforms in the marine industry. In terms of pollutants, the injection technology concept significantly impacts the concentrations of exhaust compounds. While possibly not considered at first sight, the amount of incompletely or unburnt hydrocarbon compounds significantly impacts NO_X conversion in SCR systems and may impact emission compliance when moving from Diesel to methanol operation. Furthermore, toxic side products (like HCN and HCHO) are formed during the SCR process due to the presence of methanol and ammonia.

An oxidation catalyst downstream of the SCR to remove side products can be even more detrimental to the observed NO_X conversion performance. However, three feasible pathways for avoiding any impact to NO_X compliance or the emission of toxic side products are presented. The options come with specific advantages and restrictions, but all enable engine operation on methanol also for any combustion concepts chosen on the engine side. Exact dimensioning depends as usual on the exhaust conditions, the emission compounds and their concentration. In general, the more the exhaust characteristics in methanol operation resemble typical Diesel fuel exhaust gas, the less additional modifications compared to a Diesel engine aftertreatment system are required. Close collaboration between engine and aftertreatment system design ensures optimized setups.

In contrast to methane slip issues still encountered for dual fuel gas combustion and hard to abate with aftertreatment technology, methanol does not bring along unresolvable emission challenges in terms of greenhouse gas emissions or other pollutants. For instance, laughing gas emissions were also monitored, as raw emissions and due to the use of the different aftertreatment concepts, they remained under all circumstances on Diesel combustion engine levels. Generally, particle emissions from methanol combustion have the potential to be significantly below typical Diesel fuel combustion emissions. However, for ultra-low emission vessels, the ambition is to achieve also ultra-low particulate mass and particle number emissions. In order to achieve these goals, methanol dual fuel engines can be additionally equipped with a wall-flow DPF, the first vessels will be delivered in 2026. Hug Engineering has developed solutions to support engine builders and operators to enable their transition to low net CO_2 engine operation, for methanol and other future fuels.

4 ABBREVIATIONS

CH_3OH: methanol

CO: carbon monoxide

DPF: diesel particulate filter

HCHO: formaldehyde

HCN: hydrogen cyanide / prussic acid

MeOH: methanol

Oxi: oxidation catalyst

PGM: platinum group metal

SCR: selective catalytic reduction

T: temperature

5 ACKNOWLEDGMENTS

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