

## Ammonia measurement challenges in SCR units

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### Abstract

SCR (Selective Catalytic Reduction) technology has been utilized in energy production and nowadays also in large marine diesels. To study and test these catalyst units in a smaller scale VTT has developed a test bench which utilizes a proper exhaust gas from a medium speed diesel engine. SCR utilizes ammonia ( $\text{NH}_3$ ) in the form of water solutions of urea for reducing  $\text{NO}_x$  to  $\text{N}_2$ . Naturally the amount of urea or ammonia is to be optimized in order to avoid ammonia emissions downstream of SCR. To measure ammonia, several methods can be used such as FTIR and laser based methods which use a heated sampling line from the SCR unit, in-situ laser method which requires optical access to exhaust piping, and wet chemical method using impinger sampling. In present study we have used both FTIR and a laser based method to measure ammonia slip when SCR was utilized to reduce  $\text{NO}_x$  emissions from a medium speed diesel engine exhaust. In addition we have utilized wet chemical method where unfiltered exhaust gas is bubbled through a reagent liquid and then analysed with a spectrometer. The results show that FTIR with heated sampling line seems to give lower ammonia values than impinger sampling in some test cases. (\*) In addition to the reactions between ammonia and sulphur, a further complication in these measurements may arise from possible storage effects in the exhaust piping and in the sampling lines. In a recent field study we compared FTIR and in-situ laser method and found systematic differences between ammonia results. Both high sulphur fuel and low sulphur fuel were utilized in testing and differences were found in ammonia results.

### Introduction

International Maritime Organization (IMO) has been creating regulation to prevent air pollution from ships /1/. It is well known that ship emissions contribute significantly to global emissions and to local emissions at ports. The regulation by IMO includes rules and limit values to decrease emissions of sulphur compounds and nitrogen oxides. There is regulation also on energy efficiency of ships which includes greenhouse gas emissions, and regulation on VOC emissions. The emission levels of sulphur compounds and particles will be decreased by rules on the sulphur contents of fuel. These rules gradually set the maximum allowed sulphur percentage in fuel to 0.5% globally by the year 2020, and to 0.1 % in specific emission control areas by the year 2015. Ships can also comply with these rules by installing an after-treatment system for  $\text{SO}_x$  removal. Also  $\text{NO}_x$  emissions are restricted gradually in marine diesel engines and the limits referred as Tier I, II and III are given as specific emissions (g/kWh) based on the maximum operating speed of the engine. The current Tier II standard can be met by optimization of combustion process, but Tier III standards which are planned to come into force in 2016 are expected to require an after-treatment unit for emission control.

The tight requirements set by IMO Tier III can be met by utilizing SCR technology (Selective Catalytic Reduction). In this technology a solid catalyst and injected ammonia is used for the reduction of NO<sub>x</sub> to N<sub>2</sub>. Instead of using ammonia as such, urea in water solution can be used as a reductant.

Theoretically, the amount of ammonia to be injected should be based on a molar ratio of ammonia to NO<sub>x</sub>, which is numerically the same as the NO<sub>x</sub> removal efficiency (based on the dominant reaction, see e.g. Majewski & Khair 2006 /2/). In addition to the amount of ammonia (urea) injected, the mixing of ammonia and gas is relevant for effective NO<sub>x</sub> removal operation. In practice, water solutions of urea are injected into the exhaust gas stream and evaporated, followed by decomposition of urea. The decomposition of urea to ammonia and the mixing of ammonia with the gas should happen well upstream of the SCR unit to allow the use of the SCR catalyst for the NO<sub>x</sub> reduction only (not for the urea decomposition).

Obviously, the target is to have the ammonia fully used for the NO<sub>x</sub> reduction. In practice, however, this is not always the case and excess residual ammonia (ammonia slip) can be found downstream of the SCR unit. The excess ammonia is environmentally harmful. In addition, if sulphur-containing fuels are used the ammonia can react with the SO<sub>3</sub> to form ammonium sulphates. These ammonium sulphates contribute to the formation of particle emissions and/or can deposit on the catalyst or downstream equipment, causing performance deterioration. For the formation of sulphates the temperature is in key role. In general, the lower the temperature the higher the potential of ammonium sulphate formation is.

In the operation of SCR unit the emission of ammonia or the ammonia slip is, however, not regulated by emission limit values by IMO. Instead, a general recommendation is given to prevent reductant emission: *When SCR uses urea solution as reductant, measures to prevent reductant slip should be provided to avoid supply of an excessive amount of reductant in the system. The reductant injection system should be designed to prevent emissions of any harmful substance from the system. /1/.*

To optimize the urea injection in practice and to avoid ammonia slip formation, there is a need for actual ammonia measurements. For this, several methods can be used such as FTIR and laser based methods which use a heated sampling line, and in-situ laser method which requires optical access to exhaust.

In the present study we have used both FTIR and a laser based method to measure ammonia slip. In addition, we have utilized an impinger sampling where exhaust gas is bubbled through a reagent liquid and then analysed with a spectrometer. Tests have been performed in three different applications: a medium speed diesel engine utilizing both LFO (light fuel oil with very low sulphur level) and HFO (heavy fuel oil with high sulphur level) as fuels and a gas engine utilizing natural gas (no sulphur) as fuel.

The research of ship emissions at VTT is focused on bench scale testing of catalytic units at laboratory, optimization of urea injection, and characterization of emissions. Moreover, we

carry out field measurement campaigns at diesel and gas power stations and at the ships with SCR units. These studies include the development of sampling and measurement methods, and the utilization of accredited standard methods for emission characterization.

At VTT a test bench has been constructed for SCR studies /3, 4/. This system makes it possible to vary several experimental parameters in wide range and independently of each other, which is typically not possible at production scale facilities. The test bench utilizes the exhaust gas of a 1.6 MW diesel engine creating realistic conditions for catalyst studies.

## Experimental

Ammonia slip measurements were conducted in three different applications. A medium speed diesel engine utilizing both LFO and HFO as fuels was employed as well as a gas engine utilizing natural gas (no sulphur) as fuel. In all the applications we used a FTIR device with a heated sampling line and compared it with other methods.

The first application is at VTT's medium speed engine laboratory. In this case we have utilized an emission control test bench (Fig.1), presented previously by Lehtoranta et al. /3/.

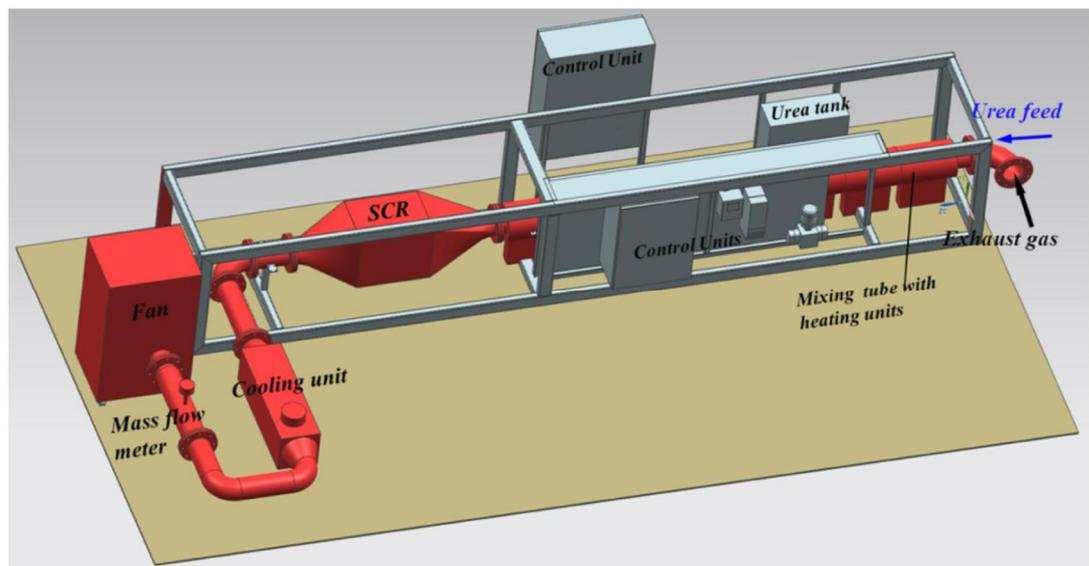


Figure 1. SCR test bench with urea mixing unit, SCR unit, and exhaust gas cooling and heating units /3/.

Heavy fuel oil with sulphur level of 2.4% was utilized as fuel and a vanadium based SCR to reduce NO<sub>x</sub> emissions. In this case, the ammonia slip downstream of the SCR unit was measured by FTIR and by impinger sampling where exhaust gas is bubbled through a reagent liquid and then analysed with a spectrometer. With the impinger sampling of this study, a known volume of exhaust gas was bubbled through the impinger containing water. Further, a sample was taken to ammonium cuvette test and analysed for the ammonium with spectrophotometer.

The second application was another medium speed diesel engine. Both heavy fuel oil and light fuel oil (with very low sulphur level) were in use and a vanadium based SCR. The ammonia slip was measured with FTIR and with an in-situ laser based method.

The third application was a gas engine equipped with a side-flow SCR unit. In this case, we again utilized FTIR, but now in parallel with a laser based method using the same heated sampling line for both instruments.

The actual target of this field campaign was to compare different catalyst setups by varying exhaust flow and urea feed but it was also possible to compare the  $\text{NH}_3$  results with different measurement methods. This SCR unit is constructed for R&D purposes and it contains several sampling points for extractive sampling. In Fig. 2 a schematic view of the SCR unit is shown with a movable sampling probe. The gas samples from different points between the catalyst plates were measured with FTIR and laser spectroscopy.

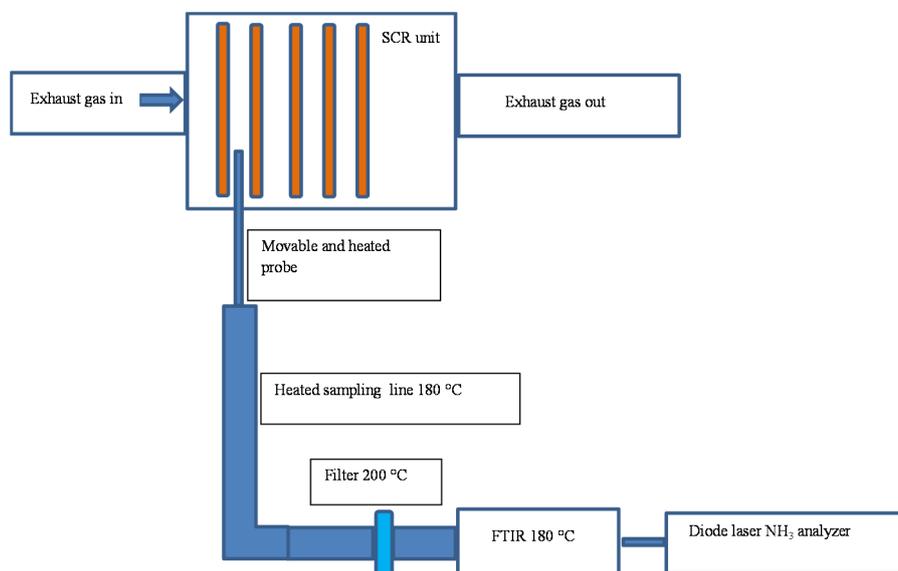


Figure 2. A schematic view of the SCR test unit in a side-flow of a gas engine.

## Results and discussion

The ammonia measurements with FTIR and with impinger sampling were compared in four different cases (ammonia slips between 4-46ppm). The results revealed to be either at the same level or the FTIR was found to give lower values. Especially when the FTIR resulted to very low level of 4ppm ammonia slip, the result from the impinger sampling followed by spectrophotometer analysis was 18 ppm.

In the second application ammonia slips were measured downstream of the SCR and the engine was run both with HFO and LFO. Two different FTIR units were utilized in measurements and compared to the in-situ laser measurement. For FTIR a laboratory calibration was carried out before the experiment and factory calibration settings were used

for in-situ laser. When running the engine with LFO, all the devices measured rather similar values for ammonia slips. However, when running on HFO (with high sulphur level) both FTIR instruments resulted to lower ammonia values than what was measured with the in-situ laser device. E.g. when the FTIR showed values of 20-30ppm for ammonia, the in-situ laser resulted to 50-56ppm. This might indicate that the sulphur related reactions can cause interference to the ammonia measurements with FTIR which requires sampling. Reactions between ammonia and sulphur compounds can lead to ammonium sulphates deposits in the piping line. The sampling line and a particle filter are possible places for such deposits.

In the third application the gas sample is fed to FTIR and laser device through the same sampling line as indicated in Fig. 2. The results indicated that there is a systematic difference between the NH<sub>3</sub> results for these instruments. During the two week campaign the laser device gave systematically 15-30% larger values than FTIR instrument. A reason for these differences could not be found. The use of the same sampling line and natural gas as fuel eliminates factors such as storage effects in sampling line and reactions between sulphur compounds and ammonia as in previous cases. The laser device was operated by using factory settings for NH<sub>3</sub> analysis. No corrections were made to the data for other substances as the diode laser's narrow beam should ensure the specificity of NH<sub>3</sub> measurement. The calibration of FTIR instrument was carried out at laboratory before the measurement period with reference gases (NH<sub>3</sub> in N<sub>2</sub>). During the field measurements only zero gas was tested daily. Further laboratory tests with calibration gases are under way to clarify the reason for these differences in NH<sub>3</sub> results.

## Acknowledgement

The study was conducted in CLEEN Oy's FCEP (Future Combustion Engine Power Plant) and MMEA (Measurement, Monitoring and Environment Efficiency Assessment) research programs funded by TEKES and several Finnish companies and research institutes. The authors would like to thank the personnel running the engines and contributing to emission measurements.

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