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Onboard measurements of diesel engine exhaust gas components

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Abstract

Against the background of future international regulations for marine diesel exhaust gas, the paper describes in brief the purpose of the intended IMO-Code on the emission of nitrogen oxides. In this connection, the joint research project CLEAN and the tasks of Germanischer Lloyd (GL) will be presented as dealing with the measurement technology used to analyse the gaseous components of marine diesel exhaust gas and to sample exhaust particles. Equipment and procedures are presented shortly whilst discussing the necessary knowledge to assess the exhaust emission behaviour of a diesel engine.

Emphasis will be laid on the description, measurement and the analysis of the particulate matter in the diesel engine exhaust gas. The method as well as the equipment used for sample collection and analysis of the composition of the particles will be described more closely. General requirements for onboard measurement equipment are stated.

1. Air Pollution from Ships

The increasing demands for environmental protection in shipping as well as in other fields are being answered by the International Maritime Organization (IMO) with further development of the rules. At present, an "Air Pollution" Annex to MARPOL is being compiled. Its purpose is inter alia to regulate the emission limits for the oxides of nitrogen (NOx) and sulphur (SO_2). A 'step by step' solution for implementation of the limit values for the nitrogen oxides is intended. This means that the permissible limit values defined in the Annex will be reduced further in phases according to technical progress and environmental needs at later stages.

Diverse strategies for implementing low-emission ship propulsion plants are also in the centre of the deliberations: progressive port duties as an economic incentive for low-emission propulsion units, for example. It may be expected that future developments will be characterized by more stringent limit values, by an extension with respect to the size and number of regions with special status and correspondingly low limit values, as well as by the inclusion of further diesel emission components in environmental considerations.

Looking closer to the IMO and regarding the NOx emission from ships, MARPOL's target is to achieve a reduction of 30 % from the 1990 levels for all marine diesel engines. The proposed regulations are laid down in the draft "Technical Code on Emission of Nitrogen Oxides from Marine Diesel Engines" with the purpose of specifying the requirements for the testing, survey and certification of marine diesel engines in order that the engines comply with the NOx emission limits. These limits are represented by the engine-speed/NOx-emission-limits curve which results from the peculiar characteristics in the formation of NOx across the engine speed ranges. This curve will be referred to later in this paper.

For a smooth and technically practicable implementation, the emission limits shall only apply to new engines with a power output of more than 130 kW. The total emission of nitrogen oxides should be determined using the relevant test cycles and measurement methods as specified in the NOx guidelines. The test cycles are distinguished for different marine applications, such as:

- constant-speed marine engines for ship main propulsion, including diesel electric drive and variable-pitch propeller sets - test cycle type **E 2** -
- propeller-law operated main engines and propeller-law operated auxiliary engines - test cycle type **E 3** -
- constant-speed auxiliary engines - test cycle type **D 2** -
- variable-speed, variable-load auxiliary engines - test cycle type **C 1** -

The applicable limit value and the actual weighted value of the engine shall be stated in the "Engine International Air Pollution Prevention Certificate" (EIAPP Certificate). The engine's certification will be part of a ship's initial certifications for the issuance of the ship's "International Air Pollution Prevention Certificate" (IAPP Certificate).

2. The CLEA*N* Project

Against this background, it is considered highly probable that by the end of this decade the emission limits of marine diesel engines will have become a decisive criterion in competition, and will enjoy priority over optimum efficiencies. Finding a satisfying solution to fulfil both criteria simultaneously is one of the primary tasks of the joint project CLEA*N*. In November 1995 the research project "Low-Emission Ship Propulsion Plant" was officially launched at Germanischer Lloyd Head Office in Hamburg. The project is financially supported by the German Federal Ministry for Education, Science, Research and Technology (BMBF).

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Verbundvorhaben Emissionsarme Schiffsantriebsanlage

For identification purposes, the acronym CLEA*N* was chosen for the project. CLEA*N* stands for Clean and Low Soot Engine with Advanced Techniques for NOx Reduction. The following companies and institutions are involved in the joint research project with own financial contributions:

- Forschungsvereinigung für Verbrennungskraftmaschinen e.V. (Research Association for Combustion Engines)
- FMC - Fiedler Motoren Consulting
- Siemens Energieerzeugung (KWU), Product Division for Catalytic Reactors
- TT-Line GmbH & Co.
- Germanischer Lloyd
- AVL Graz
- Dieselmotorenwerk Vulkan (DMV)
- MaK Motoren GmbH
- MAN B&W Diesel AG
- Motoren-Werke Mannheim AG (MWM)
- SKL Motoren- und Systemtechnik
- Woodward Governor Germany

In order to monitor, coordinate and control the joint project, the project partners entrusted Germanischer Lloyd with the overall project management.

Coming back now to the engine-speed/NOx-emission-limits curve, today's state of technology and the aims of the joint project are shown in Fig. 1. The aims of the project go beyond the IMO limit values expected for the near future. These figures already represent a 30-percent reduction of the usual NOx emission values of the year 1990. The joint endeavour is aiming at a further decrease in NOx emissions, so that a reduction by approx. 50 % will become possible by engine-internal measures and about 95 % by SCR (Selective Catalytic Reaction) units. However, the specific fuel consumption as well as the emissions of soot and particles should not deteriorate, rather the second objective is to reduce the emissions of visible soot radically, particularly during non-steady engine operations and under partial load.

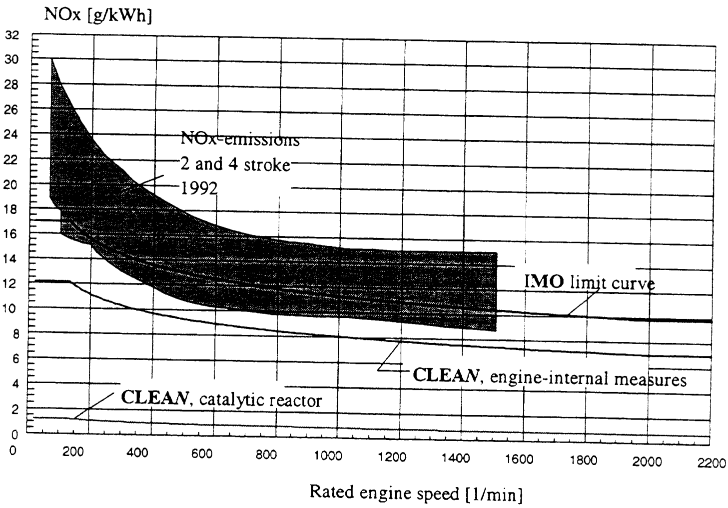

Fig 1: State of Technology and Aims of CLEA*N*

Although no national or international rules have been initiated yet for allowable particle emissions, corresponding efforts are expected in the foreseeable future. For particles also, the main efforts will be to reduce their formation through design and enhanced process control.

The approaches towards reduction of exhaust emissions in sea transport range from fundamental questions concerning the most favourable transportation and propulsion systems, over operational measures to be taken by the shipowners, up to detailed solutions for the propulsion plant and the marine diesel engine (Fig. 2).

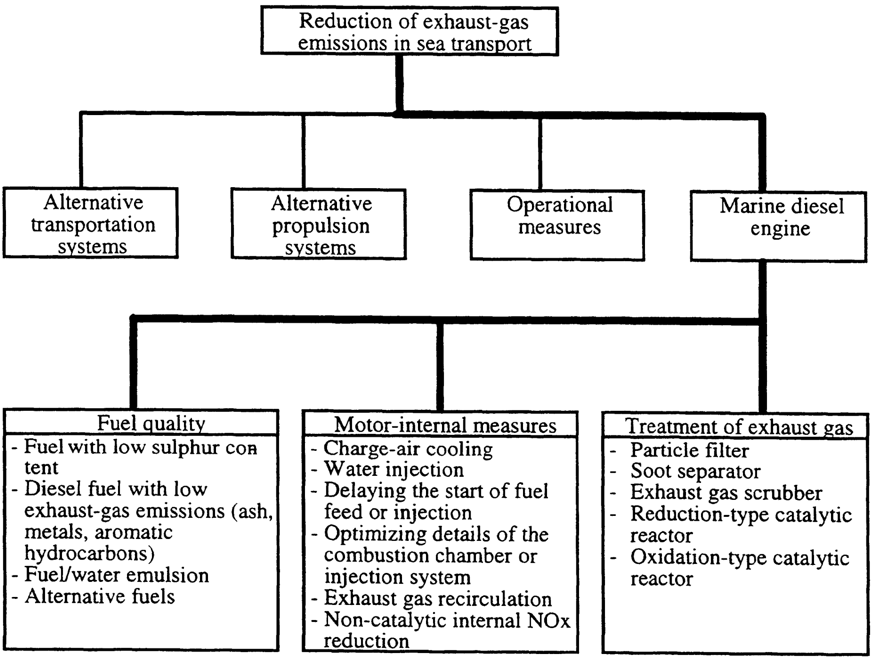

Fig. 2: Options for Emission Control

The work in the joint project is concentrating on the propulsion plant, with the main emphasis on prevention of NOx and particle formation during combustion. Exhaust gas treatment systems are also being investigated.

The objective of CLEA*N* is to significantly reduce the NOx and the particle/soot emissions - if possible without an increase in fuel consumption, to which the CO_2 emission level is proportional. The problematic nature of this dependency, namely the counteractive relationship between optimization of the design for optimum fuel-consumption and for minimum NOx, is generally referred to as the 'diesel dilemma'.

The engine design point for the emission characteristics is not all that important, if the diesel engine exhaust system is equipped with an SCR and/or a particle/soot separator.

As a basis for future engine and catalytic-reactor designs, theoretical and experimental research, developments on laboratory and test-bench scale as well as test series on engine test-beds are being conducted in this joint project with a distribution of tasks amongst the partners. Investigative sea trials on a ferry ship are to determine whether and under what conditions electronically controlled fuel injection systems and catalytic reactors for after-treatment of the exhaust gas can be implemented during normal operation at sea, in order to reduce the emissions reliably and effectively.

Based on fundamentals, which also include an experimental evaluation of the current emission level of modern engines, engine-internal measures and exhaust gas after-treatment systems are being developed. The experiments and the development work of the engine manufacturers and their associates with respect to the optimization of the combustion process will lead to generalized design criteria. The solutions found for the 2-stroke and 4-stroke test engines of different sizes and different engine-internal measures are the prerequisite for further improvements by means of engine management systems with electronically controlled fuel injection.

To reduce NOx emissions further, an SCR will be needed. A catalyst which works by addition of urea to the exhaust gas flow has been installed onboard a ferry operating in the Baltic Sea. For the storage and supply of urea to the exhaust, a special system with associated control is necessary. Hence a new design without urea supply, and hopefully without any reduction agent, is to be developed in the project. Further investigations comprise the application of catalytic reactors to 2-stroke engines and their operation downstream of engines burning heavy fuel oil. The investigations and developments of exhaust gas treatment systems will be generalized and requirements for such plants will be derived.

If a propulsion plant consists of several engines, the plant management should distribute the power demand to the engines such that best overall emission values are reached. This management should also include the control of fuel treatment and charge air systems as well as applicable exhaust gas after-treatment systems.

At the current stage of development, results cannot be presented in this paper yet. This will be up to the decision of each partner for the specific results obtained. Within the project a free exchange of information is agreed and contractual provisions for a future use of these findings foreseen.

In the following, the tasks of Germanischer Lloyd in this project will be described briefly:

- coordination of the joint project
- measurement of the emissions of the latest generation of marine diesel engines in service burning heavy fuel oil

- measurements of NOx emissions on the test beds of the partners as a basis for comparison and future certification
- onboard and test-bed sampling as well as laboratory analysis of diesel particles
- characterization of particles
- development of procedures suitable for the measurement of the particle emissions of marine diesel engines
- elaboration of proposals for potential guidelines for the assessment of the particle emissions of marine diesel engines
- investigation of characteristics relevant to safety and definition of the corresponding requirements relating to electronically controlled fuel injection systems and onboard catalytic converters.

3. Onboard Measurements

Germanischer Lloyd is carrying out PC-controlled measurements for the assessment of the exhaust gas emission behaviour of marine diesel engines under service conditions. Besides the nitrogen oxides, some additional gaseous components are registered using special analysers, such as:

- oxygen - O_2 -
- sulphur dioxide - SO_2 -
- hydrocarbons - HC -
- carbon monoxide - CO -
- carbon dioxide - CO_2 -

In cooperation with a maker of measurement devices for exhaust gas particles, a special sampler has been developed for mobile use on board ships.

In addition to the exhaust gas measurements, some essential operating data are measured to assess the respective engine operating conditions for all test cycles:

- engine or shaft torque
- engine or shaft revolutions
- charge air pressure and temperature
- ambient air conditions: temperature, pressure, humidity
- fuel rack position
- fuel consumption
- exhaust gas temperatures

GL has assembled portable measurement devices to meet the difficult and varying conditions aboard all kinds of ships. The combination of all parts of the equipment is shown below.

In general, the measurement programme includes the registration of time records of ship manoeuvres during entry into and departure from ports, as well as the performing of the IMO-related test cycles.

4. Combustion in Diesel Engines and Particulate Matter

The combustion process of hydrocarbons is governed not only by the kinetic reaction, but also by diffusion, thermal conduction and convection. In spite of a very lean mixture, with $\lambda = 1.2$ ranging up to $\lambda = 2.0$, zones with an oxygen

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deficiency arise when the heterogeneous mixture in the cylinder is burnt; here the hydrocarbon fractions emerged by cracking do not oxidize completely. A consequence of this is the visible diesel soot, consisting of fine aerosol-like components.

Since only oxygen is consumed by the combustion, the gaseous emissions comprise 75 % nitrogen (N_2) by weight and, because of the lean mixture, about 6 % oxygen (O_2) by weight. Further primary components are water vapour (H_2O) as well as carbon dioxide (CO_2), in about the same proportions with 9 % and 10 % by weight respectively.

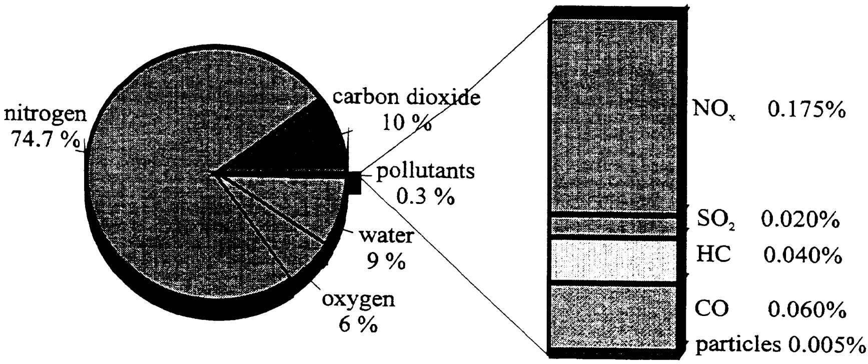

Fig. 3: Composition of diesel exhaust gas

The actual contaminant gases CO, NOx and HC do not even make up 1 % by weight of the entire emission. Nevertheless, they must be given the most attention. The "HC proportion" is a complex mixture of aldehydes and other volatile organic substances. The concentrations of the various substances range from the ppb level up to several hundred ppm. During dilution with ambient air, these molecules can attach themselves to the solid particles contained in the exhaust gas.

The diesel particles are composed of several hundred organic and inorganic compounds; mainly of elemental carbon, attached hydrocarbons and sulphate with attached water.

These diesel particles, 80 % of which have an aerodynamic diameter of $dp_{ae} < 0.3\ \mu m$, carry toxic and carcinogenic substances which can reach the alveolar part of the human respiratory tract. Moreover, it is now suspected that the elemental carbon also has a carcinogenic effect.

The chemical composition of the particles is usually described in the form of 'particle fractions' for reasons of simplification. Depending on the type of analysis, the individual substances are then classified into material groups of the same chemical characteristics (extraction process) or physical characteristics (thermal process).

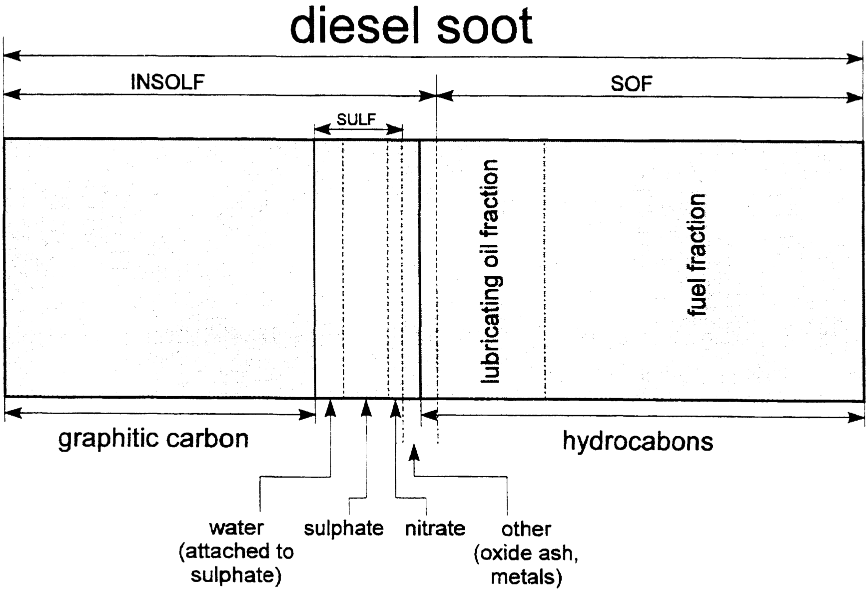

Fig. 4: Diesel soot fractions according to the chemical characteristics of the particles

The fraction that can be extracted in an aqueous solution is named the 'sulphate fraction' (SULF) after its main constituent, and for the classification shown in Fig. 3 is simply assigned to the insoluble fraction, which cannot be dissolved in homopolar organic solvents. The sulphate fraction characterizes the fuel's influence on the particulate emissions and should therefore always be shown separately.

The particulate fraction that can be extracted by a Soxhlet or ultrasonic process in organic solvents, such as toluene, consists of a multitude of condensed hydrocarbon compounds which originate from the gaseous phase and are attached to the solid particles. The individual organic compounds can be quantified, either by the chemical methods of trace analysis, such as HPLC (High Performance Liquid Chromatography) or GC (Gas Chromatography), or by evaporation at 200°C for 20 hours, whereby separation into a solid and a volatile particle phase is achieved.The insoluble particle phase consists mainly of soot, ash and various metal compounds. The ash-like particle components originate directly from the fuel or from the oxidation of lubricant additives. Iron, calcium and zinc compounds are the chief members of this group of materials. Oxide ash plays an important role in the combustion of heavy fuel oil in large diesel engines. The chemical analysis of oxide ashes is most time-consuming, and is therefore only being performed for selected samples by Germanischer Lloyd within the scope of "CLEA*N*".

The organically soluble particle phase

In characterizing the organic particle fraction, the methods of chemical trace analysis are generally applied; capillary gas chromatography is used at Germanischer Lloyd. The particle mass that is soluble in organic solvents consists mainly of the following groups of compounds:

- unburnt hydrocarbons from the fuel oil and the lubricating oil
- partially oxidized fuel and lubricant compounds, e.g. aldehydes, ketones and organic acids
- products of the pyrolysis process; these include polyaromatics and polymer compounds, amongst others.

Although several hundred different organic compounds can be detected in diesel particles, the organic particulate mass of the paraffin fraction consists mainly of unburnt fuel and lubricating oil.

The inorganically soluble particle components

The prime representatives of the inorganically soluble particle fraction are sulphate compounds. In terms of weight, nitrates, phosphates and other salts are only subordinate.

The formation of sulphate particles is primarily characterized by the sulphur content of the fuel and the conversion rate of the combustion process, which determines the proportion of fuel sulphur to be found as sulphate emission in the diesel exhaust gas. Depending on the engine type and load condition, the conversion rate is about 0.9 % up to a maximum of 6 %.

From the combustion chamber through the exhaust duct up to mixing with surrounding air, there is a continuous change in the physical and chemical characteristics of the particles:

In the combustion chamber of the diesel engine, finely dispersed elemental carbon is formed and introduced into the exhaust duct. For fuels with mineral components, these also pass into the hot exhaust gas as oxide ash particles. Organic materials and sulphuric acid are present in gaseous or vapour phases, owing to the high temperatures.

After passing into the exhaust duct, the exhaust gas is cooled by dilution and mixing with the surrounding air. As a result, organic compounds condense on the particles. The temperature falls below the dewpoint of sulphuric acid, which then also settles on the particles from the diesel exhaust gas and the surrounding air, thereby increasing the particle mass and changing the particle composition. This effect is avoided by performing the particle sampling according to the ISO 8178 or EPA requirements, in that the exhaust gases are diluted with filtered, particle-free ambient air.

5. Technological State of Particle Measurement

Evaluation Criteria for Particle Emissions

In order to assess the particle emissions of diesel engines, the method of gravimetric determination of the particle mass concentration is applied in the hot exhaust gas as per German Technical Specification for Air (*TA-Luft*), or in the diluted exhaust gas as per EPA requirements.

With regard to motor vehicle engines, the term 'particle' groups together all solid and liquid components of the exhaust gas that are precipitated on certain types of filters (Teflon-coated fibre glass filters, Teflon membrane filters) after cooling, through dilution, to a temperature equal to or less than 52°C. For the assessment of the engine emission characteristics the concentration is calculated from the particulate matter in the diluted exhaust gas stream and the actual exhaust mass of the engine.

The particle sampling for stationary diesel engines is performed according to German guideline VDI 2066, whereby the dry dust mass concentration of the raw exhaust gas is determined. The emission values are expressed with reference to an oxygen volume content of 5 percent.

Gravimetric Determination of the Particle Mass

A partial stream is taken from the diesel exhaust gas, and the particles are precipitated on special filters. The particle mass is then determined from the difference in mass between the clean and the used filter, whereby defined conditions for humidity and temperature are needed for the weighing process. Gravimetric processes provide the reference for all assessments of limit values that refer to the overall particle mass.

To achieve sufficient measurement accuracy, the particles must reach a certain minimum mass over the sample collection time. For ships, sampling with a exhaust gas dilution system is proposed, by analogy with vehicle engines. A special system is required for sampling on board ships, this being available at Germanischer Lloyd.

6. Outlook

By increasing experience in onboard measurements, the results of CLEA*N* will provide a valuable basis for the general assessment of particles and, regarding NOx, for the practical performance of engine certification.