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Methane and Formaldehyde Emissions of Gas Engines

By CIMAC WG 17, Gas Engines

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Content

1 Summary

Unburned Methane emissions from gas engines are of concern because of their contribution on global warming. Formaldehyde – a toxic interstage product of the Methane oxidation process – is known for its strong smell and carcinogenic properties. The amount of and the reasons for these emissions depend very much on the gas engine design and its combustion system. This results in different engine internal and engine external strategies for optimizing Methane and Formaldehyde emissions. Due to their combustion system lean burn Otto-Gas-Engines generally show the highest rates of unburned Methane emissions among different gas engine concepts. But compared to Diesel engines modern gas engines definitely contribute to an effective reduction of NO^x, CO^2 and other toxic emissions in the exhaust gas. Due to their savings in CO^2-emissions gas engines even with unburned Methane emissions close to 2% still show a lower Green House Gas (GHG) factor than comparable Diesel engines.

After treatment systems for Formaldehyde-oxidation are proven technology (for natural gas) and already in use in the gas engine market. However, reliable after treatment systems with catalysts to oxidize the residuals of unburned Methane are not available yet. For current systems the exhaust gas temperature of gas engines is significantly lower than that needed for efficient conversion. After treatment systems for Methane-oxidation definitely require further development.

The further optimization of the gas engine combustion process, the gas engine design and the after-treatment system is a major interest of the gas engine industry. Much effort is spent on the continuous development of new improved solutions.

2 Background

Comparing with gas turbines modern reciprocating piston gas engines show higher electrical efficiency, lower capital investment and lower maintenance cost in a power range approximately up to 50MW. Together with their ability to respond to higher load steps piston engines are predestined (or the only solution) for smaller power plants, mechanical applications and propulsion.

Efficiency and power density are key factors for the development of modern gas engines. The efficiency of modern gas engines can be even higher than those of Diesel engines. Moreover, gas engines are especially known for their very low toxic emissions. Global oil resources are expected significantly to drop in the next decades, whereas the exploration/extraction of natural gas and the usage of biogas still have big potential for growth. Therefore, natural gas is seen as one of the main energy sources for the future and gas engines usage is expected to increase. Despite all these advantages gas engines also are facing serious challenges:

(1) Although the oxidation of natural gas (Methane, CH^4) generally produces less CO^2 than Diesel combustion of fuel oil, residuals of unburned Methane in the exhaust gas can worsen the overall green-house effect of gas engines. Since the green-house factor of Methane is about 23 times that of CO^2, even small amounts of Methane are very significant. In this respect the so-called “Methane-slip” is a characteristic for almost all gas engines and can vary from below 1% to over 5% of the total gas consumption.

(2) Although gas engines have a very low toxic emission level compared to diesel engines some of their oxidation products must not be neglected. Among these Formaldehyde is

very significant. The International Agency for Research and Cancer (IARC, belonging to the WHO) has categorized Formaldehyde as a carcinogenic substance. The regulations of TA-Luft limit the emissions of Formaldehyde to 60mg/m^3. It is to be expected that the limit for Formaldehyde will be reduced even further. German legislation, for example, has already defined 40mg/m^3 as a basic requirement for the approval of financial aids for cogeneration plants.

3 Introduction

In contrast to steady state operated gas turbines with their spatial separated sections for compression, combustion and decompression, the design principle of reciprocating gas engines combines all these sections into one basic (combustion) chamber. This single chamber basically fulfills all necessary functionalities in a cyclic, time-sequential order. Due to the reciprocating movement of the piston each phase is limited in time and characterized by rapidly changing temperature and pressure levels.

The combustion mixture and the combustion itself inside a piston gas engine never experience steady state conditions. Many design parameters and variables of the engine system show significant time-dependent impact on the combustion process as well as on the development of emissions. The engine's bore and speed, the power output, the design of the combustion chamber, the combustion system, the motion of the combustion mixture and last but not least the composition of the burned air/gas mixture itself are the most relevant key-parameters.

3.1 Classification of the combustion system of gas engines

Gas engines cover a wide range of different applications. In order to achieve highest performance levels their combustion and ignition systems must reflect the specific constraints of the applications they are designed for. There is no unique combustion and ignition system suitable for all gas engine applications. The different combustion and ignitions systems of gas engines can be categorized/classified as follows:

- *Rich/lean burn gas engines:* Near-stoichiometric mixture systems (rich burn systems) are generally dominating in automotive applications. Their mean effective pressure is moderate - however, the required engine's speed variability is very high. Near-stoichiometric systems are easy to ignite and to burn out and usually, their exhaust gas temperatures are very high which is very beneficial to exhaust gas after treatment systems.
  Lean burn gas engines are the preferred system for off-road, marine and power-generation applications with high power-density. Lean burn combustion systems reduce thermal loading and the risk of knocking. Lean burn systems require advanced ignition technologies and - in contrast to rich burn systems - their exhaust gas temperature is significantly lower.
- *Air/Gas mixture formation:* The air/gas mixture formation for Otto-Gas-Engines can be differentiated between in-cylinder mixing procedures (e.g. port injection or direct injection into the combustion chamber) and homogeneous charge mixing strategies upstream the cylinders often referred to as mixture charged engines. The most relevant aspects for selecting one of these methods is the available gas supply pressure, the required engine's load step profile and safety regulations of the plant or engine. Port injection and direct injection systems are advantageous for applications with high dynamic load profiles. Homogeneous charge mixing strategies can be operated with the lowest gas supply pressure whereas direct injection

systems require gas supply pressures up to 200 – 300 bar. The direct injection technology is very attractive especially in combination with LNG-storage locations and LNG-carriers.

- *Internal combustion principle:* Based on the applied air/gas mixture strategy the internal combustion of gas engines can be classified into two basic categories: The pre-mixed and the Diesel-like diffusion based combustion. Mixture charged as well as port injection gas engines are characterized by a pre-mixed combustion. Diffusion based combustion systems require direct injection. Both combustion principles have their individual advantages and limitations with regard to emissions, efficiency and operating range.
- *Ignition source:* The most common ignition types of modern gas engines are the spark-ignition (for rich and lean burn systems) and the ignition by pilot Diesel-fuel injection (for lean burn systems). The ignition source might be amplified by additional pre-chambers. Pilot Diesel-fuel injection is the preferred ignition technology of dual-fuel engines in gas mode and gas engines with direct gas injection. Dual fuel engines combine the positive characteristics of Diesel and gas engines. With their ability to burn Diesel as well as gaseous fuels (modern dual-fuel engines can switch between gas and Diesel mode during operation) they are predestined for applications where fuel flexibility and low emissions are required.

Methane and Formaldehyde are characteristic emissions mainly of gas engines with a pre-mixed combustion system. Gas engines with direct injection and a Diesel-like diffusion based combustion show a very different emission behavior in which unburned Methane and Formaldehyde play only a minor role (refer to Fig. 5). Due to this fact this position paper focuses on gas engines with homogeneous charge mixing or port injection and a pre-mixed combustion.

3.2 Motivation for lean burn gas engines (pre-mixed combustion)

Fig. 1 illustrates the characteristic combustion diagram of pre-mixed combustion gas engines. The stable and usable operating range of reciprocating gas engines is mainly dominated by the limits of knocking and misfiring. Both limits get very close to each other for higher values of Lambda and/or BMEP (Break Mean Effective Pressure). Low-NO^x gas engines are trapped between these limits – their operating range must follow these naturally given constraints. Hence, optimizing gas engines with regard to NO^x, BMEP and efficiency can be realized only by leaning out the combustion mixture. Fig. 1 is representative for all Otto-Gas-Engines in a qualitative point of view. Specific values and limits, however, depend highly on the gas properties but also on the combustion system (e.g. ignition source, port or direct injection) and the engine design (e.g. speed and bore).

3.3 Challenges for the development of lean burn gas engines (pre-mixed combustion)

This combustion strategy for highly efficient lean burn gas engines is facing challenges. On the one hand, very lean mixtures require - especially for large bore gas engines - amplified ignition sources (e.g. pre-chamber or Diesel-pilot injection) to extend the misfiring limit. On the other hand advanced engine control techniques must protect the engine from mechanical damages due to knocking events because of the narrow operating window at high loads.

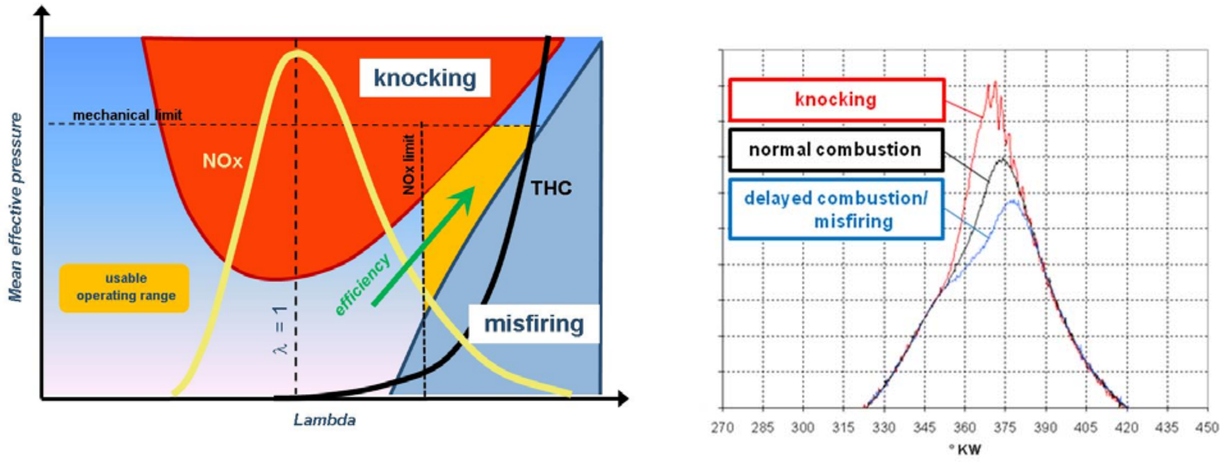


Fig. 1: Combustion diagram for gas engines. The relation between emissions, efficiency, power density and operating limits.

4 Reasons for CH^4 and Formaldehyde emissions of gas engines

4.1 Relation between CH^4 and Formaldehyde

CH^4 and Formaldehyde emissions result from unburned or only partially burned air/fuel mixtures. Formaldehyde is an early interstage product of the Methane oxidation. Its formation starts at low temperatures but gets fully oxidized only above a certain minimum temperature level (800-900°C). Some "cold regions" in the combustion chamber (like crevice areas or the fireland) show temperature levels typically varying within these limits. Such areas are the main sources of Formaldehyde emissions. Generally the amount of Formaldehyde emissions increases with the amount of unburned Methane in the exhaust gas.

4.2 Sources of CH^4 and Formaldehyde

The amount of unburned/partially burned air/fuel mixtures highly depends on a complex relationship between the reaction kinetics of the fuel, the design parameters of the combustion chamber, the timing of the scavenge process and last but not least the combustion system itself. Therefore, the specific type of gas engine technology has a significant impact on the resulting CH^4 and Formaldehyde emissions. Usually, differences in engine design and combustion system will result in different CH^4 and Formaldehyde emission levels. In reciprocating gas engines the main sources of CH^4 and Formaldehyde are:

(1) *Scavenging process, losses during valve overlap*

During the valve overlap at the beginning of the suction phase temporarily a direct path between the inlet and outlet port may exist. In case of turbocharged gas engines where the pressure level of the charge air intake manifold is higher than the pressure level in the exhaust manifold, fresh air or unburned air/gas mixture can escape during this phase into the exhaust gas system. CH^4 losses due to valve overlap are mainly significant for homogenous charge gas engines and for port injection systems with long injection timings.

The scavenging process/valve overlap has only a minor impact on the total Formaldehyde emissions, however.

(2) *Quenching effects in lean mixture zones*

The flame propagation in combustion zones is stable only under certain conditions. The type of fuel, the equivalence ratio, the pressure and temperature level as well as the intensity of the turbulence limit the range of stable flame propagation and reaction kinetics. Too high or too low values might lead to significant quenching effects resulting in unburned or partially burned Methane emissions. Fig. 2 shows schematically the impact of equivalence ratio, temperature and turbulence level on the chemical flame stability. The range of stable flame propagation highly depends on the equivalence ratio and decreases rapidly with lower temperatures in the combustion chamber. The flame stability of Methane/air mixtures is usually very good up to lambda values of 2 and decreases significantly for leaner mixture rates. Mixture ratios close to Lambda 3 can be seen as the outer limit for state of the art ignition and combustion systems of gas engines with a pre-mixed combustion. Even if the overall mixture rate in a combustion chamber would allow a stable flame propagation, local in-homogeneities might result in zones with gas/air mixtures close or beyond Lambda 3.

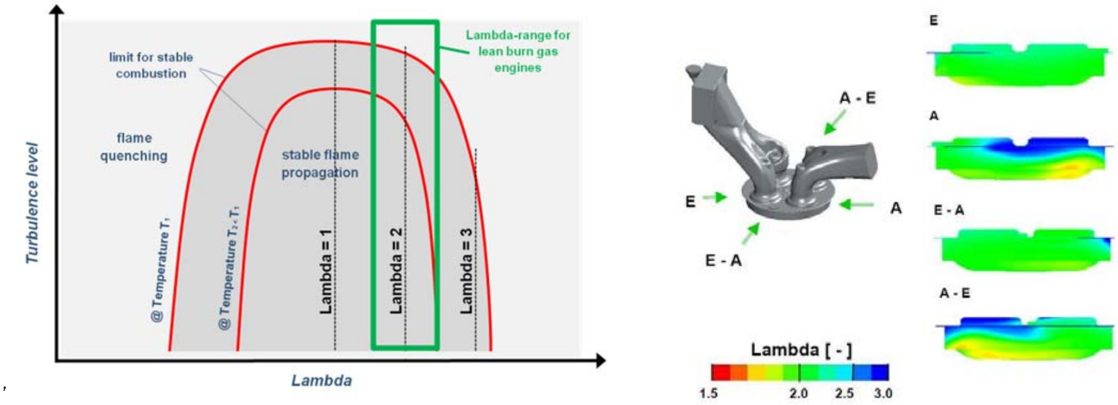


Fig. 2: Left hand side: Range of stable flame propagation

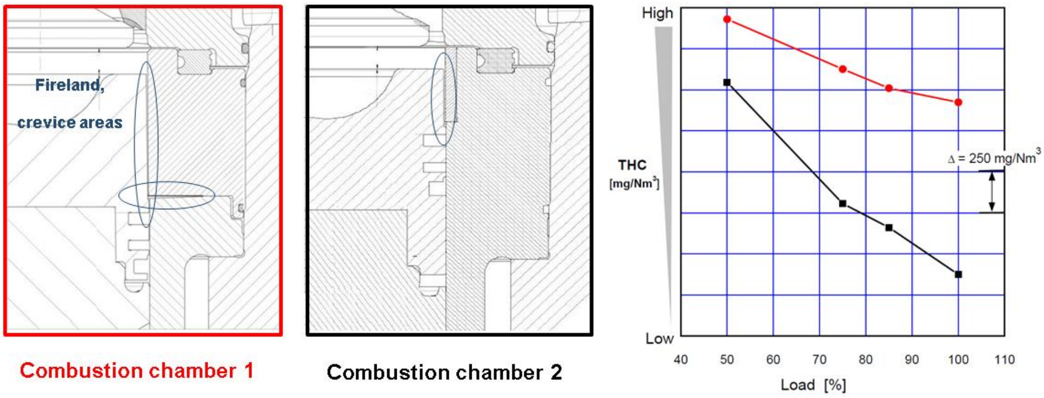
Right hand side: Stratified charge mixture in the combustion chamber of large bore engine shortly before ignition [2]

(3) *Quenching effects near walls*

Heat losses of the burning gas/air mixture close to walls in the combustion chamber are very significant. Such heat losses reduce the temperature level in boundary layers and can impact/slow down the reaction kinetics of the oxidation process (compare fig. 2). This will result in unburned fuel emissions. Boundary layers not only suffer from heat losses over the walls of the combustion chamber but also from a decrease in turbulence. The reduction of the turbulence level slows down the propagation velocity of the local combustion process. The time window of the combustion cycle might be insufficient to complete the slower combustion.

(4) *Trapped methane in fireland*

Crevice areas in the combustion chambers are characterized by high surface/volume ratios. In such crevice areas heat losses are very high and the turbulence levels are significantly reduced. As described above both properties negatively affect the reaction kinetic and lead to increased unburned and partly oxidized CH^4 emissions. In general, the amount of CH4 and Formaldehyde emissions grows equally with the total volume of the crevice areas in the combustion chamber. For mixture charged and port injection gas engines the most significant CH^4 and Formaldehyde source is the fireland above the piston rings. Typically more than 50% of the total CH^4 emissions result from the fireland if CH^4 is trapped in this area during the compression cycle.



Combustion chamber 1

Combustion chamber 2

Fig. 3: Impact of crevice areas on the emission level of Methane [2]

(5) *Delayed combustion/misfiring*

Another important source of CH^4 emission are incomplete or delayed combustion processes including events of misfiring. The risk of such events is usually higher for leaner mixtures. Especially during the starting process of port injection gas engines the combustion mixture might reach very lean conditions (around Lambda 3). Unusual high CH^4-emissions of a gas engine might also come from wrongly adjusted ignition systems or failures due to worn components of the ignition system.

5 The relation between engine design, combustion system and CH4 emissions (pre-mixed combustion)

(1) *The dilemma of efficiency and CH^4:*

Highly-efficient turbo-charged gas engines with high power densities must be operated with lean mixtures since the knocking intensity of gas/air mixtures grows with the mean effective pressure. The higher the engine's mean effective pressure is the leaner the combustion mixture must be (compare Fig. 1). The use of gases with low Methane numbers worsens the situation. Leaner combustion mixtures show the trend towards higher rates of unburned CH^4 as a consequence of reduced reaction temperatures (Fig. 4).

(2) *The dilemma of NO^X and CH^4:*
Similar to the dilemma of efficiency and CH^4 there is also a dilemma with regard to NO^X and CH^4. When just focusing on the reduction of unburned CH^4-emissions the enrichment of the combustion mixture would be a very effective measure. By reaching almost stoichiometric conditions this measure alone would reduce the unburned CH^4 emissions well below 1% of the total amount of gas. But reducing the amount of unburned CH^4 by enrichment of the gas/air mixture will result in increased NO^X and CO emission rates (Fig. 1).

(3) *The dilemma of engine bore and CH^4:*
Due to mechanical limitations the engine speed must drop with larger bores. As a direct consequence of the engine's speed the combustion and emission characteristics are different for small, medium and large bore gas engines: With increasing engine speeds the internal combustion process gets faster. This effect helps to reduce the time-dependent formation of NO^X and the risk of knocking events. Within the category of pre-mixed combustion systems large bore gas engines are therefore more affected by the constraints of the chemical reaction kinetics than small bore engines. Consequently large bore engines with pre-mixed combustion must be run under leaner conditions in order to keep the same NO^X emissions and the same margin to the knocking limit as small bore engines. This of course affects the unburned CH^4 emissions.

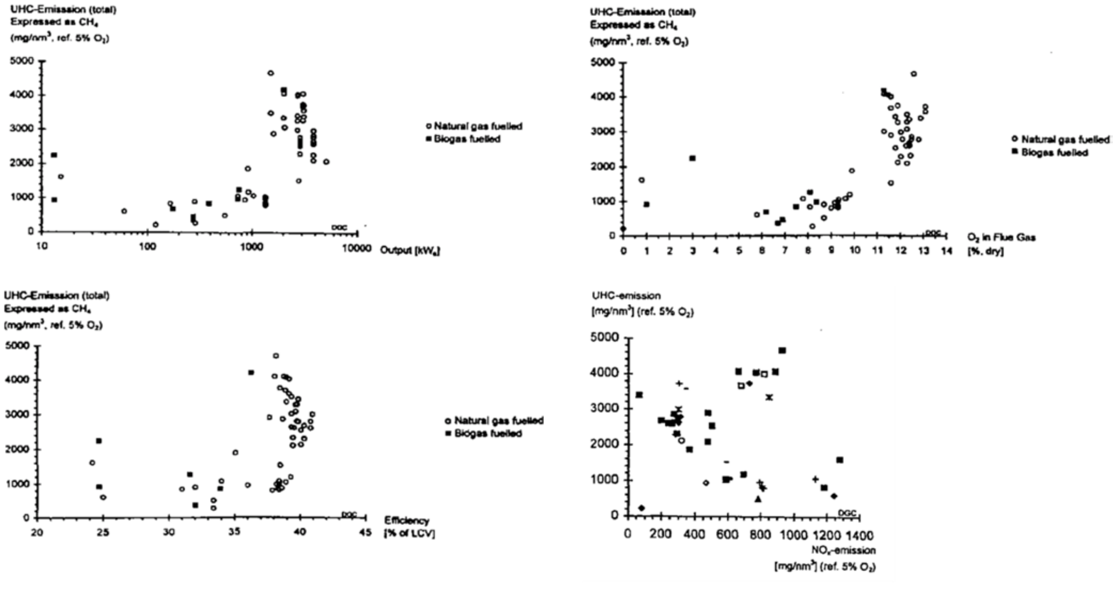


Fig. 4: CH^4-emissions in the context of multi-disciplinary engine optimization [1]

Fig. 5 compares the CH^4-emssions of different gas engine designs and combustion systems from a qualitative point of view. Each source of unburned CH^4-emissions is evaluated with regard to its relative contribution.

A comparison between rich burn and lean burn systems clearly shows that learn burn gas engines generally have disadvantages regarding the amount of CH^4-emissions. 4 out of 5 sources of CH^4-emissions are assessed higher for lean burn systems. Most relevant source is the trapped Methane in the fireland and similar crevice areas.

The analysis between small bore and large bore engines reveals an almost similar result. 3 out of 5 possible sources of CH^4 emissions are dominating in large bore engines. For small bore as well as for large bore engines trapped CH^4 in the fireland is again the most significant source of unburned Methane and Formaldehyde.

The impact of the fireland and other crevice areas on the CH^4-emssions can be significantly reduced by the choice of the gas mixing system. In port-injection and homogenous charge systems parts of the combustion mixture are trapped within the fireland during the compression cycle. This can be avoided by injecting the gas into the combustion chamber shortly before ignition.

Combustion System	**scavenging process, valve overlap**	**quenching effects in lean mixture zones**	**quenching effects near walls**	**trapped Methane in fireland**	**delayed combustion/misfiring**
same engine speed					
Rich burn combustion system (SI)	**medium**	**low**	**low**	**medium**	**Low**
Lean burn combustion system (SI/DF)	**low**	**medium**	**medium**	**higher**	**medium**
same NO^x level, same gas admission system					
Lean combustion: small bore – high speed (SI/DF)	**medium**	**low**	**low**	**higher**	**Low**
Lean combustion: large bore – medium speed (SI/DF)	**low**	**medium**	**medium**	**higher**	**medium**
same NO^x level					
Homogenous charge (SI/DF)	**medium**	**low**	**low**	**higher**	**Low**
Port injection (SI/DF)	**medium**	**medium**	**low**	**higher**	**Low**
Direct injection (SI/DF)	**low**	**medium**	**low**	**low**	**medium**

Fig. 5 Comparison of different Otto gas engine and combustion systems with regard to relative CH^4-emissions

6 Engine internal measures to reduce CH^4-emissions

The reduction of unburned CH^4-emissions in the internal combustion process is a natural interest of gas engine manufacturers since this represents a significant potential for further efficiency improvement (see Fig. 6). The reduction of CH^4-emissions by 1% results in up to 0.5% gain in efficiency. The challenge for future gas engines will be to burn as lean as necessary and to keep the balance with unburned CH^4-emissions. It is the responsibility of the industry not only to reduce emissions but also to save energy. Preventing CH^4-slip during the scavenging process, reducing crevice areas in the combustion chamber and the realization of a fast and complete combustion are key technologies for advanced gas engines with high thermal efficiency. However, material and design/application constraints of the engine as well as the individual physical reaction kinetics of the burned gas/air mixture make advancements in these areas difficult.

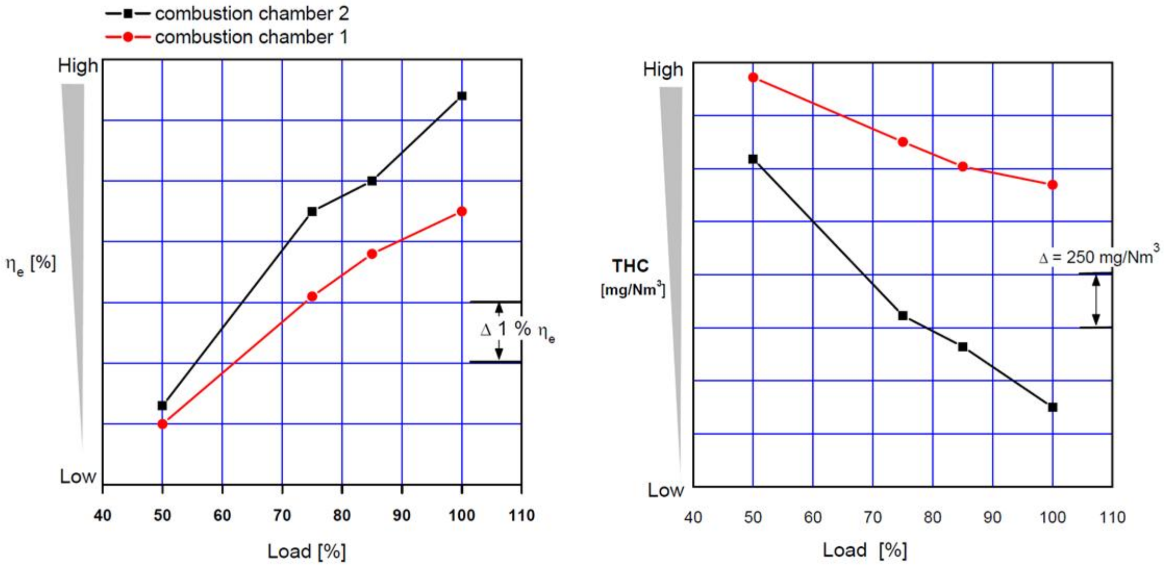


Fig. 6: Efficiency enhancement due to the reduction of Methane-slip [2]

(1) *Measures to reduce CH_4-emissions due to scavenging processes and valve overlap*

The timing optimization of the valve lifting curves and the gas admission is standard procedure for gas engine manufacturers. Minimizing the inlet/outlet valve overlap and a precise control of the gas admission can reduce the scavenge losses of unburned Methane very close to 0%. This target, however, is realistic only if the engine can be optimized for a certain application. In dynamic operation with load response (longer injection timings, see CIMAC Position Paper “Transient Response Behavior of Gas Engines”, March 2011) higher Methane emissions are to be expected.

In case of dual-fuel engines (which are designed for gas as well as Diesel operation) the valve overlap cannot be chosen as small as in pure gas engines (Diesel operation requires additional cooling of the exhaust valves). The larger the valve overlap has to be, the more difficult is the prevention of scavenge losses of unburned Methane. In the same way, engines which are operated with high as well as low calorific gases might have higher unburned Methane emissions since the timing of the gas admission and the valve lifting cannot be optimized for all operating conditions. Technologies with fully variable valve timing could improve this situation but these technologies are not yet available for serial 4-stroke engines.

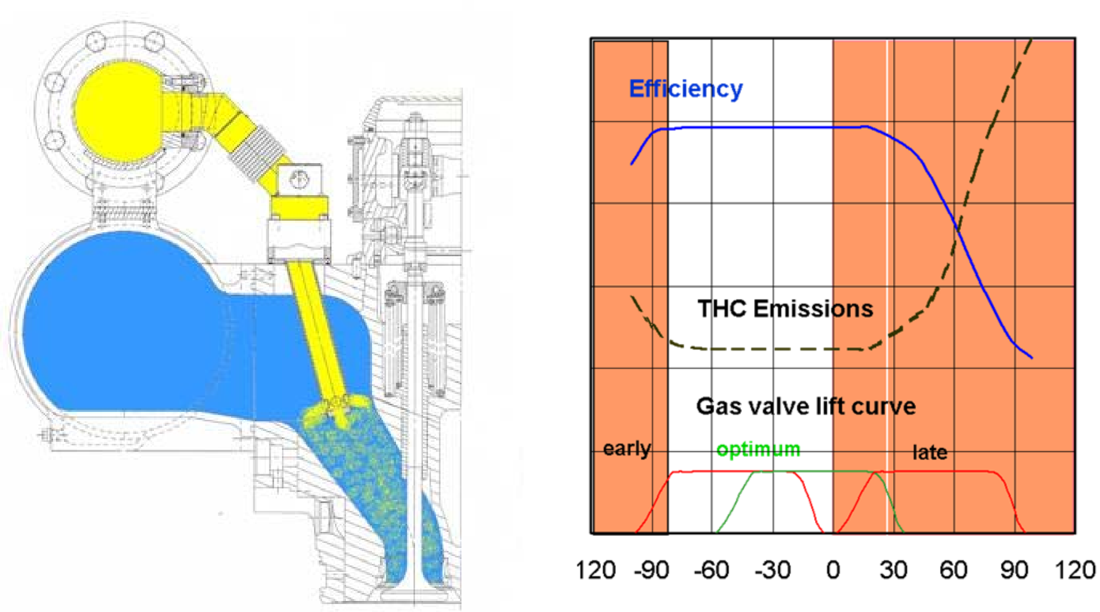


Fig 7: Blow-by-losses of unburned Methane during the valve overlap [2]

(2) and (3) *Measures to reduce quenching effects near walls and in lean mixture zones*
When focusing just on the reduction of unburned CH^4-emissions enriching the combustion mixture would be a very effective measure. Close to stoichiometric conditions unburned CH^4 emissions are reduced beyond 1% of the total amount of gas without any other measure. But taking into account other (toxic) emissions, the overall engine efficiency and the available power density the enrichment of the combustion mixture is generally no alternative. Lean burn gas engines require advanced gas/air mixing strategies to prevent chemically low-reactive zones in the combustion chamber. As leaner the combustion system is the better the mixture homogeneity must be. Much effort is spent by the gas engine manufacturers to continuously improve and to adjust the mixing process.

(4) Measures to reduce CH^4-emissions due to trapped methane in crevice areas (fireland)
As a main source for CH^4-emissions, crevice volumes in the combustion chamber (namely the fireland) are very important. A significant amount of gas can be trapped into these crevices during the compression phase.

Another strategy is reducing the volume of the fireland. This is for non-direct injecting gas engines one of the most effective measures to reduce the emission of unburned CH^4 and Formaldehyde. The effectiveness of this measure grows with the Lambda-value of the combustion mixture (especially above Lambda 2). Hence, for lean burn gas engines the manufactures reduce the fireland as much as possible. The technical limit is the thermal loading of the top piston rings. For state of the art gas engines much effort is spent on optimizing the cooling of the rings and finding new high-temperature resistant materials. The piston rings in dual-fuel engine must also resist the thermal loading under heavy duty Diesel operation. The fireland-height in dual-fuel engines cannot be optimized in the same way as for pure gas engines. Because of this fact dual-fuel engines will have higher CH^4-emissions if not equipped with direct injection systems.

(5) *Delayed combustion/misfiring*
Improved starting procedures like the temporarily de-activation of cylinders can help to avoid over-lean mixtures. In such starting procedures cylinders which are under load can burn richer since they take over the power from the other “cold” cylinders. This helps to ensure a reliable ignition and high burn-out ratios. Changing the ignition sequence of an engine, however, can severely impact its torsional vibration properties.

Measuring the exhaust gas temperature cannot detect single misfiring in the cylinders. Advanced monitoring systems for the ignition system to detect single misfiring events are in development. In SI-systems the probability of misfiring increases as the spark plug approaches its lifetime limit.

Over-lean mixtures or over-rich mixtures can lead to misfiring, as the equivalence ratio must be in a limited range for successful spark ignition. Such conditions might occur temporarily with the dynamic operation of gas engines (see also CIMAC Position Paper “Transient Response Behavior of Gas Engines”, March 2011)

7 Engine external measures to reduce CH^4-emissions: Exhaust gas after-treatment

As described above, unburned CH^4-emissions are an inherent characteristic of piston gas engines especially with a pre-mixed combustion. Unburned CH^4-emissions generally increase with leaner combustion mixtures which are required for high efficient and high power density engines. Unburned CH^4-emission can be reduced in-cylinder by enriching the combustion mixture with the common effect that other (toxic) emissions raise and the engine efficiency reduces. To escape these dilemmas exhaust gas after-treatments are a feasible solution:

Near stoichiometric conditions of the combustion mixture the 3-way catalyst is a very reliable and efficient technical solution. 3-way catalysts reduce the content of NO^x, CO, CH^4 and other unburned hydrocarbons. But 3-way catalysts do not work for lean gas mixtures. Under lean conditions different exhaust gas after-treatment technologies must be foreseen. Following scenarios are feasible:

(1) *Reduction of unburned CH^4-emissions by the usage of enriched mixtures*: The increased NO^x-emission which follows may be reduced with SCR-technology. Disadvantages might be losses in the thermal efficiency of the engine and additional investment and maintenance cost for the SCR.

(2) *Reduction of unburned CH^4-emissions in a regenerative thermal oxidation reactor*. Non catalytic oxidation processes of CH^4-molecules get activated at temperatures above 800°C. Using an inter-stage thermal reactor for the exhaust gas at temperatures above 800°C unburned CH^4-emissions can be successfully oxidized. Once reaching the temperature level of 800°C an auto-thermal operation of the reactor is possible, if the concentration of unburned CH^4 is at least $2 g/nm^3$ exhaust gas @5%O2. Thermal reactors are very big and expensive. Due to their heat capacity it requires a lot of time till its operating temperature is reached. Such thermal inertias are not suitable for dynamic operation.

(3) *Reduction of unburned CH^4 by EGR:* Recirculation of exhaust gas can help to reduce the final concentration of unburned CH^4. The rate of CH^4 reduction is about proportional to the amount of exhaust gas used for EGR. Modern applications use up to 30 percent of the exhaust gas for EGR. High efficiency EGR-application requires inter-cooling of the re-

circulating exhaust gas from typically 300-400°C (exhaust gas temperature) to 40-50°C (suction/charge air temperature). Since the chemical composition of the exhaust gas has a positive effect on the knocking behavior of the combustion charge the replacement of air by cold exhaust gas can improve the combustion stability. However, inter-cooling is very problematic. Economic affordable inter-coolers can be installed in such areas only where sufficient cooling is possible. EGR application is also quite critical for turbocharged engines in which the pressure after the turbine is lower than the intake manifold pressure. In such cases the exhaust gas must be fed back to the suction air in front of the turbocharger. Particles in the exhaust gas and water mist due to inter-cooling can significantly affect the wearing behavior of the turbocharger.

(4) *Catalytic oxidation of Formaldehyde emissions*. The efficiency of oxi-cat technology for formaldehyde is high even at moderate exhaust temperatures. The technology of catalytic oxidation of Formaldehyde is proven technology. Disadvantages are additional invest and maintenance costs for the oxi-cats. Methane emissions are not affected by formaldehyde oxidation. However, poisoning of the catalytic materials by even small amounts of H^2S and passivation effects by dust in the exhaust gas severely impact the effectiveness of the oxi-cat. In general biogas applications with oxi-cat require additional sulfur filtration technologies.

(5) *Catalytic oxidation of Methane and Formaldehyde with special catalytic materials at higher temperature levels*: Reliable catalytic Methane oxidation requires exhaust gas temperatures above 500 to 600°C. In this temperature range conversion rates of 90% and more can be realized. Below 400 to 500°C the conversion rate decreases rapidly. The choice of the catalytic material defines the temperature dependent conversion rate. In this aspect Palladium based catalytic alloys show better performance than Platinum based alloys. The higher the mean effective pressure and the engine's thermal efficiency the lower the exhaust temperature will be. Hence, catalytic Methane oxidation becomes more and more ineffective as the combustion mixture rates get leaner and the engine's mean effective pressure is increased. That means that the current trend in advanced engine design is basically counterproductive for the catalytic Methane oxidation. Heating up the exhaust gas temperature by additional heat sources can help to bridge the technologies of advanced engine design and catalytic Methane oxidation. However, the additional investment cost for such systems are currently very high. Today such systems are imaginable only for Combined Cycle Process (CCP) and Combined Heat and Power (CHP) applications where the heat of the exhaust gas is used.

Besides the significant temperature depended conversion rate oxidation catalysts get poisoned very fast even by small amounts of H^2S or similar components. The application of catalytic methane oxidation for gases with Sulfur content like biogas is very problematic. Palladium based catalytic alloys (good conversion rate at low temperatures) get poisoned by H^2S concentrations as low as 1ppm in the exhaust gas. Platinum based catalytic alloys show more robustness against poisoning but have the disadvantage of lower conversion rates at decreased temperatures.

8 Conclusion(s)

As described above, unburned CH^4-emissions are an inherent characteristic of piston gas engines with pre-mixed combustion. Unburned CH^4-emissions usually increase with the lambda ratio of the combustion mixture. CH^4-emissions legislation must take into account that uniform emission restrictions cannot be applied for all gas engines. Any restriction should be defined in accordance with the physical limits of the different types of gas engines. In this perspective the allowed CH^4-concentration in the exhaust gas should correlate with the engine's bore or speed (like already done in the IMO regulations for NOx-emissions), its specific power and efficiency. The strength of lean burn gas engines is their ability to combine high efficiency with low CO^2 and low toxic emissions without additionally installed expensive exhaust gas after-treatment devices and should be valued.

Unburned CH^4-emissions in the exhaust gas can be further reduced by after treatment systems like catalytic oxidation. However, current catalyst technology does not yet fulfill all present and future requirements of gas engines. Main target must be to raise the conversion rate even at low exhaust gas temperatures and to make the oxidation catalyst resistant against poisoning. Systems which require exhaust gas heating before catalyst should be seen only as intermediate solutions. In any case exhaust gas after-treatment always means significant additional invest and maintenance cost.

The further optimization of the gas engine combustion process, the gas engine design and the after-treatment system is a major interest of the gas engine industry. Much effort is spent on the continuous development of new improved solutions.

Dual fuel engines combine the positive characteristics of Diesel and gas engines. With their ability to burn Diesel oil as well as gas (modern dual fuel engines can switch between gas and Diesel mode during operation) they are preferred for many applications where high reliability and low emissions are required. Since the combustion system in dual fuel engines must bridge the requirements of Diesel and gas engines these engines cannot be purely optimized either for Diesel or gas. Many technologies which help to reduce unburned Methane emissions in gas engines cannot be realized in dual fuel engines due to mechanical and thermal constraints. Legislation should consider this fact. For many applications (which require an immediate Diesel fall back solution) dual fuel engines are the only alternative for a clean energy supply.

(1) CH^4 emissions of gas engines definitely influence their impact on the Green House Gas (GHG) factor. But one must not forget that gas engines also have a significant CO^2 advantage over the Diesel engines (about 20%). And this CO^2 advantage compensates CH^4-emissions till 1,5 - 2%. Taking into account that only a very minor part of the global CH^4 emissions comes from the gas engines exhaust gas, legislation should keep in mind that gas engines should not be disadvantaged to Diesel engines since natural gas has many other positive benefits and will be an energy source of the future.

(2) Formaldehyde cannot be completely avoided in gas engines with port injection or homogenous charge supply. The main source of Formaldehyde is the fireland. Reducing its volume and using richer mixture ratios reduce the emissions very effectively. For engines where these measures cannot be implemented as required, oxi-cats (plus additional sulfur filtration devices) are an appropriate alternative. Such oxi-cats, however, mean additional

space, invest and maintenance costs. This raises the question if such an after-treatment system is necessary for locations and applications far away from populated areas.

9 Source(s)

[1] Emission of Unburned Hydrocarbons from Gas Engines for Cogeneration, Jan de Wit, Malene Nielsen, Fourth International Conference Technologies for a Clean Environment, 1997, Lisbon, Portugal

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