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Lean-Burn Natural Gas Engines: Challenges and Concepts for an Efficient Exhaust Gas Aftertreatment System

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Abstract

High engine efficiency, comparably low pollutant emissions, and advantageous carbon dioxide emissions make lean-burn natural gas engines an attractive alternative compared to conventional diesel or gasoline engines. However, incomplete combustion in natural gas engines results in emission of small amounts of methane, which has a strong global warming potential and consequently makes an efficient exhaust gas aftertreatment system imperative. Palladium-based catalysts are considered as most effective in low temperature methane conversion, but they suffer from inhibition by the combustion product water and from poisoning by sulfur species that are typically present in the gas stream. Rational design of the catalytic converter combined with recent advances in catalyst operation and process control, particularly short rich periods for catalyst regeneration, allow optimism that these hurdles can be overcome. The availability of a durable and highly efficient exhaust gas aftertreatment system can promote the widespread use of lean-burn natural gas engines, which could be a key step towards reducing mankind's carbon footprint.

Keywords Catalyst reactivation · Emission control · Gas engines · Methane oxidation · Palladium · Reductive pulsing

1 Introduction

The continuous technological progress initiated by industrialization resulted in our modern globalized world with a society whose energy supply is mainly based on carbon-containing fossil resources like coal, oil, and natural gas. Combustion of these resources releases energy, but also leads to considerable pollutant emissions. While undesired side-products such as carbon monoxide (CO), nitric oxide (NO_x), or particulate matter (PM) are toxic for mankind and environment, the main combustion product carbon dioxide (CO_2) is considered a key driver for global warming.

Since climate change is one of the most urgent issues of our modern society, ambitious targets for the reduction of global CO_2 emissions have been formulated in recent years, which becomes particularly obvious in the case of future CO_2 requirements for light-duty vehicles. Europe, for instance, aims at reducing its CO_2 emissions compared to 2020 by 37.5% by 2030 in the light-duty sector, while the USA strives for approximately 23% reduction in the same time frame [1, 2]. Overall, the European aspirations for a climate-neutral economy, mobility and society are most ambitious, culminating in the goal to achieve net-zero greenhouse gas emissions by 2050 [1].

However, modern combustion engines are already highly optimized and further substantial reduction of fuel consumption is technologically more and more challenging, hence alternative approaches are mandatory. In this regard, replacement of conventional gasoline or diesel fuels by natural gas that consits mainly of methane (CH_4) seems an attractive solution. Since CH_4 has the highest hydrogen-to-carbon ratio of all hydrocarbons, natural gas has a superior carbon balance resulting in advantageous CO_2 emissions that oil-based fuels cannot outperform. In addition, besides small amounts of unburnt hydrocarbons, gas engines emit comparably low levels of toxic CO and only moderate amounts of NO_x. All these aspects make gas engines a technology with outstanding potential on the way towards a modern and sustainable energy supply.

An upward tendency of the global natural gas production and an all-time production record of 3937 billion cubic meters in 2018 underscores the growing interest in natural gas as an energy source [3]. Already today, natural gas is widely used

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for both stationary and mobile applications, i.e., in combined heat and power (CHP) plants for energy production or as a fuel for heavy-duty vehicles (Fig. 1). A fast transition from a mainly diesel- and gasoline-based energy supply in the near future, especially in the on-road and marine sector, towards a natural gas–based system as illustrated in Fig. 1 may benefit from the fact that many countries already have an existing natural gas infrastructure. This is an essential prerequisite for a widespread usage within the next years. Although fossil sources currently represent the main feedstock for natural gas, promising alternative concepts like biomethane and power-to-gas technologies can open up a sustainable access to the highly valuable energy source methane. In addition, such carbon-neutral approaches terminate gas emissions that typically occur during the production of fossil natural gas, which increases the sustainability of the whole value chain even further.

2 Engine Operation and Emissions of Lean-Burn Gas Engines

Especially smaller gas engines are commonly operated under stoichiometric conditions that allow an exhaust gas aftertreatment with the well-established compact three-way catalyst (TWC) [4]. In contrast, lean combustion is frequently preferred for large-bore gas engines, as it maximizes the engine efficiency and additionally contributes to minimizing raw emissions. Under the assumption that a lean-burn natural gas engine consumes 150 g fuel per kWh and CO_2 is the only greenhouse gas emitted, a greenhouse gas advantage of up to 35% compared to a diesel engine can be achieved [5]. However, CO_2 is not the only component emitted, making a modern and highly efficient aftertreatment system capable of meeting future ultra-low emission limits imperative.

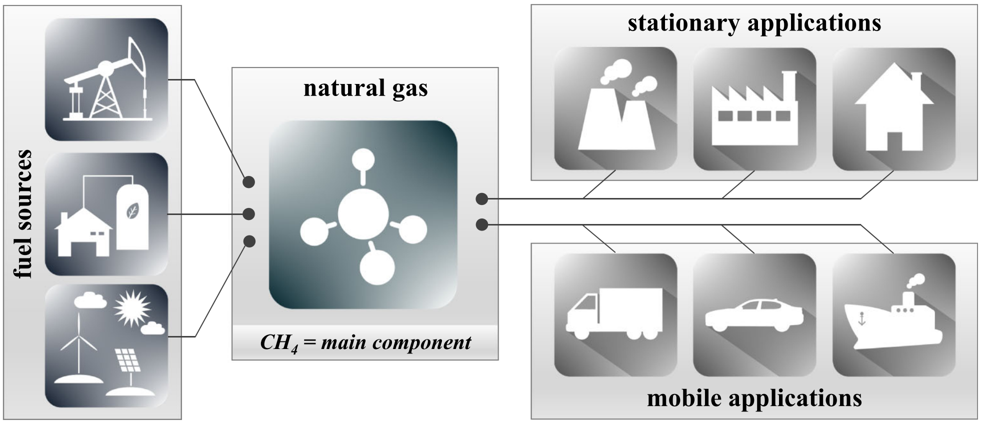
PM, which forms in local areas in the combustion chamber that do not exhibit an ignitable mixture, is only a minor issue. In comparison to diesel and even gasoline engines, natural gas engines emit less PM with overall particle emissions in the magnitude of a diesel engine equipped with a diesel particulate filter (DPF) [6]. Besides, the contact between combustion flame and lube oil used in the engine typically leads to partial combustion of oil, resulting in hydrocarbon and oil ash emissions. Oil ash consists of elements like calcium, magnesium, zinc, phosphorous, or sulfur and is emitted as particulate matter or acts as a catalyst poison [7].

Moreover, the engine's operational point strongly influences the pollutant emissions (Fig. 2). While considerable amounts of CO, NO_x, and hydrocarbons (HC) are emitted during stoichiometric operation, especially NO_x emissions can be minimized by lean operation [8, 9], since NO_x mainly forms during a high temperature reaction between oxygen and nitrogen, which is suppressed by the low combustion temperatures during lean operation. In this respect, at least slightly lower NO_x emissions in comparison to diesel engines, which also exhibit low combustion temperatures, are reported [10]. However, tightening environmental legislation will make a dedicated NO_x abatement, i.e., by a system for selective catalytic reduction (SCR) [11], imperative. Hence, despite the lower engine efficiency, the call for stoichiometric operation may grow louder in the future, as additional space-consuming and potentially costly measures for NO_x control will be redundant if a TWC is used for emission control.

Furthermore, partial combustion of methane results in formaldehyde emissions [12]. The recent classification as potentially carcinogenic substance by the European Union (EU) [13] will result in ultra-low emission standards, which can only be met when applying noble metal catalysts, mostly on platinum basis [14]. Since catalytic formaldehyde conversion is a mass transport limited process, optimized catalyst geometries with respect to the channel shape and a homogeneous washcoat distribution are required to overcome low diffusion rates due to the small concentration gradient [15, 16].

Amongst the emissions of gas engines, the most important hurdle, however, is methane slip, typically present in the exhaust gas in a magnitude of up to over 3000 ppm, due to incomplete combustion. Methane has a more than 20 times stronger greenhouse potential compared to carbon dioxide, which drastically

Fig. 1 Schematic value chain from production to application for a methane-based energy system



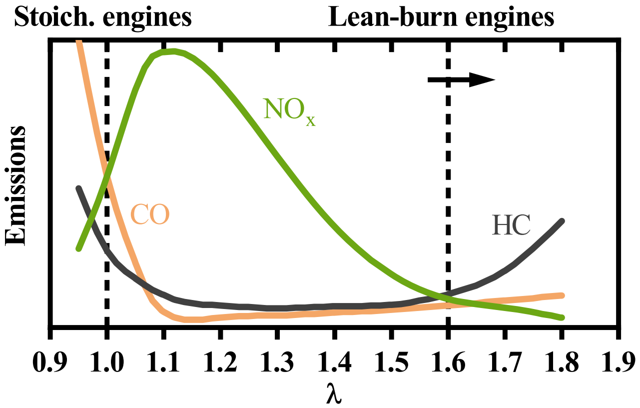


Fig. 2 Emissions of CO, HC, and NO_x versus lambda (air-to-fuel-ratio). Based on graphs and data from [8, 9]

reduces the benefit of using gas engines if such amounts of methane are released into the atmosphere. The typically low exhaust gas temperatures impede catalytic combustion of the methane molecule with its high stability and low reactivity, necessitating a highly active catalyst that exhibits excellent stability and durability. In this respect, palladium has been in the focus of scientific interest for decades since it shows the highest activity [17] for catalytic methane conversion.

3 Methane Oxidation over Palladium: Overcoming Water Inhibition and Sulfur Poisoning

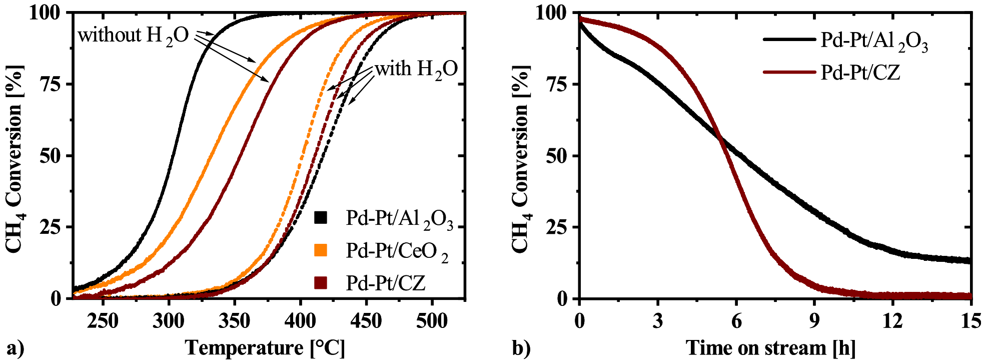
Despite the initially high activity, palladium catalysts have to cope with two main challenges. Firstly, the inevitable combustion product water, which is also produced by the catalytic methane oxidation reaction itself, leads to pronounced inhibition and continuous deactivation, especially at low temperatures (Fig. 3a). Hydroxyl accumulation on both, the support material and the noble metal, blocks the active sites, which are then unavailable for methane adsorption and conversion [18]. Usage of ceria-based supports with a high oxygen mobility reduces the negative impact of steam, however, this cannot sufficiently redeem the inhibition [19].

Secondly, sulfur compounds (SO_x) that originate either from the natural gas itself or from deliberately added odorants act as a strong catalyst poison. As shown in Fig. 3b, the presence of only 5 ppm of SO_2 in the gas stream already leads to severe catalyst degradation due to poisoning within very short time frames. Poisoning of the palladium phase by $Pd(SO)_4$ formation can lead to a complete loss of activity and support materials such as alumina that form support-related sulfates, hereby acting as a sulfur sink, can only partially protect the noble metal [20, 21].

Since the development of materials and catalyst formulations that permanently withstand the negative impact of these species proceeds only slowly, rationally designed process control and reaction engineering approaches pose possible alternatives to ensure high catalytic conversion. Any procedure for catalyst reactivation needs to be an optimized process that takes engine operation and catalyst operation parameters into account, as methane conversion over Pd-based catalysts is particularly sensitive towards the feed gas composition [22]. Rich treatment, for instance, can remove adsorbed surface species blocking the catalyst's active sites, which allows to regenerate catalysts that were deactivated by water or poisoned by sulfur [20, 23, 24]. To avoid a re-poisoning of the noble metal by the remaining support-related sulfur species, the reductive treatment should be conducted at elevated temperatures to ensure full regeneration of both, the noble metal and the support material [25, 26]. The feasibility of reductive pulsing during lean operation for regenerative purposes has not only been demonstrated in the lab, but also in a gas engine operated under realistic conditions. Hereby, the introduction of short reductive phases every 30 min resulted in a stabilization of methane conversion at approximately 70%, which is considered an adequate level for moderate exhaust gas temperatures of about 450 °C [27].

Besides temporary changes of the engine's operational point, also the upstream placement of a three-way catalyst in front of a methane oxidation catalyst was reported to enhance the durability [28]. Finally yet importantly, exploitation of gas-phase chemistry, which is particularly relevant at elevated temperatures and pressures as typically found for pre-turbo applications, may be a step forward. NO_x that is always

Fig. 3 CH_4 oxidation activity of bimetallic 2.0 wt% Pd–0.4 wt% Pt catalysts supported on Al_2O_3, CeO_2, and CeO_2-ZrO_2 ("CZ") in (**a**) 3200 ppm CH_4, 10% O_2, 0/12% H_2O, and balance N_2 during heating with 3 °C/min; and (**b**) 3200 ppm CH_4, 10% O_2, 12% H_2O, 5 ppm SO_2, and balance N_2 during steady-state operation at 450 °C. GHSV = 80,000 h^{-1}



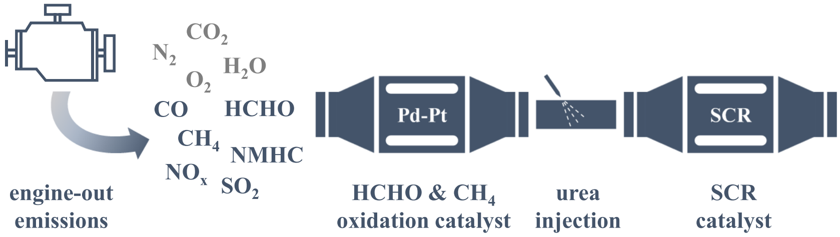


Fig. 4 Typical engine-out emissions and a possible future design of an exhaust gas aftertreatment system for lean-operated natural gas engines

present in the exhaust of gas engines significantly promotes the homogeneous oxidation of light alkanes like methane but also the formation of further HCHO [29]. Therefore, suppressing the formation of undesired side-products and secondary emissions such as HCHO or N_2O is another challenge in optimizing the aftertreatment system.

4 Conclusions and Outlook

In conclusion, based on a comprehensive fundamental understanding, the combination of different well-established technologies and careful process control can pave the way towards a durable and efficient exhaust gas aftertreatment system for lean-operated natural gas engines. Modern state-of-the-art aftertreatment systems have substantially grown compared to the simple oxidation catalyst originally proposed for emission control by pioneer Eugene J. Houdry [30]. The careful combination of optimally adapted and coordinated measures, i.e. including exhaust gas recirculation, allowed meeting tight emission limits for lean-operated diesel engines in the past [31]. Hence, there is confidence that the remaining technical challenges for meeting forthcoming ultra-low emission standards can similarly be solved for lean-operated natural gas engines, possibly via a system as schematically proposed in Fig. 4. Future exhaust gas aftertreatment systems may be amended by implementing a state-of-the-art urea-based SCR system for NO_x control in addition to the oxidation catalyst. This necessitates a careful choice of both, engine operation parameters for controlling engine-out emissions and catalyst formulation for minimizing secondary emissions, for instance since HCHO and NH_3 can form highly toxic HCN over several SCR catalysts [32, 33]. However, as this approach is already well-established in the context of lean-burn diesel engines, the technological hurdles for extending the overall system are expected to be moderate, allowing a fast realization and transfer into serial production. Entirely novel approaches as utilization of non-linear flow channels may further contribute to finding a holistic solution [34].

Looking forward, the widespread use of natural gas engines is not only a scientific-technical issue, but also a political one. Although many countries strive for an electrification of the on-road sector, combustion engines will remain indispensable at least in stationary and heavy-duty applications in the near future. This may lead to a more diverse global energy system where natural gas engines can play an important role. In this context, an efficient exhaust gas aftertreatment system for lean-operated natural gas engines is essential for ecological and economic competitiveness. Particularly, the recent progress on catalyst operation, activation, and regeneration strategies is encouraging and allows optimism that natural gas engines can significantly contribute to reducing mankind's carbon footprint.

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Compliance with Ethical Standards

Competing Interests The authors declare that they have no competing interests.

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