Efficiency and raw emission benefits from hydrogen addition to methane in a Prechamber–Equipped engine

Patrik Soltic*, Thomas Hilfiker

Automotive Powertrain Technologies Laboratory, Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, Dübendorf, 8600, Switzerland

HIGHLIGHTS

• Hydrogen accelerates combustion and extends the lean limit.
• Hydrogen addition reduces tailpipe CO2 emissions by substituting carbon by hydrogen.
• The energy conversion efficiency increases by hydrogen addition.
• Small amounts of hydrogen massively reduce hydrocarbon emissions.
• Hydrogen addition avoids the need of prechamber fueling for hard-to-ignite mixtures.

ARTICLE INFO

Article history:
Received 3 March 2020
Received in revised form 2 June 2020
Accepted 12 June 2020
Available online 31 July 2020

Keywords:
Turbulent jet ignition
CNG
HCNG
Internal combustion
Ignition chamber

ABSTRACT

Providing high ignition energies to low reactivity (hard-to-ignite) fuels in premixed combustion modes is a challenging task. This is especially true if diluted combustion and high compression ratios are applied which are desirable for achieving high efficiency levels. One promising technology is to decouple the ignition process from the conditions in the main chamber using a prechamber, which is able to ignite the charge in the engine’s main combustion chamber using turbulent jets. In this study, experimental results of a prechamber-equipped four-cylinder engine with 2 L displacement are discussed. The engine is designed to provide high efficiency using natural gas as a fuel. The prechamber is able to be fueled externally (called active prechamber mode), e.g. the air–fuel equivalence ratio λ can be decoupled from the λ in the main combustion chamber. Besides of pure methane operation, the engine is operated with the addition of 22.5 mol% (3.5 mass%, 8.0 energy%) hydrogen to methane. The results show that it is beneficial to use auxiliary fueling of the prechamber in pure methane operation mode in order to achieve highest possible efficiency at low NOx levels at λ of around 1.7. When adding hydrogen, λ of around 1.7 still provides highest efficiency but auxiliary fueling of the prechamber is not necessary any more to enable fast and robust combustion. Compared to the active prechamber operation with methane, the 3.5 mass% (8.0 energy%) addition of hydrogen is able to reduce the engine’s fuel energy demand by 1.3–3.3% in relevant engine operating points, which leads to tailpipe CO2 reductions of 9.2–11%. Additionally, hydrogen addition is able to disproportionately lower the engine’s unburned hydrocarbon (HC) emissions: The addition of 3.5 mass% hydrogen lowers HC mass emissions by impressive 30–40%. Simultaneously, at the lean conditions considered, CO and NOx emissions are lowered by around 20%.

* Corresponding author.
E-mail addresses: patrik.soltic@empa.ch (P. Soltic), thomas.hilfiker@empa.ch (T. Hilfiker).

https://doi.org/10.1016/j.ijhydene.2020.06.123

0360-3199/© 2020 The Author(s). Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
sustainably produced bio-methane as well as other bio-fuels are not large enough for completely replacing fossil sources. As renewable electricity can be harvested in comparably simple and cost-efficient ways and the quantities are practically unlimited, the main focus in many regions worldwide lies on increasing renewable electricity production, mainly by building-up windmills or photovoltaics. With increasing shares of such fluctuating renewable power, the need emerges to store temporal overproduction for day/night balancing, for weekly balancing, or even for seasonal balancing. For short-term storage of smaller amounts of energies, batteries are likely to be a feasible solution. For medium-to long-term storage of large amounts of energy, chemical energy carriers are presumably the most sensible solution [2–5]. Hydrogen is the simplest chemical energy carrier. It can be produced efficiently from water electrolysis, coal or biomass gasification, or natural gas reforming and a small number of hydrogen filling stations for vehicles already exists [6,7]. However, large-scale storage of hydrogen is challenging, especially for seasonal balancing [8] so that synthetizing hydrocarbons from hydrogen and CO₂ makes it easier and more cost-efficient to store and distribute [9]. The simplest hydrocarbon with an existing storage- and distribution system in many regions is methane which can synthetically be produced by the exothermal Sabatier process that can be realized with different catalysis technologies [10–12]. Therefore, hydrogen and methane can be considered as synergetic chemical storage means for fluctuating renewable energies [13] and engine technologies using methane and hydrogen may play an important role in a future energy system. Clearly, the electrification of certain segments of the on-road mobility has a potential to lower CO₂ emissions but only a meaningful combination of electrification and renewable fuels is able to maximize the CO₂ benefits at reasonable costs [14–17].

Internal combustion engines are cost-efficient, robust and durable converters from chemical to mechanical energy and they are adaptable to the fuel they use. The dominating technology for modern natural gas engines in the road mobility sector is a classical spark ignition setup where a premixed stoichiometric natural gas/air mixture is ignited by a spark plug in an open combustion chamber and the engine’s pollutant emissions are reduced to virtually zero using three-way-catalytic conversion [18]. However, the stoichiometric combustion with comparably low compression ratios leads to lower efficiencies compared with compression ignition engines as they combine lean combustion with a higher compression ratio. Applying such compression-ignition-engine-like process parameters (diluted combustion, high compression ratio) leads to difficult conditions for ignition, early flame growth and turbulent combustion as well as to in-cylinder peak pressure levels that are unusually high for spark ignition engines. One way to enable robust ignition and fast combustion under such...
difficult circumstances is the use of a prechamber ignition setup. A prechamber for spark ignition engines hosts an igniting device - usually a classical spark plug - where combustion is initiated with comparably small energies in the magnitude of 100 mJ [19]. Hot turbulent jets exiting the prechamber catch a large portion of the main chamber and ignite the charge of the main combustion chamber with much higher energies than a classical spark breakdown process can deliver [20]. A prechamber can either have auxiliary fueling or not [21,22]. Prechambers without auxiliary fueling, often called passive prechambers, have a similar air-fuel equivalence ratio (\(\lambda\)) in the main combustion chamber and in the prechamber. They enable, to a certain extent, fast combustion in diluted mixtures [23–26]. With auxiliary fueling (active prechambers), \(\lambda\) in the prechamber can be lowered and very lean mixtures in the main combustion chamber can be ignited [27,28]. Adding air and fuel to a prechamber adds additional degrees of freedom and benefits, but increases the complexity of the system [29]. Prechamber technologies have been widely studied in 1970ies [22] and have currently gained attention again, also in racing applications [30].

From research on classical (non-prechamber) natural gas engines it is known that adding comparably small amounts of hydrogen to natural gas leads to several advantages. The initial flame phase is shortened which leads to faster and more stable combustion, the exhaust gas recirculation tolerance is enhanced and the unburned hydrocarbon emissions are lowered [31–37]. However, to what extent these known advantages of hydrogen addition to methane in classical engines transfers to prechamber-equipped engines is not clear. Research shows that ultra-lean hydrogen mixtures can be ignited by hot turbulent jets [26,38–40], or that hydrogen injection into a prechamber is beneficial for lean ethanol or gasoline combustion [41–43] but available data on methane/hydrogen mixtures is very limited.

**Materials and methods**

A light-duty four-cylinder engine has been build-up in a collaborative project in the framework of the Horizon 2020 research program of the European Union, which is equipped with a prechamber with auxiliary fueling and optimized for highest efficiencies using natural gas. The prechamber and combustion chamber geometries have been extensively optimized using numerical and experimental methods [44–49]. The final results of this engine running on natural gas are reported in [50,51]. Using natural gas, it turns out to be the best strategy to operate the engine at an overall \(\lambda\) of 1.7 and injecting very small amounts of fuel to the prechamber to lower \(\lambda\) in the prechamber to around 1.2. Doing so, this 2-Liter natural gas engine enables brake efficiency levels of 45%, which is an unusual high value for an engine in the 120 kW class. This paper presents experimental results for exactly this engine fueled with a mixture consisting of 22.5 mol% hydrogen and 77.5% mole% methane and compares it with pure methane operation.

The engine is based on a serial-production diesel engine (Volkswagen EA288) but it has a redesigned cylinder head holding a prechamber with the possibility for auxiliary fueling, redesigned pistons (piston bowl, piston rings) and an air path with a gas mixer and a throttle. A rapid prototyping engine control unit is used to control the engine (e.g. fueling, ignition, throttle, turbocharger) based on feedback signals from sensors (e.g. \(\lambda\) sensors, pressure sensors, temperature sensors). Feedback combustion phasing control is implemented by near-real-time evaluation of the apparent heat release and setting center of combustion (COC) to the desired value of 8 °CA after top dead center [22]. This value of 8 °CA is found to deliver highest efficiency levels for this engine and it is kept constant for all experiments described here.

In the case of external prechamber fueling, the \(\lambda\) situation in the prechamber itself is rather complex as a mixture of a given stoichiometry is pushed into the prechamber during compression and dilutes the amount of fuel injected to the prechamber. Therefore, the stoichiometry in the prechamber depends not only on the stoichiometry of the main chamber and the amount of injected prechamber-fuel, but also on the crank angle. Additionally, the fuel and residual gas distributions in the prechamber are not very homogeneously as detailed CFD simulations [45]. In order to have a tool to roughly estimate the prechamber fueling during calibration, \(\lambda\) in the prechamber at ignition crank angle is feedback-controlled but, as it is not possible to measure \(\lambda\) in the prechamber using \(\lambda\) sensors, the control is based on real-time prechamber \(\lambda\) model. The control model is described in [52]. However, as it is not possible to validate \(\lambda\) in the prechamber for this engine, the prechamber \(\lambda\) of the used model is only a rough estimation of unknown precision. The desired overall air–fuel equivalence ratio \(\lambda\) is also feedback-controlled, the feedback signal is provided by wide-band \(\lambda\) sensors and checked with the \(\lambda\) value determined from emissions measurements [53]. The \(\lambda\) values from these two methods proves to be within 1%, so the overall \(\lambda\) values are very precise.

The engine is operated on a state-of-the-art engine test bench equipped with an automotive certification-grade emission measurement system. Fig. 1 shows a sketch of the experimental setup, Table 1 lists the main characteristics and Fig. 2 shows the engine’s combustion chamber and the prechamber.

Experiments are performed at fully warmed-up engine conditions for steady-state operating points. In order to assess operating points which are relevant for light duty vehicle use in a European context, the frequency of operating points is simulated for a mid-sized passenger car driving the homologation cycles NEDC and WLTC and clustered into six classes for each cycle, each class with the same time share per cycle. Fig. 3 shows the results of the resulting points A...F for the NEDC and F...K for the WLTC (the operating point F is identical for NEDC and WLTC). The amount of fuel spent in each class is represented by the diameter of the bubble.

For the engine experiments presented in this study, the operating points E, F and K are chosen as they represent a good cross-section along the relevant speed- and load range:

- **E** (1200 min⁻¹, brake torque = 30 Nm, BMEP = 1.9 bar, brake power = 3.8 kW) is a relevant point with lowest power,
- **F** (1500 min⁻¹, brake torque = 100 Nm, BMEP = 6.4 bar, brake power = 15.7 kW) is the most relevant operating point regarding fuel consumption considering both cycles,
K (2000 min⁻¹, brake torque = 220 Nm, BMEP = 14.0 bar, brake power = 46.1 kW) a relevant point with highest power and load.

All three operating points are measured in active prechamber mode (i.e. fuel is injected into the prechamber) for a λ region from minimum prechamber injection quantity up to the active prechamber lean limit. In addition, operating point F is measured in passive prechamber mode (i.e. without fuel injection to the prechamber), from λ = 1 up to the passive prechamber lean limit.

The water supply to the intercooler is controlled such that a desired intake manifold temperature is achieved. For the operating points E and F, the intake manifold temperature is set to 30 °C (±1 °C) and for operating point K to 32 °C (±1 °C). Since it is a priori unclear which type of exhaust gas treatment is necessary for which combustion strategy and in combination with which fuel, no exhaust gas treatment system is mounted and only the original muffler of the engine is present in the exhaust line. This setup leads to backpressure levels after turbine of roughly zero for operating point E, to 2...5 hPa for operating point F and to 16...20 hPa for operating point K. Such a setup may be representative for stationary engine applications where the engine’s raw emissions are low enough to meet the limits, the backpressure levels are certainly too low for on-road applications where exhaust catalysis is needed.

Table 2 lists the main parameters of the used fuels, which were delivered by a gas supplier in pressurized cylinders. Before use, the gases were analyzed using a Siemens MicroSAM process gas chromatograph. The gases are referred as CH₄ for the pure methane and HCH₄ for the methane-hydrogen-blend throughout this paper.

**Results and discussion**

**Influence of hydrogen addition on combustion**

In this section, the combustion characteristics are discussed for all three operating points E, F, K operated in active prechamber mode at an overall λ of 1.7 whereas operating point F is also operated in passive prechamber mode for HCH₄. For CH₄, it is not possible to run at λ = 1.7 in passive mode (see section Influence of hydrogen addition on prechamber fueling demand and on combustion stability). The relevant governing equations used for the evaluation can be found in [54,55]. In all figures of this paper, data of active prechamber measurements is plotted with solid lines and data from passive prechamber measurements is plotted with dashed lines. HCH₄ data is colored in red/orange for the three operating points considered, while CH₄ data is plotted in variations of blue.

Fig. 4 shows the pressure difference between the prechamber and the main chamber versus the crank angle for the three operating points. Additionally, the crank angle of ignition is marked. The measurements are performed in cylinder #1, they represent averaged values over 300 consecutive cycles and they show a noticeable pressure difference buildup only a few crank angle degrees after ignition. In active prechamber
operation, the pressure difference buildup is clearly more intense for the HCH₄ cases where more energy is released whereas the passive HCH₄ case behaves similarly to the active CH₄ case. The increased reactivity of the fuel proves to be beneficial for the early flame stage, as [26] predicts numerically. For the active HCH₄ cases, the peak pressure buildup equals to about 5% (case E), 7% (case F) and 9% (case K) of the cylinder pressure level in the main chamber and roughly half as much for the CH₄ cases.

Combustion is analyzed with a software implementation of a two-zone combustion model [56], i.e. the combustion is divided into two zones (fresh gas, burned gas) of equal

| Table 1 – Main characteristics of the used engine and the test infrastructure. |
|----------------------------------|----------------------------------|
| # of cylinders / valves per cylinder | 4/4 |
| Bore/stroke [mm], Displacement [cm³] | 81.0/95.5, 1968 |
| Compression ratio | 14.5 |
| Piston bowl geometry | Omega shape, fully symmetric |
| Ignition system/spark plugs | Inductive/M10 thread, spark gap 0.6 mm |
| Intake fueling | 4 Bosch NGI2 injectors, via mixer |
| Prechamber fueling | Bosch NGI2 injectors (throttled), via cannula and check valve |
| Prechamber volume | 1.8 cm³ |
| Prechamber orifice configuration | 7 holes, 1.5 mm diameter each |
| Boosting | VTG turbocharger |
| Intercooler | Water/air |
| External EGR | Not present |
| Exhaust gas after treatment | Not present (muffler is present) |
| ECU | Rapid prototyping unit (dSPACE Microautobox), powered via an external power supply |
| Lambda sensors | Wide-band Bosch LSU 4.9 |
| Cylinder pressure sensor | All 4 cylinders using water-cooled piezoelectric sensors (Kistler) |
| Prechamber pressure sensor | Prechamber of cylinder 1, using uncooled piezoelectric sensor (Kistler) |
| Engine test bench | EcoDyn 265M using a HBM T40B torque transducer |
| Engine test bench automation | Horiba STARs |
| Combustion air supply | Air conditioning system, set to 23 °C and 50 %RH |
| Combustion air flow measurement | ABB Sensyflow P thermal flow meter |
| Intake fuel flow measurement | Rheonik RHM015 Coriolis flow meter |
| Prechamber fuel flow measurement | Bronkhorst EL-FLOW Select |
| Emission measurement system | Automotive certification-grade system Horiba MEXA-ONE-D1-EGR emission bench using heated filters and heated sampling lines, 24 bit ADC for all analyzers, digital communication with test bench automation, automatic calibration using calibration gases with 1% tolerance, all analyzers with a measurement precision of ±0.5% of the maximum range value, automatic range switching, all analyzers linearized using a Horiba GDC gas divider |
| NO/NOx analyzer | Dual chemiluminescence detector (with a NOx converter for NOx measurement) Horiba CLA-02HV (wet measurement) |
| CO analyzer | Non-dispersive infrared detector Horiba AIA-11 (dry measurement) |
| CO₂ analyzer | Non-dispersive infrared detector Horiba AIA-33 (dry measurement) |
| O₂ analyzer | Magnetopneumatic detector Horiba MPA-01 (dry measurement) |
| THC/CH₄ analyzer | Dual flame ionization detector with catalytic methane cutter for CH₄ measurement Horiba FIA-02H-ND (wet measurement) |

Fig. 2 – Visualization of the combustion chamber layout (left), picture of the prechamber assembly (right).
Residual gas fraction is modeled using Cheng’s approach [59]. Blow-by is modeled using a labyrinth-seal approach [60]. Caloric properties are determined assuming chemical equilibrium for 18 species and considering dissociation [61], real gas effects are considered.

Fig. 5 shows the calculated normalized fuel mass burn rates using the combustion chamber pressure sensor as the experimental input. It is evident that H₂ addition to methane considerably shortens the initial phase of combustion. The heat release in the prechamber is more intense and the ignition can be delayed by about 5 °CA for all three operating points and active prechamber operation to maintain the center of combustion at 8 °CA after TDC. Looking at operating point F, the early combustion phase using passive HCH₄ prechamber operation is slightly more intense then the active CH₄ case. Already with CH₄ prechamber operation, combustion is very fast as ignition timing is at around 15 °CA before TDC for a center of combustion at 8 °CA after TDC. With H₂ addition, combustion is further accelerated and the combustion duration is even shorter. However, the normalized fuel mass burn rates differ only very slightly between the considered operating points.

Hydrogen addition directly lowers the methane number (MN), in the case described here from a MN of 100 for the pure methane to a MN of 77.5 for the hydrogen-enriched methane. One could therefore expect potential knock problems in the engine used here which has a relatively high compression ratio of 14.5. However, as the prechamber enables very fast combustion and, as a consequence, late ignition, no knock tendencies are observed with methane or with the methane-hydrogen mixture whatsoever.

Fig. 6 shows the simulated temperatures of the cylinder charge. The average temperatures are plotted as well as the temperatures of the growing burned zone. These results are
based on the measured cylinder pressure using the in-cylinder sensor. For all three operating points, the peak temperatures of the burned zone appear to be very similar, even for the HCH₄ cases with later ignition and faster combustion. Therefore, it is expected that the thermal NOₓ emissions originating from combustion in the main chamber are very similar for all cases (which is confirmed by the NOₓ measurements, see section Influence of hydrogen addition on NOₓ emissions).

**Influence of hydrogen addition on prechamber fueling demand and on combustion stability**

In passive prechamber mode, a λ sweep is made from λ = 1 up to the point when combustion stability becomes poor. Combustion stability is assessed by evaluating the coefficient of variance of the indicated mean effective pressure (COVIMEP) over 300 cycles. In the prechamber design process using

Fig. 5 – Normalized fuel mass burn rates in the main chamber for λ = 1.7 for the operating points E, F and K.

Fig. 6 – Simulated temperatures of the burned zone and for the average cylinder charge (center of combustion for all cases: 8 CA after TDC, λ = 1.7) for the operating points E, F and K.
numerical methods, a special focus was given to keep remaining burned gases in the prechamber away from the spark plug location [62]. In passive prechamber mode, $\lambda$ in the prechamber is therefore expected to be very close to $\lambda$ in the main chamber.

In active prechamber mode, a $\lambda$ sweep is made from $\lambda = 1.4$ up to the point when combustion stability becomes poor. Active prechamber mode gives two additional degrees of freedom, namely the phasing of the prechamber injection and the amount of fuel injected to the prechamber. The prechamber phasing is optimized for lowest THC emissions, which turned out to be when prechamber injection starts at 300 °CA before TDC across all operating points. The amount of fuel injected to the prechamber is optimized for each operating condition individually. In a first range of $\lambda$ between 1.4 and about 1.6, the smallest amount is injected which the injectors can robustly deliver by setting the injection duration to 1 ms. For higher $\lambda$, the amount of prechamber fuel is primarily optimized for best combustion stability (i.e. lowest value of COVIMEP) considering also low THC emissions and engine efficiency.

Fig. 7 shows the share of prechamber fueling (left) as well as the estimated $\lambda_{\text{prechamber}}$ (right). It shows that the percentage of prechamber fuel can be decreased with increasing load and that HCH$_4$ demands less prechamber fuel than CH$_4$. Fig. 8 shows the resulting combustion stability, expressed as the coefficient of variance of the indicated mean effective pressure (COVIMEP). The engine runs stable in passive prechamber mode and using CH$_4$ up to $\lambda$ of about 1.65. With HCH$_4$, the passive prechamber mode is extended up to $\lambda$ of about 1.9. In active prechamber mode, CH$_4$ is able to run stable to $\lambda$ of around 2. With HCH$_4$, the active prechamber mode is extended up to $\lambda$ of about 2.2. Leaner combustion is, in principle, also possible by a further reduction of $\lambda$ in the prechamber [63] but as the hydrocarbon emissions strongly increase, this operation mode is not considered in this work.

**Influence of hydrogen addition on NO$_x$ emissions**

In a prechamber-equipped engine, NO$_x$ can either origin from the prechamber or from the main combustion chamber. The situation in the prechamber is quite complex as the fuel and residual burned gas distribution is inhomogeneous, the article [45] shows numerical results for the prechamber used here. Shortly after ignition, the flame can be quenched again because of high strain rates and heat losses [64], which leads to the desired turbulent jets of hot radicals exit the prechamber as article [48] shows. From research on large prechamber engines it is known that NO$_x$ emissions created in the prechamber can be significant and that smaller prechambers lead to less NO$_x$ emissions [65,66]. In smaller engines with small prechambers, NO$_x$ from the prechamber is reported to be rather insignificant [67]. Operated at very lean conditions where NO$_x$ from the main chamber gets to virtually zero, practically all NO$_x$ measured in the exhaust originates from the prechamber [68].

Fig. 9 (left) shows the NO$_x$ emissions of the engine considered here and it shows that NO$_x$ tends to very low values for $\lambda$ above about 2 for CH$_4$ and to even lower values for

---

**Fig. 7** — Percentage of fuel mass injected to the prechamber (left) and estimation of $\lambda_{\text{prechamber}}$ (right) for the operating points E, F and K.

**Fig. 8** — Coefficient of variance of the indicated mean effective pressure versus $\lambda$ for the operating points E, F and K.
HCH₄. Most likely, these NOₓ emissions in the magnitude of 10…100 ppm origin from the prechamber. The general engine-out NOₓ levels follow the expected trends: they peak at slightly lean conditions and decrease thereafter. Fig. 9 (right) shows a relative comparison of the NOₓ levels with HCH₄ (active and passive) versus active CH₄ operation. The NOₓ levels of HCH₄ show to be above the NOₓ levels of CH₄ operation up to a λ of about 1.7—1.8 and below at leaner mixtures. The reason for this behavior is that for very lean mixtures, the prechamber NOₓ dominates and λ in the prechamber is set leaner for HCH₄, thus leading to less thermal NOₓ creation. For lower global λ values, NOₓ is dominantly created in the main chamber and the higher flame temperature of hydrogen leads to increased NOₓ levels.

**Influence of hydrogen addition on hydrocarbon emissions**

Hydrocarbon emissions from engines fueled with methane are critical as methane is a very stable hydrocarbon and its catalytic oxidation is difficult. Albeit methane is not toxic, it is a powerful greenhouse gas and minimizing engine-out emissions is important. Hydrocarbon emissions origin from flame quenching at walls and from releasing hydrocarbons tapped in crevices [54]. As the flame quenching distance is reduced

---

*Fig. 9 – Brake specific engine-out NOₓ emissions versus λ for the operating points E, F and K (left), comparison of HCH₄ NOₓ emissions versus the active CH₄ case (right).*

*Fig. 10 – Brake specific engine-out THC emissions versus λ for the operating points E, F and K.*

*Fig. 11 – Molar shares of methane to total hydrocarbons versus λ for the operating points E, F and K.*
with increasing pressure, a reduction of THC emissions can generally be observed when load increases. Hydrogen addition reduces the flame quenching distance as well as the density of the fuel. A reduced flame quenching distance reduces therefore the hydrocarbon emissions directly and the reduced hydrocarbon density leads to a lower hydrocarbon content in the quenched zone. As Fig. 10 shows, the net effect is impressive as the addition of 22.5 mol%/3.5 mass%/8.0 energy% hydrogen reduces THC mass emissions by 30...40% for all load conditions.

As the engine is fueled with pure methane and a mixture of pure methane with hydrogen, respectively, the majority of the THC emissions are expected to be methane. The used emission bench is able to measure THC as well as methane simultaneously. This gives the possibility to quantify the methane- and non-methane emissions and Fig. 11 shows the results. For very lean conditions, the majority of the THC emissions is methane indeed and only a small portion of a few percent are synthesized to other, most likely longer-chained, hydrocarbons. When moving towards richer mixtures and especially pronounced for pure methane fueling, a considerable amount of non-methane hydrocarbons is synthesized: at \( \lambda = 1 \), nearly 20% of the hydrocarbons are non-methane. The presence of hydrogen, however, reduces the build-up of non-methane hydrocarbons quite strongly.

**Influence of hydrogen addition on CO emissions**

Reducing the amount of carbon by adding hydrogen to hydrocarbons leads directly to a reduction of carbon monoxide emissions. A dampening of this effect is possible by the water gas shift reaction \([69]\) \((H_2 + CO_2 \leftrightarrow CO + H_2O)\) because of the large amount of available hydrogen. Fig. 12 shows the measured CO emissions and it shows the expected pattern with high CO emissions towards \( \lambda = 1 \) and lower CO emissions in lean conditions. At conditions of best engine efficiency, a reduction of the CO emissions of around 20% due to the H\(_2\) addition can be observed, see Fig. 12 (right). However, as the reduction depends quite strongly on \( \lambda \), a competition of CO-reducing and CO-increasing effects can be assumed. Lowering engine-out CO levels is not necessarily beneficial since CO may be beneficial for catalytic methane oxidation \([70]\).

**Influence of hydrogen addition on engine efficiency**

As hydrogen addition is able to accelerate combustion this usually leads to increased engine’s brake thermal efficiencies. This effect can also be observed for the pre-chamber engine considered here, as Fig. 13 shows. A shift of \( \lambda \) for best efficiency toward leaner mixtures results, since hydrogen addition extends the lean limit. For operating point F, where also passive prechamber operation is performed, best efficiency can be seen for HCH\(_4\) for passive prechamber operation at \( \lambda = 1.7 \). Table 3 compares the fuel energy savings for the most efficient settings for HCH\(_4\) versus the most efficient setting for CH\(_4\) and also versus
operation at $\lambda = 1$ and it lists tailpipe CO$_2$ reductions. As the results regarding lean operation show, a few percent fuel energy can be saved. The fuel saving effect is more pronounced at lower loads. Comparing lean with $\lambda = 1$ operation, the fuel savings are much higher.

As the amount of unburned hydrocarbons increases with leaner combustion, the energy loss attributed to unburned fuel increases as well. To quantify the significance of unburned fuel, a fuel utilization efficiency $\eta_{\text{fuel}}$ is defined:

$$\eta_{\text{fuel}} = 1 - \frac{\sum (m_{\text{emissions}} \cdot LHV_{\text{emissions}})}{m_{\text{fuel}} \cdot LHV_{\text{fuel}}}$$

with $m_{\text{emissions}}$ being the mass emission of species having a lower heating value $LHV_{\text{emissions}}$ and $m_{\text{fuel}}$ being the fuel mass provided to the engine with its lower heating value $LHV_{\text{fuel}}$. In the experiments described here, hydrogen emissions are not measured and regarding hydrocarbon emissions, only the differentiation between methane and total hydrocarbons is made. The fuel utilization efficiency is therefore simplified by just considering the hydrocarbons and the carbon monoxide and assuming that all hydrocarbons exiting the engine have the LHV of methane. This leads to the following approximation:

$$\eta_{\text{fuel}} \approx 1 - \frac{m_{\text{THC}} \cdot LHV_{\text{CH}_4} + m_{\text{CO}} \cdot LHV_{\text{CO}}}{m_{\text{CH}_4 \text{ to engine}} \cdot LHV_{\text{CH}_4}}$$

with $m_{\text{CH}_4 \text{ to engine}}$ being the mass of methane provided to the engine, $m_{\text{THC}}$ being the mass of total hydrocarbon emissions and $m_{\text{CO}}$ being the mass of carbon monoxide emissions. To distinguish the importance of hydrocarbon- and carbon monoxide emissions, a utilization efficiency is defined which considers only the hydrocarbon emissions:

$$\eta_{\text{THC}} \approx 1 - \frac{m_{\text{THC}} \cdot LHV_{\text{CH}_4}}{m_{\text{CH}_4 \text{ to engine}} \cdot LHV_{\text{CH}_4}}$$

Fig. 14 shows the resulting fuel utilization efficiencies considering only hydrocarbon losses (left) and losses of
hydrocarbons and carbon monoxide (right). The unused fuel leaving the engine in the form of hydrocarbon emissions considerably increases with leaner mixtures, which points out that a significant effect for efficiency decrease at very lean mixtures, is the increase of wasted fuel. The behavior of this engine is very similar to the behavior of a diesel pilot ignition engine of similar size reported in [71] (only hydrocarbon emissions are considered there). Carbon monoxide, whose lower heating value is about five time lower than the one of methane, has only a small energetic effect at lean condition. However, at conditions towards $\lambda = 1$ the energy loss due to CO emissions becomes more significant. For all cases, hydrogen addition is able to reduce the amount of wasted fuel considerably which is, besides of faster heat release, the main reason for the observed increase in brake thermal efficiency.

**Turbine outlet temperature levels**

Exhaust temperature levels are mainly affected by engine and turbine efficiencies, fuel type, exhaust gas recirculation, amount of air excess, heat losses along the exhaust piping and turbine housing. Since the in-cylinder temperatures for CH$_4$ and HCH$_4$, for a given $\lambda$, are rather similar (Fig. 6) also similar exhaust temperature levels are expected. Fig. 15 shows the resulting temperature levels after turbine and, as expected, not much difference can be seen between CH$_4$ and HCH$_4$ combustion. Generally, the temperature levels are rather low for low load and for high air excess. Only 489 K after turbine are observed for HCH$_4$ operation in operating point E and $\lambda$ of 2.2.

**Conclusions**

As hydrogen increases the laminar flame speed, a distinct shortening of the ignition- and early flame phase is observed by hydrogen addition. For center of combustion at efficiency-optimal stoichiometry settings and at $8^\circ$ CA after TDC, ignition is set to around $10^\circ$ CA before TDC which is about $5^\circ$ CA later than for pure methane. Despite the lower methane number of the hydrogen enriched fuel, no kock problems occur.

Hydrogen addition is able to extend the lean limit of combustion, both in active and in passive prechamber mode. With H$_2$ addition, NO$_x$ emissions can be lowered in the very lean operation regime, as thermal NO$_x$ creation is reduced. Hydrogen addition shows to be able to disproportionally lower the engine’s hydrocarbon emissions: The addition of 22.5 mol %/3.5 mass%/8 energy% hydrogen lowers the THC emissions by 30–40%. Hydrogen addition proves also to lower CO emissions by around 20% for the efficiency optimal settings. Faster combustion, less THC and CO emissions leads to an increase in brake thermal efficiency. This results in fuel energy savings of the magnitude of 1.3–3.3% in the operating conditions considered here, which leads to tailpipe CO$_2$ reductions of 9.2–11%. In summary, the use of hydrogen-enriched methane in prechamber engines proves to be beneficial for all aspects considered. To achieve maximum benefits from hydrogen addition, the engine’s settings have to be adapted (i.e. ignition angle, amount of prechamber fuel). In practical applications with changing fuel compositions, this asks for either a feedback combustion control or a feedforward control based on signals from a fuel composition sensor [72,73]. While the NO$_x$ and CO emissions of such an engine can be efficiently reduced using known after treatment technologies such as selective catalytic reduction and catalytic oxidation, the methane emissions remain a problem, especially for the low temperature levels associated with lean combustion. An efficient lean methane reduction technology has to be developed before such a combustion concept can be transferred to on-road use. Some approaches are currently being discussed in the scientific community, for example the use of zeolites [74,75], graphene confinements [76] or electric fields [76]. However, for non-road applications without strict methane emission limits, the engine technology presented here may be already mature enough to be transferred into products.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgements**

The authors express their gratitude to the project partners for their invaluable scientific and technical contributions and the collaboration during the design and build-up of the prechamber engine. Namely the Aerothermochemistry and Combustion Systems Laboratory of ETH (Zürich, Switzerland) for their fundamental research on prechamber combustion using numerical and optical tools, the Institute of Combustion Engines and Transport of the Poznan University of Technology (Poznan, Poland) for single cylinder engine experiments, Ricardo Software (Shoreham-by-Sea, U.K.) for developing their simulation tools for prechamber simulation and Volkswagen Group Research (Wolfsburg, Germany) for optimization work and for designing and providing prototype hardware.

Special thanks go also to the technical staff of Empa (H. Ehrensperger, R. Spühler) who set-up the experiments with great care.

**References**

[1] NGV Global. Current Natural Gas Vehicle Statistics (n.d). http://www.iangv.org/current-ngv-stats/ (accessed February 12, 2020).

[2] Kotter E, Schneider L, Sehnke F, Ohnmeiss K, Schroer R. The future electric power system: impact of Power-to-Gas by interacting with other renewable energy components. J Energy Storage 2016;5:113–9. https://doi.org/10.1016/j.est.2015.11.012.

[3] Vandewalle J, Bruninx K, D’Haeseleer W. Effects of large-scale power to gas conversion on the power, gas and carbon sectors and their interactions. Energy Convers Manag 2015;94:28–39. https://doi.org/10.1016/j.enconman.2015.01.038.

[4] Michalski J. Investment decisions in imperfect power markets with hydrogen storage and large share of...
intermittent electricity. Int J Hydrogen Energy 2017;42:13368–81. https://doi.org/10.1016/j.ijhydene.2017.01.141.

[5] Le Duigou A, Bader AG, Lanoix JC, Nadau L. Relevance and costs of large scale underground hydrogen storage in France. Int J Hydrogen Energy 2017;42:22987–3003. https://doi.org/10.1016/j.ijhydene.2017.06.239.

[6] Schmidt O, Gambhir A, Staffell I, Hawkes A, Nelson J, Few S. Future costs and performance of water electrolysis: an expert elicitation study. Int J Hydrogen Energy 2017;42:30470–92. https://doi.org/10.1016/j.ijhydene.2017.06.239.

[7] Kurtz J, Sprik S, Bradley TH. Review of transportation hydrogen infrastructure performance and reliability. Int J Hydrogen Energy 2019;44:12101–23. https://doi.org/10.1016/j.ijhydene.2019.03.027.

[8] Andersson J, Gronkvist S. Large-scale storage of hydrogen. Int J Hydrogen Energy 2019;44:11901–9. https://doi.org/10.1016/j.ijhydene.2019.03.063.

[9] O’Kelly-Lynch PD, Gallagher PD, Borthwick AGL, McKeogh EJ, O’Kelly-Lynch PD, Gallagher PD, Borthwick AGL, McKeogh EJ. Fossil fuels: feasibility study in a depleted gas field. Proc Inst Mech Eng Part A J Power Energy 2020;234:226–36. https://doi.org/10.1177/0957650919851001.

[10] Ronsch S, Schneider J, Matthiaschke S, Schlüter M, Götz M, Lefebvre J, et al. Review on methanation - from fundamentals to current projects. Fuel 2016;166:276–96. https://doi.org/10.1016/j.fuel.2015.10.111.

[11] Ricca A, Truda L, Palma V. Study of the role of chemical support and structured carrier on the CO2 methanation reaction. Chem Eng J 2019;377:120461. https://doi.org/10.1016/j.cej.2018.11.159.

[12] Delmelle R, Terreni J, Remhof A, Heel A, Proost J, Borgschulte A. Evolution of water diffusion in a sorption-enhanced methanation catalyst. Catalysts 2018;8:1–15. https://doi.org/10.3390/catal8090341.

[13] Gotz M, Lefebvre J, Mors F, McDaniel Koch A, Graf F, Bajohr S, et al. Renewable Power-to-Gas: a technological and economic review. Renew Energy 2016;85:1371–90. https://doi.org/10.1016/j.renene.2015.07.066.

[14] Eser P, Chokani N, Abhari RS. Impacts of battery electric vehicles on renewable integration within the 2030 European power system. Int J Energy Res 2018;42:4142–56. https://doi.org/10.1002/er.1611.

[15] Reitz RD, Ogawa H, Payri R, Fansler T, Kokjohn S, Moriyoishi Y, et al. IJER editorial: the future of the internal combustion engine. Int J Engine Res 2019. https://doi.org/10.1177/1468087419877990. 1468087419877999.

[16] Kramer U, Stollenwerk S, Ortloff F, Sava X, Janssen A, Eppler S, et al. FVV fuel study: options for the defossilization of the transportation sector (100 % scenarios). In: Liebl J, Beidl CMW, editors. Int. Mot. Baden-Baden: Springer Vieweg, 2019. p. 1–21. https://doi.org/10.1007/978-3-658-26528-1_1.

[17] Senecal PK, Leach F. Diversity in transportation: why a mix of propulsion technologies is the way forward for the future fleet. Results Eng 2019;4:100060. https://doi.org/10.1016/j.rineng.2019.100060.

[18] Bach C, Lammle C, Bill R, Soltic P, Dyantar D, Janner P, et al. Clean engine vehicle a natural gas driven Euro-4/SULEV with 30% reduced CO2-emissions. SAE Tech Pap. 2004. https://doi.org/10.4271/2004-01-0645.

[19] Kammermann T, Kretzner W, Trottmann M, Merotto L, Soltic P, Bleiner D. Spark-induced breakdown spectroscopy of methane/air and hydrogen-enriched methane/air mixtures at engine relevant conditions. Spectrochim Acta Part B At Spectrosc 2018;148:152–64. https://doi.org/10.1016/j.sab.2018.06.013.

[20] Gholamisheeri M, Wichman IS, Toulson E. A study of the turbulent jet flow field in a methane fueled turbulent jet ignition (TJI) system. Combust Flame 2017;183:194–206. https://doi.org/10.1016/j.combustflame.2017.05.008.

[21] Toulson E, Schock H, Attard WP. SAE Tech Pap Ser. A review of pre-chamber initiated jet ignition combustion systems, 1; 2010. https://doi.org/10.4271/2010-01-2263.

[22] Alvarez CEC, Couto GE, Roso VR, Thiriet AB, Valle RM. A review of prechamber ignition systems as lean combustion technology for SI engines. Appl Thermo Eng 2018;128:107–20. https://doi.org/10.1016/j.aplthermeng.2017.08.118.

[23] Xu G, Kotzagiannii M, Kyrtatos P, Wright YM, Boulouchos K. Experimental and numerical investigations of the uncavitated prechamber combustion in a rapid compression and expansion machine under engine-like conditions. Combust Flame 2019;204:68–84. https://doi.org/10.1016/j.combustflame.2019.01.025.

[24] Benajes J, Novella R, Gomez-Soriano J, Martinez-Hernandiz PJ, Libert C, Dabiri M. Evaluation of the passive pre-chamber ignition concept for future high compression ratio turbocharged spark-ignition engines. Appl Energy 2019;248:576–88. https://doi.org/10.1016/j.apenergy.2019.04.131.

[25] Syrovatka Z, Vitek O, Vavra J, Takats M. SAE Tech Pap Ser. Scavenged pre-chamber volume effect on gas engine performance and emissions, 1–17, 2019. https://doi.org/10.4271/2019-01-0258.

[26] Qing-he L, Bai-gang S, Yong-li G, Xi W, Han W, Ji-bin H, et al. The effect of equivalence ratio, temperature and pressure on the combustion characteristics of hydrogen-air pre-mixture with turbulent jet induced by pre-chamber sparkplug. Int J Hydrogen Energy 2019;44:20470–81. https://doi.org/10.1016/j.ijhydene.2019.05.238.

[27] Getzlaff J, Pape J, Gruenig C, Kuhnert D, Latsch R. Investigations on pre-chamber spark plug with pilot injection. SAE Tech Pap Ser. 2007. p. 776–90. https://doi.org/10.4271/2007-01-0479.

[28] Desantes JM, Novella R, De La Morena J, Fagano Ing V. Achieving ultra-low combustion using a pre-chamber spark ignition system in a rapid compression-expansion machine. SAE Tech Pap Ser. 2019. p. 1–12. https://doi.org/10.4271/2019-01-0236.

[29] Tolou S, Schock H. Experiments and modeling of a dual-mode, turbulent jet ignition engine. Int J Engine Res 2019. https://doi.org/10.1080/14680874.2019.85880. 1468087419875888.

[30] Sassi L, Kitsopanidis I, Lovett G. Evolutions in F1 engine technology: pursuing performance from today's power unit through efficiency. In: Proc. 37th int. Vienna engine symp, 2016.

[31] Dimopoulos P, Bach C, Soltic P, Boulouchos K. Hydrogen-natural gas blends fuelling passenger car engines: combustion, emissions and well-to-wheels assessment. Int J Hydrogen Energy 2008;33:7224–32. https://doi.org/10.1016/j.ijhydene.2008.12.026.

[32] Thurnheer T, Soltic P, Dimopoulos Eggenschwiler PS. I. engine fuelled with gasoline, methane and methane/ hydrogen blends: heat release and loss analysis. Int J Hydrogen Energy 2009;34:2494–503. https://doi.org/10.1016/j.ijhydene.2008.12.048.

[33] Hao D, Mehra RK, Luo S, Nie Z, Ren X, Fanhua M. Experimental study of hydrogen enriched compressed
natural gas (HCNG) engine and application of support vector machine (SVM) on prediction of engine performance at specific condition. Int J Hydrogen Energy 2019;45:5309–25. https://doi.org/10.1016/j.ijhydene.2019.04.039.

[35] Verhelst S, Wallner T. Hydrogen-fueled internal combustion engines. Prog Energy Combust Sci 2009;35:490–527. https://doi.org/10.1016/j.pecs.2009.08.001.

[36] Mehra RK, Duan H, Juknelevicius R, Ma F, Li J. Progress in hydrogen enriched compressed natural gas (HCNG) internal combustion engines - a comprehensive review. Renew Sustain Energy Rev 2017;80:1458–9. https://doi.org/10.1016/j.rser.2017.05.061.

[37] Luo S, Ma F, Mehra RK, Huang Z. Deep insights of HCNG engine research in China. Fuel 2020;263:116612. https://doi.org/10.1016/j.fuel.2019.116612.

[38] Biswas S, Qiao L. Ignition of ultra-lean premixed H2/air using multiple hot turbulent jets generated by pre-chamber combustion. Appl Therm Eng 2018;132:102–14. https://doi.org/10.1016/j.applthermaleng.2017.11.073.

[39] Wang N, Liu J, Chang WL, Lee C fon. A numerical study of the jet ignition process. University of Melbourne; 2008.

[40] Toulson E. Applying alternative fuels in place of hydrogen to the jet ignition process. 2014.

[41] Santos NDSA, Alvarez CEC, Roso VR, Baeta JGC, Valle RM. Combustion analysis of a SI engine with stratified and homogeneous pre-chamber ignition system using ethanol and hydrogen. Appl Therm Eng 2019;160:113985. https://doi.org/10.1016/j.applthermaleng.2019.113985.

[42] Toulson E. Applying alternative fuels in place of hydrogen to the jet ignition process. University of Melbourne; 2008.

[43] Toulson E. Applying alternative fuels in place of hydrogen to the jet ignition process. 2014.

[44] Bolla M, Shapiro E, Tiney N, Kyrtatios P, Kotzagianni M, Boulochous K. Numerical simulations of pre-chamber combustion in an optically accessible RCEM. SAE Tech. Pap. 2019-01-0224. SAE International; 2019. https://doi.org/10.4271/2019-01-0224.

[45] Bolla M, Shapiro E, Kotzagianni M, Kyrtatios P, Tiney N, Boulochous K. Numerical study of fuel and turbulence distributions in an automotive-sized scavenged pre-chamber. Combust Engines 2019;176:61–7. https://doi.org/10.19206/CE-2019-108.

[46] Shapiro E, Tiney N, Kyrtatios P, Kotzagianni M, Bolla M, Boulochous K, et al. Experimental and numerical analysis of pre-chamber combustion systems for lean burn gas engines. SAE Tech Pap Ser. 2019. p. 1–11. https://doi.org/10.4271/2019-01-0260.

[47] Pielecha I, Wislocki K, Cieslik W, Fiedkiewicz L. Prechamber selection for a two stage turbulent jet ignition of lean air-gas mixtures for better economy and emission. E3S Web Conf 2018;70:03010. https://doi.org/10.1051/e3sconf/20187003010.

[48] Kotzagianni M, Kyrtatios P, Boulochous K. Optical investigation of prechamber combustion in an RCEM. Combust Engines 2019;176:10–5. https://doi.org/10.19206/CE-2019-102.

[49] Bolla M, Shapiro E, Tiney N, Kyrtatios P, Kotzagianni M, Boulochous K. SAE Tech Pap Ser. Numerical study of turbulence and fuel-air mixing within a scavenged pre-chamber using RANS and LES, 1. 2019. p. 1–11. https://doi.org/10.4271/2019-01-0198.

[50] Soltic P, Hilfiker T, Hutter R, Hanggi S. Experimental comparison of efficiency and emission levels of four-cylinder lean-burn passenger car-sized CNG engines with different ignition concepts. Combust Engines 2019;176:27–35. https://doi.org/10.19206/CE-2019-104.

[51] Soltic P, Hilfiker T, Haenggi S. Efficient light-duty engine using turbulent jet ignition of lean methane mixtures. Int J Engine Res 2019. https://doi.org/10.1177/1468088319889383.

[52] Hanggi S, Hilfiker T, Soltic P, Hutter R, Onder C. Control-oriented analysis of a lean-burn light-duty natural gas research engine with scavenged pre-chamber ignition. Combust Engines 2019;176:42–53. https://doi.org/10.19206/CE-2019-106.

[53] Brettschneider J. Extension of the equation for calculation of the air-fuel equivalence ratio. SAE Tech. Pap. 972989. SAE International; 1997. https://doi.org/10.4271/972989.

[54] Heywood JB. Internal combustion engine fundamentals, 21. McGrawHill Series in Mechanical Engineering; 1988.

[55] Nguygen HH, Horak V, Coriniç S. Theory of the internal combustion engine cycle with the thermochemical model of combustion. In: ICMT 2019 - 7th int. Conf. Mil. Technol. Proc., Brno; 2019. https://doi.org/10.1109/MILTECHCS.2019.8870076.

[56] Obrecht P. Aerothermochemistry and Combustion Systems Laboratory of ETH Zurich - WEC: Benutzerhandbuch und Programmdokumentation. 2016.

[57] Waschini G. A universally applicable equation for the instantaneous heat transfer coefficient in the internal combustion engine. SAE Tech Pap 670931. 1967.

[58] Bargende M. Ein Gleichungsansatz zur Berechnung der instationären Wandwärmeübergänge im Hochdruckteil von Ottomotoren. TH Darmstadt; 1990.

[59] Fox JW, Cheng WK, Heywood JB. A model for predicting residual gas fraction in spark-ignition engines. SAE Tech. Pap. 931025. SAE International; 1993. https://doi.org/10.4271/931025.

[60] Grote H-H, Feldhusen J. Stromungsmaschinen, verluste, wellendichtung. In: Dubbel Taschenb. für den Maschinenbau; 2014.

[61] Kee RJ, Rupley FM, Miller JA. Chemkin II: a Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. 1989.

[62] Shapiro E, Tiney N, Kyrtatios P, Kotzagianni M, Bolla M, Boulochous K, et al. Experimental and numerical analysis of pre-chamber combustion systems for lean burn gas engines. SAE Tech. Pap. 2019-01-0260. SAE International; 2019. https://doi.org/10.4271/2019-01-0260.

[63] Gussak LA. The role of chemical activity and turbulence intensity in prechamber-torch organization of combustion of a stationary flow of a fuel-air mixture. SAE Tech Pap Ser. 1983. https://doi.org/10.4271/830592.

[64] Bradley D, Shehata M, Lawes M, Ahmed P. Flame extinctions: critical stretch rates and sizes. Combust Flame 2020;212:459–68. https://doi.org/10.1016/j.combustflame.2019.11.013.

[65] Gingrich JW, Olsen DB, Puzinaskas P, Willson BD. Precombustion chamber NOx emission contribution to an industrial natural gas engine. Int J Engine Res 2006;7:41–9. https://doi.org/10.1243/146808706X30602.

[66] Redtenbacher C. Analyse und Optimierung von Vorkammerbrennverfahren für Großgasmotoren. TU Graz; 2012.

[67] Konishi M, Nakamura N, Oono E, Baika T, Sanda S. Effects of a prechamber on NOx formation process in the SI engine. SAE Tech Pap 790389. 1979.

[68] Uyehara OA. Prechamber for lean burn for low NOx. SAE Tech Pap 950612. 1995. https://doi.org/10.4271/950612.

[69] Vickland CW, Strange FM, Bell RA, Starkman ES. A consideration of the high temperature thermodynamics of internal combustion engines. SAE Tech Pap 620564. 1962. https://doi.org/10.4271/620564.
[70] Hutter R, De Libero L, Elbert P, Onder CH. Catalytic methane oxidation in the exhaust gas aftertreatment of a lean-burn natural gas engine. Chem Eng J 2018;349:156–67. https://doi.org/10.1016/j.cej.2018.05.054.

[71] Hutter R, Ritzmann J, Elbert P, Onder C. Low-load limit in a diesel-ignited gas engine. Energies 2017;10:1–27. https://doi.org/10.3390/en1001001450.

[72] Soltic P, Biffiger H, Prêtre P, Kempe A. Micro-thermal CMOS-based gas quality sensing for control of spark ignition engines. Measurement 2016;91:661–79. https://doi.org/10.1016/j.measurement.2016.05.098.

[73] Heinrich S, Hien M, Knittel T. Novel thermal method for determining properties of compressed natural gas. Combust Engines 2019;176:56–62. https://doi.org/10.19206/CE-2019-107.

[74] Petrov AW, Ferri D, Krumeich F, Nachtegaal M, Van Bokhoven JA, Krocher O. Stable complete methane oxidation over palladium based zeolite catalysts. Nat Commun 2018;9. https://doi.org/10.1038/s41467-018-04748-x.

[75] Petrov AW, Ferri D, Krocher O, Van Bokhoven JA. Design of stable palladium-based zeolite catalysts for complete methane oxidation by postsynthesis zeolite modification. ACS Catal 2019;9:2303–12. https://doi.org/10.1021/acscatal.8b04486.

[76] Cui X, Li H, Wang Y, Hu Y, Hua L, Li H, et al. Room-temperature methane conversion by graphene-Confined single Iron Atoms. Chem 2018;4:1902–10. https://doi.org/10.1016/j.chempr.2018.05.006.