

## Methane Emission Control

### A review of mobile and stationary source emissions abatement technologies for natural gas engines

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Natural gas is of increasing interest as an alternative fuel for vehicles and stationary engines that traditionally use gasoline and diesel fuels. Drivers for the adoption of natural gas include high abundance, lower price and reduced greenhouse gas emissions compared to other fossil fuels. Biogas is an option which could reduce such emissions further. The regulations which cap emissions from these engines currently include Euro VI and the US Environmental Protection Agency (EPA) greenhouse gas legislation. The regulated emissions limits for methane, nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) for both stoichiometric and lean burn compressed natural gas engines can be met by the application of either palladium-rhodium three-way catalyst (TWC) or platinum-palladium oxidation catalyst respectively. The drivers, policy and growth of this Pd based catalyst technology and its remaining challenges to be overcome in terms of cost and catalyst deactivation due to sulfur, water and thermal ageing are described in this short review.

#### Introduction

There is increased interest in recent years in replacing traditional gasoline and diesel fuels with natural gas for

a number of reasons, such as increasing energy prices, depletion in oil resources and political uncertainty, but mainly due to increasing concern about global warming (1). Natural gas is composed mainly of methane (typically 70–90%) with variable proportions of other hydrocarbons such as ethane, propane and butane (up to 20% in some deposits) and other gases (2, 3). It can be commercially produced from oil or natural gas fields and is widely used as a combustion energy source for power generation, industrial cogeneration and domestic heating. It can also be used as a vehicle fuel. Natural gas has a number of environmental benefits: it is a cleaner burning fuel typically containing few impurities, it contains higher energy (Btu) per carbon than traditional hydrocarbon fuels resulting in low carbon dioxide emissions (25% less greenhouse gas emissions), and it has lower emissions of PM and NO<sub>x</sub> compared to diesel and gasoline. In the EU there is an aim for more than a 60% reduction in CO<sub>2</sub> emissions from transport by 2050 from 1990 levels (4) and using natural gas as a vehicle fuel can contribute to this (1). From the economic point of view, natural gas can be less expensive than diesel and gasoline. For example **Table I** displays gasoline, diesel and natural gas prices during 2014 and 2015 (5, 6).

The production cost is low and governments worldwide are promoting its usage by providing financial incentives. Political benefits, in countries such as the USA, could include secured national resources for energy, and less dependency on imported oil from other countries. Partly due to these factors, there is a rapid increase in interest in use of natural gas with a

**Table I Comparison between Gasoline, Diesel and Natural Gas prices 2014–2015 (5, 6)**

Fuel	Price, US\$ per GGE <sup>a</sup>	
	July 2014	October 2015
Gasoline	3.70	2.35
Diesel	3.51	2.30
Natural Gas	2.17	2.09

<sup>a</sup>GGE = gasoline gallon equivalent

predicted 30% average annual growth especially in internal combustion engines.

This short review focuses on the demand, policies and growth of natural gas globally and methane abatement *via* aftertreatment systems for mobile and stationary applications.

### Legislation and Challenges

Natural gas engines emit very low PM and NOx (up to 95% and 70% less, respectively) compared to heavy-duty and light-duty diesel engines. Presently, methane is not included in criteria emissions regulations, but the US EPA greenhouse gas legislation caps methane emissions at 0.1 g bhp<sup>-1</sup> h<sup>-1</sup> for heavy-duty engines and 0.05 g mile<sup>-1</sup> for pickup trucks and vans (7). Euro VI natural gas vehicles are required to meet both total hydrocarbon (THC) and methane emissions limits and therefore need methane emission control aftertreatment devices. The current EU emission standards for heavy-duty gas engines are shown in **Table II**. The methane limits apply for only gas engines and the PM limit is not an issue for CNG vehicles.

The US EPA has also proposed new standards towards meeting the US government’s pledge to reduce the methane emissions mainly from the oil and gas sectors by 40–45% by 2025 from 2012 level (9).

This is further emphasised recently in May 2016 to limit methane emissions from industry leaking compressors, wells and pumps (10).

### Natural Gas Resources and the Natural Gas Vehicles Market

Natural gas is available in abundance worldwide. As shown in **Figure 1**, the worldwide proven reserves of natural gas exceed 204.7 × 10<sup>12</sup> m<sup>3</sup> and world gas reserves will last for 537 years, another 161 years in Europe (1).

The worldwide natural gas vehicle population increased at an average growth rate of 20% per annum between 1991 and 2007 and some sources predict it to increase further as shown in **Figure 2** (11).

### Fuel Options

Natural gas can be used as transportation fuel in the form of CNG and liquefied natural gas (LNG). CNG is carried in tanks pressurised to 3600 psi (~248 bar) and has an energy density around 35% of gasoline per unit volume (12). LNG has an energy density 2.5 times that of CNG and is mostly used for heavy-duty vehicles. It is cooled to liquid form at –162°C and as a result the volume is reduced 600 fold meaning LNG is easier to transport than CNG (2). In general, natural

**Table II EU Emission Standards for Heavy-Duty Gas Engines: Transient Testing (8)**

Stage	Date	Test	Limit, g kWh <sup>-1</sup>				
			CO	NMHC	CH <sub>4</sub>	NOx	PM
Euro V	October 2008	European Transient Cycle (ETC)	4.0	0.55	1.1	2.0	0.03
Euro VI	January 2013	World Harmonised Transient Cycle (WHTC)	4.0	0.16	0.5	0.46	0.01

Courtesy of Dieselnet

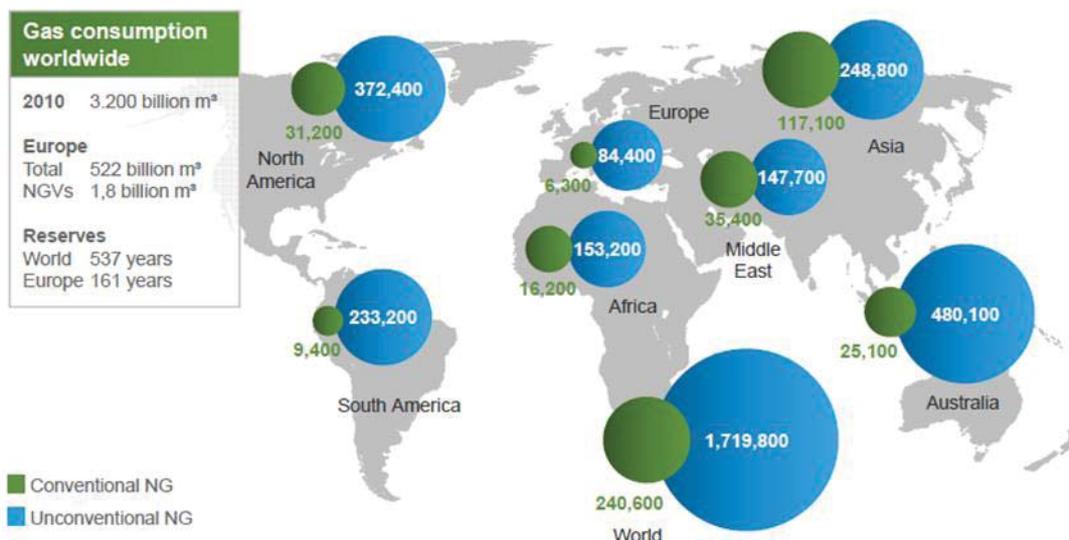


Fig. 1. Worldwide natural gas reserves (units = 10<sup>9</sup> m<sup>3</sup>) (1). Source: NGVA Europe

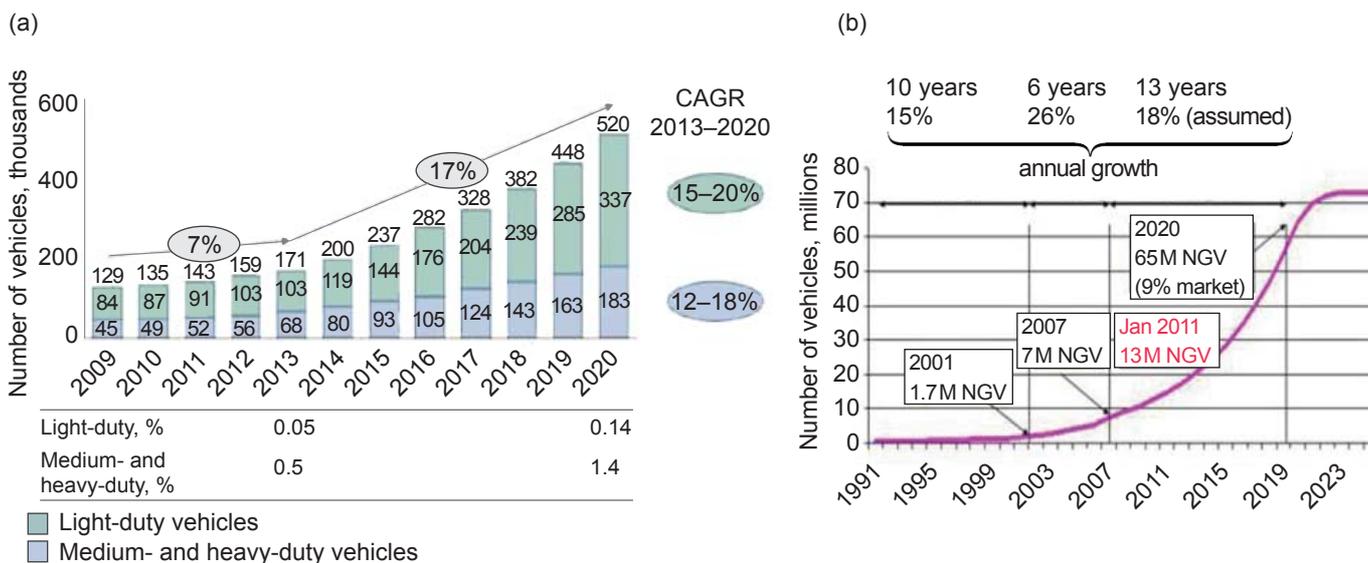


Fig. 2. CNG vehicles in: (a) USA, where CAGR ranges are based on different assumptions regarding CNG vehicle adoption and penetration (in %) is calculated relative to all vehicles currently in use in the USA; and (b) Europe markets as a proportion of worldwide natural gas vehicle with 5% market share for Europe in 2020 and 9% possible for Europe in 2030 (11) (Reproduced with kind permission from Eunseok Kim, Heesung Catalysts, South Korea)

gas vehicles are more expensive than petrol or diesel vehicles mainly due to the cost of the high-pressure or insulated fuel tank which is required to store LNG or CNG.

Alternatively, using gas-to-liquids (GTL) technology (13), the natural gas can be converted to liquid fuels which have ignition characteristics similar to diesel or gasoline fuels and can be used for transportation purposes. Other options include reforming natural gas

to generate hydrogen for hydrogen fuel cell vehicles and generation of electricity for electric vehicles by firing a power plant by natural gas (14).

Bio-LNG could be an alternative to natural (fossil) gas, being produced from biogas, derived by anaerobic digestion from organic matter such as landfill waste or manure (15–17). Its use would further reduce vehicle greenhouse gas emissions (18) and would also be cheaper than diesel, partly because of government

incentives such as reduced duties in various countries or regions (19).

### Emission Aftertreatment Technologies

Based on the combustion conditions, two main operating modes are used for methane fuelled engines: stoichiometric conditions ( $\lambda = 1$ ) and lean burn conditions ( $\lambda \geq 1.3$ ). **Figure 3** (11) shows the CO<sub>2</sub> emission comparison of the various technologies, and it can be seen that natural gas contributes lower emissions than diesel under all conditions.

Methane is the least reactive hydrocarbon and high energy is required to break the primary C–H bond. The

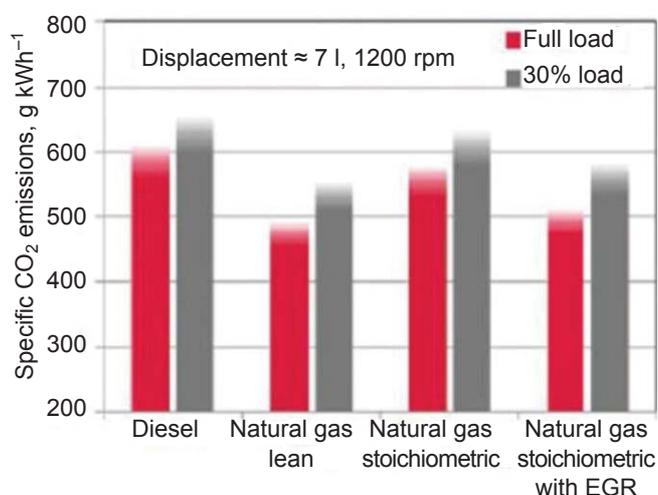


Fig. 3. CO<sub>2</sub> emission dependence on technologies in HDD CNG engines (11). EGR = exhaust gas recirculation (Reproduced with kind permission from Eunseok Kim, Heesung Catalysts, South Korea)

ignition temperature of alkanes generally decreases with increasing fuel to air ratio and increasing hydrocarbon chain length which correlates with the C–H bond strength. Palladium-based catalysts are well known as the most active type of catalyst for methane oxidation.

**Figure 4** illustrates how different hydrocarbon species are converted to CO<sub>2</sub> and H<sub>2</sub>O under lean conditions with increasing exhaust temperature over a Pd based catalyst. It is shown that methane has a higher light-off temperature compared to other hydrocarbons, reaching 50% conversion at 550°C.

When operating in stoichiometric conditions ( $\lambda = 1$ ), a TWC is used as an effective and cost efficient aftertreatment system to combust methane. Mostly bimetallic Pd-Rh catalysts with high total platinum group metal (pgm) loadings of >200 g ft<sup>-3</sup> are needed for high levels of methane conversion to meet end of life THC regulations due to the very low reactivity of

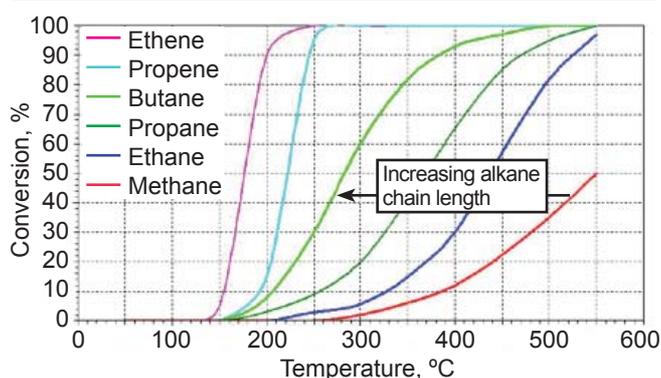


Fig. 4. Hydrocarbon species conversion of Pd based catalyst as a function of temperature under lean conditions

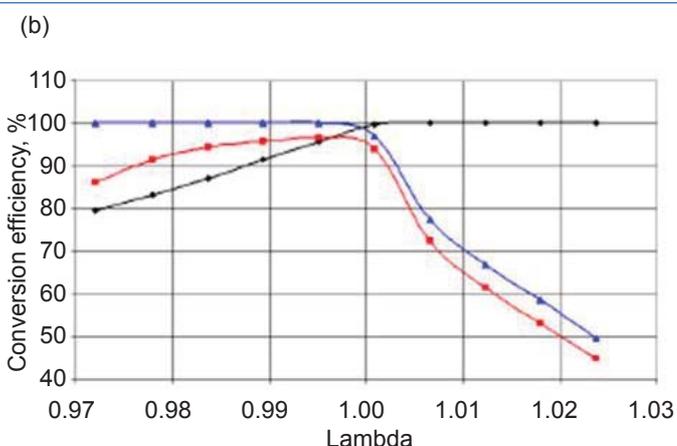
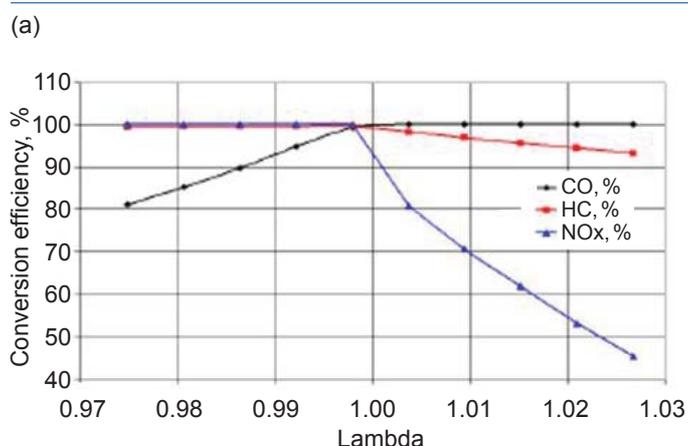


Fig. 5. Comparison of the performance of an aged Pd:Rh (120/0:11:1) TWC as a function of lambda at 450°C on: (a) a gasoline engine; (b) a stoichiometric CNG engine

this hydrocarbon and catalyst deactivation *via* thermal and chemical effects. **Figure 5** shows the performance of a typical Pd-Rh TWC as a function of engine lambda on a standard gasoline engine compared to a stoichiometric CNG engine (a gasoline engine fuelled by CNG). Stoichiometric operation is chosen for CNG because it is easier to reduce both methane and NOx emissions under stoichiometric conditions than under lean conditions. It is evident that in the gasoline engine going from rich to lean operation, carbon monoxide combustion improves and reaches 100% above  $\lambda = 0.995$  and remains the same during lean operation. 100% HC conversion is seen on rich operation, but starts dropping slightly when going lean; NOx shows a dramatic drop with increase in  $\lambda$  value. On the stoichiometric CNG engine, the CO and NOx conversion follow a similar trend to the gasoline engine, but HC conversion is much lower especially lean of stoichiometry. Use of high pgm loadings will improve the overall HC conversion in stoichiometric CNG engines. However, high methane conversions can be achieved with relatively low pgm based on engine calibration, i.e. controlling air to fuel ratio so as to operate near stoichiometric or rich of stoichiometric; the pgm loading can also be varied corresponding to the regional legislation requirement with regards to methane and non-methane conversions.

**Figure 6** shows the difference in light-off combustion temperatures of a series of catalysts used in both gasoline and stoichiometric CNG applications. The need for high pgm loadings for CNG applications in order to attain similar light off combustion temperatures as for gasoline applications is clearly evident. The explanation lies in the fact that hydrocarbon emissions from natural gas vehicles consist mostly of methane which is much more difficult to oxidise than the alkenes,

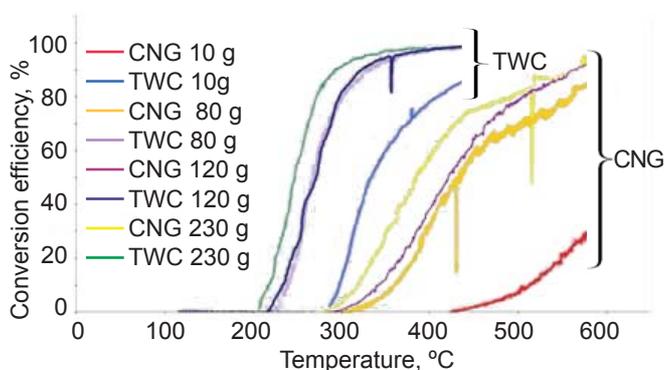


Fig. 6. Effects of pgm loadings ( $\text{g ft}^{-3}$ ) on HC conversion of Pd:Rh catalyst: gasoline (TWC) vs. CNG

aromatics and longer chain alkanes which are present in gasoline engine exhausts.

One of the advantages of using lean burn engines is high fuel economy. However, unlike with stoichiometric engines, a reductant needs to be injected into the exhaust stream in order to be able to reduce NOx in the presence of excess oxygen. This is normally in the form of ammonia ( $\text{NH}_3$ ), and thus lean burn applications require a completely different catalyst system to those that are stoichiometric, where efficient NOx reduction can be achieved with the use of CO or HC at slightly rich or stoichiometric conditions. Other technical problems with lean burn engines include the possibility of misfiring at high air-to-fuel ratios resulting in higher emissions. The reduction of NOx and oxidation of methane is also more difficult under very oxidising conditions. For lean burn CNG applications, Pd-Pt at high total pgm loadings ( $>200 \text{ g ft}^{-3}$ ) are needed for methane combustion at lower temperatures.

Due to the unreactive (or poorly reactive) nature of methane at lower temperatures, increased methane emissions result during cold start and idle situations, mainly for lean burn where the exhaust temperatures are lower than stoichiometric. In order to improve the reactivity of methane at lower temperatures, one of the options is to use high pgm loadings. **Figure 7** shows the significant benefit in methane conversion with increase in pgm loading from 100 to 200  $\text{g ft}^{-3}$  of Pd, however the benefit diminishes above 200  $\text{g ft}^{-3}$ .

## Other Challenges

CNG catalysts, especially Pd-based catalysts, suffer from poisoning by water (5–12%) and sulfur ( $<0.5 \text{ ppm SO}_2$  in lube oil) especially under lean conditions, which results in drastic reduction of conversion rate of the catalyst over time. The

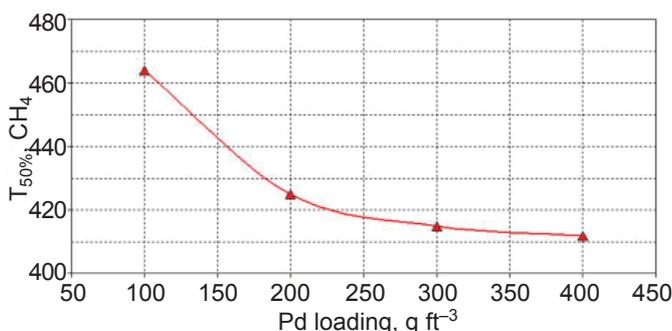


Fig. 7. Effect of Pd loading on lean burn methane conversion

deactivation due to water is significant due to the formation of hydroxyl, carbonates, formates and other intermediates on the catalyst surface (20). The activity is reversible, and can be recovered completely if water is removed (Figure 8). However, this is impractical as methane combustion feed always contains a high level of water due to the high content of H in methane. H<sub>2</sub>O can be either an inhibitor or a promoter depending on the air-to-fuel ratio, i.e. lambda. Under stoichiometric and reducing conditions, lambda ≤ 1, H<sub>2</sub>O can act as a promoter for the oxidation of hydrocarbons through the steam reforming reaction in both CNG and gasoline engines. However for lean burn CNG operating at lambdas >1, H<sub>2</sub>O acts as an inhibitor for methane oxidation. It is critical to understand the water inhibition effect and design catalysts which are more tolerant to the presence of H<sub>2</sub>O. This would allow for improvement when trying to control methane emissions from lean burn CNG.

Though the sulfur level is very low in the engine exhaust, Pd-based catalysts deactivate significantly upon sulfur exposure due to the formation of stable sulfates (21, 22). Regeneration of the catalyst in order to restore the activity following sulfur poisoning is challenging and will usually require high temperatures, rich operation or both. This is easily achievable in stoichiometric operation but more difficult in lean burn. A lean burn vehicle operates with a much higher air-to-fuel ratio than a stoichiometric vehicle and will need injection of a much higher concentration of reductant to switch to rich operation. Thermal deactivation resulting from a high level of misfire events due to poor engine transient control and ignition systems destroys the

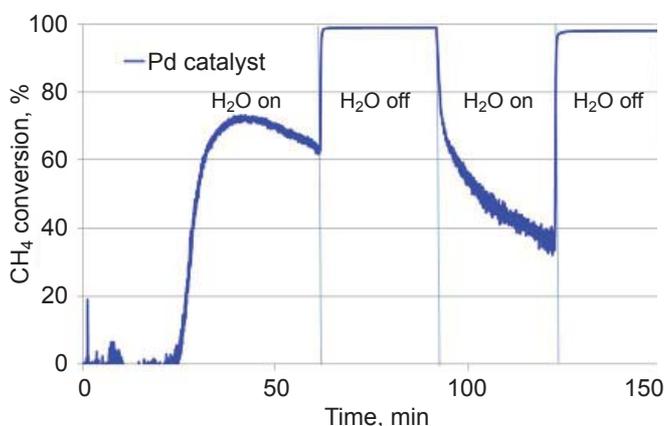


Fig. 8. Effect of water on methane conversion of Pd catalyst at 450°C

catalyst and correspondingly leads to a high level of exhaust emissions. This problem is common to all types of engine, but some catalysts are more resistant to the thermal deactivation. This leads to a high demand for catalyst efficiency and durability.

Figure 9 shows the effect of high-temperature thermal ageing and sulfur exposure on the methane conversion of a Pd-based oxidation catalyst. It is evident that the catalyst deactivates under both conditions, but sulfur poisoning has a more dramatic impact than thermal ageing. Both the thermal durability and sulfur poisoning can be improved by the addition of small amounts of Pt to the Pd catalyst (23, 24), as shown in Figures 10 and 11. Figure 11 shows that the sulfur inhibition due

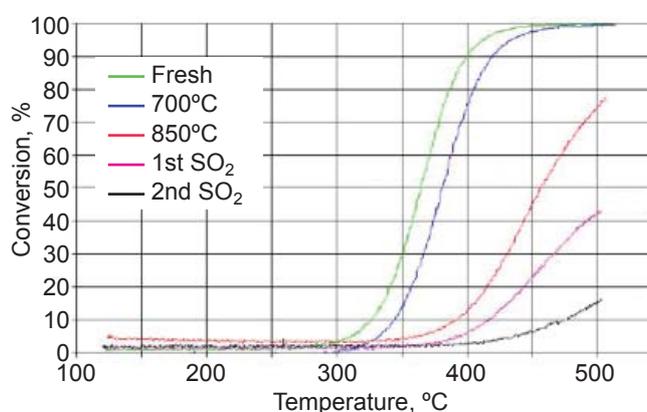


Fig. 9. Effect of thermal ageing and sulfur poisoning on a Pd-based methane oxidation catalyst. '1st SO<sub>2</sub>' and '2nd SO<sub>2</sub>' show successive sulfation

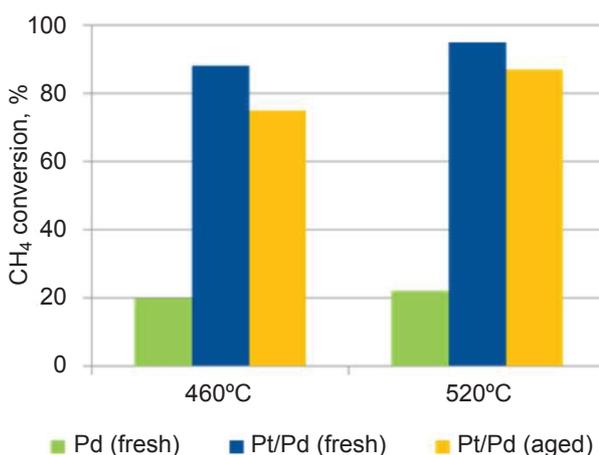


Fig. 10. Role of Pt in methane conversion (11) (Reproduced with kind permission from Eunseok Kim, Heesung Catalysts, South Korea)

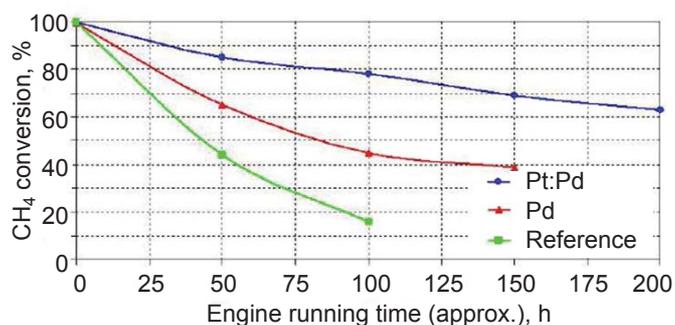


Fig. 11. Impact of Pt addition to reduce the impact of sulfur poisoning on Pd-based oxidation catalysts (25)

to formation of palladium sulfates can be reduced significantly on addition of Pt (25).

### Abbreviations

CH <sub>4</sub>	methane
CNG	compressed natural gas
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
EGR	exhaust gas recirculation
ETC	European Transient Cycle
GTL	gas-to-liquids
HC	hydrocarbons
HDD	heavy duty diesel
LNG	liquified natural gas
NMHC	non-methane hydrocarbons
NO <sub>x</sub>	nitrogen oxides
pgm	platinum group metal
PM	particulate matter
THC	total hydrocarbons
TWC	three way catalyst
WHTC	World Harmonised Transient Cycle

### Conclusions

An increased interest in the use of natural gas as an alternative fuel in mobile and stationary applications is apparent. Some of the main reasons are its relative high abundance, lower cost compared to other fuels and most importantly the urge to meet targets for the reduction of greenhouse gas emissions. Methane emissions and total hydrocarbons (including methane) are capped by regulations globally including the US EPA greenhouse gas legislation and Euro VI, requiring vehicles to use

methane emissions control aftertreatment. The obvious path for natural gas is *via* methane for stationary and mobile applications, where it can be used in the form of either CNG or LNG. With further improvement in natural gas fuelling infrastructure and an increase in the number of natural gas engines, the rate of uptake of natural gas vehicles can be enhanced to a greater extent. Pd-Rh TWC under stoichiometric conditions, while Pd-Pt catalyst under lean conditions are used to deal with methane combustion. High methane combustion can be achieved at lower temperatures by altering the pgm loading and through engine calibration depending on the regional legislation requirements. However, these might make the technology rather expensive. Further challenges include the issues with catalyst deactivation due to sulfur (from lubricant), water, thermal ageing and methane slip at low temperatures. These need to be addressed quickly so that this technology is readily available to meet the current and upcoming stricter legislation and challenges.

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