

Chapter 13

Emissions Control Technologies for Natural Gas Engines



A. Wahbi, A. Tsolakis and J. Herreros

Abstract In recent years, there has been a rising interest in alternative cleaner low-carbon fuels as they have a significant potential in decreasing the harmful exhaust emissions and contribute in decarbonising transportation. Natural gas (NG) is one of the most promising alternative fossil fuel that has been widely investigated in internal combustion (IC) engines. It is expected that global consumption of NG from 2015 to 2040 will rise 1.4% annually, accounting for the largest increase in world primary energy consumption. In this chapter, a review of the performance of NG-fuelled internal combustion engines, exhaust emissions produced from the combustion of natural gas engines and aftertreatment systems used to control those emissions is performed. In addition to the reduction of carbon dioxide (CO₂) from NG fuelling, lower levels of unburnt hydrocarbons (HC) and particulate matter emissions (PM) than conventional petrol and diesel engines have also been reported. However, they tend to produce higher nitrogen oxide (NO_x) and methane (CH₄) emissions which are difficult to oxidise, particularly at engine operation at stoichiometric conditions. On the other hand, the slow flame speed of NG is a major problem under lean-burn operation as it increases cycle-to-cycle variations, significantly compromising engine efficiency. The addition of hydrogen enhances the combustion of NG in addition to improving engine stability and reducing exhaust emissions. The difference in combustion, emission characteristics and aftertreatment systems of stoichiometric, lean-burn and hydrogen-enriched natural gas engines is outlined.

Keywords Natural gas engines • Lean-burn • Stoichiometric • Emissions
Compression-ignition • Catalyst

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13.1 Introduction

In recent years, there has been a growing concern regarding environmental pollution despite the advances in technology, with the transport sector being one of the major contributors of emitted pollutants and greenhouse gases. Emissions such as carbon dioxide (CO₂), unburnt hydrocarbons (HC), oxides of nitrogen (NO_x) and particulate matter emissions (PM) are all produced from the combustion of fossil fuel. Their adverse impact on climate change and human health has led to the introduction of increasingly stringent regulations that restrict the emission limits of automobiles. Accordingly, vehicle industries are continuously researching and rapidly developing emission control technologies that not only meet the rigorous emission standards introduced worldwide such as that set by the Environmental Protection Agency (EPA), and the EURO 6 standards, but also to satisfy consumer demands by delivering lower fuel consumption without compromising vehicle power or drivability.

Despite the environmental deterioration and global warming effect caused by the burning of fossil fuels, their use is projected to account for 77% of energy utilisation in 2040 (Fig. 13.1) (Eia.gov 2018). The use of gaseous and alternative fuels in internal combustion engines has therefore seen an increased interest in the last decade as they emit lower levels of exhaust emissions. Natural gas could play a leading role in the world’s transition to a cleaner energy. It is currently the third primary energy fuel globally and the only fossil fuel whose share of primary energy consumption is projected to grow with NG consumption increasing by 1.4% per year (Eia.gov 2018; World energy resources 2016).

The increased interest in NG is also due to the abundant proved reserves and increased production of NG, as shown in Fig. 13.2 making it a strong competitor to liquid fuels. Globally, there were 186.6 thousand cubic metres (tcm) of proven NG reserves in 2016, an increase of 19.2% from 2004 levels, which is sufficient to meet

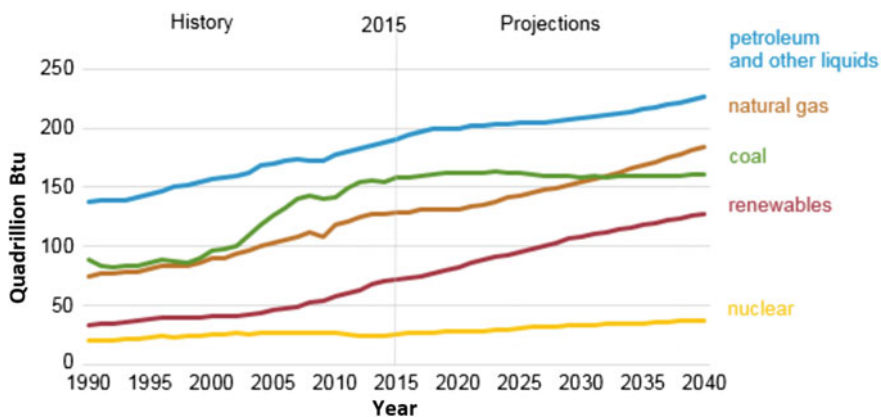


Fig. 13.1 World energy consumption by energy source (Eia.gov 2018)

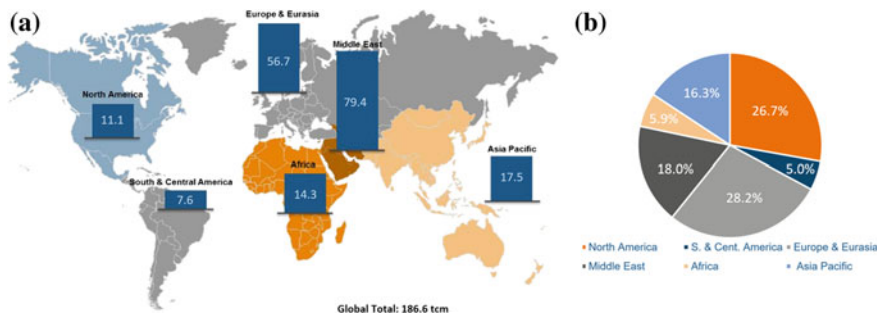


Fig. 13.2 **a** Global natural gas reserves (tcm), **b** Regional production share of natural gas
 Reproduced from BP statistical review of world energy (2017), World energy resources (2016)

Table 13.1 European emission standards for heavy-duty gas engines

Emission limits (g kWh ⁻¹)	Euro 5	Euro 6
CO	4.0	4.0
NO _x	2.0	0.46
NMHC	0.55	0.16
CH ₄	1.1	0.5
PM	0.03	0.01
Test cycle	European transient cycle	World harmonised transient cycle

more than 50 years of current global production of NG. By region, Middle-East leads the proved reserves followed by Europe with 30% of the total reserve shares while Europe has the highest global production shares commanding up to 28.2%. Low-carbon economy maps are set out worldwide. For instance, the European Commission set out a low-carbon economy roadmap that aims to cut greenhouse gas emissions in the transport sector over 60% by 2050 from 1990 levels (Communication from the Commission to the European Parliament 2011) and using NG as vehicle fuel can help meet this aim. The Euro 5 and Euro 6 emissions standards for diesel and gas engines studied on a transient test cycle are detailed in Table 13.1. With the introduction of the new Euro 6 heavy-duty emission standards, emissions of NO_x were significantly reduced by 77% from Euro 5 levels. Non-methane HCs were reduced by 71%, while methane emission from NG engines was reduced by 55% and as NG vehicles are required to meet both limits, methane emission control aftertreatment devices will be needed. In addition, the particle mass limit was reduced by 67% in the new Euro 6 emission standard which also introduced a particle number limit for the first time (not applicable for gas-fuelled engines).

These worldwide regulations will no doubt present a challenge for vehicle manufacturers to meet and will lead to the introduction of new engine technologies and aftertreatment systems or a combination of the two to guarantee the lowest

emissions, even under the most severe driving conditions. In the following sections, engine combustion and performance of natural gas in spark-ignition (bi-fuel) and compression-ignition (dual-fuel) engines are reviewed. In addition, an analysis of the exhaust products emitted from these engines and the various engine technologies and aftertreatment systems currently used to control them are described.

13.2 Natural Gas in Spark-Ignition (SI) Engines

13.2.1 Combustion of Natural Gas SI Engines

The advantage of natural gas as a vehicular fuel is that it can be utilised in both spark-ignition and compression-ignition engines. The typical combustion and physical properties of natural gas, gasoline and diesel fuels are outlined in Table 13.2. The majority of natural gas vehicles currently in use are retrofitted or converted from gasoline spark-ignition engines by adding a NG storage, supply and injection system, hence retaining the capability of being switched back to gasoline fuel (Chen et al. 2018). Although the fuel energy content in terms of mass, indicated by the lower heating value (LHV), of natural gas is higher than that of gasoline (49.5 MJ/kg for NG compared to 44.5 MJ/kg for gasoline), the engines suffer power reductions in the magnitude of 10–15% (Chen et al. 2018). This is attributed to several reasons. The volumetric heating value (VHV) of the natural gas–air mixture, which determines the amount of heat converted into mechanical work in the engine cylinder, is about 12% lower than that of gasoline–air mixture (Chen et al. 2018). In addition, the comparatively lower density of natural gas as compared to liquid fuels results in lower volumetric efficiencies (10–15% lower) as natural gas replaces a larger volume of air in the intake manifold upon injection. This limits the amount of air that can be induced into the combustion chamber and consequently less fuel is burnt leading to a reduction in power output (Korakianitis et al. 2011; Evans and Blaszczyk 1997).

Moreover, methane has a slower flame propagation speed as compared to gasoline under typical cylinder charge temperatures and pressures which extends the ignition delay time of the fuel–air mixture (Korakianitis et al. 2011; Thurnheer et al. 2009). Therefore, very advanced spark timing is employed in NG-fuelled engines which can be up to 10 CAD earlier before top dead centre (BTDC) compared to gasoline operation (Thurnheer et al. 2009). This further reduces the total power produced per engine cycle as the pre-ignited charge is working against the piston during the compression stroke. In addition, natural gas SI engines have comparatively lower thermal efficiencies to that of gasoline engines due to the relatively slower burning velocity of natural gas which reduces combustion temperatures. Therefore, gasoline engines that are converted to run on NG must be modified in order to compensate for the power loss caused by NG fuel. Engines fuelled with natural gas can run on higher compression ratios, which in combination

Table 13.2 Typical physiochemical properties of natural gas, gasoline and diesel fuels (Kakaei and Paykani 2013)

Fuel properties	Natural gas	Gasoline	Diesel
Low heating value (MJ/kg)	48.6	43.5	42.5
Heating value of stoichiometric mixture (MJ/kg)	2.67	2.78	2.79
Cetane number	–	13–17	52.1
Octane number	130	85–95	–
Auto-ignition temperature (°C)	650	310	180–220
Adiabatic flame temperature (°C)	1890	2150	2054
Stoichiometric air–fuel ratio (kg/kg)	17.2	14.56	14.3
Flame propagation speed (m/s)	0.41	0.5	–
Flammability limit in air (vol.% in air)	5.3–15	1.4–7.6	1–6
Carbon content (%)	75	85.5	87
Hydrogen content (%)	25	12–15	16–33

with forced induction (turbocharging or supercharging) allows for increase in thermal efficiency and power output by up to 50% compared to engines that are fuelled with gasoline (Cho and He 2007). This is because the octane number of natural gas, which is defined as a measure of fuel's resistance to auto-ignition, is higher than gasoline's (120 for methane and 95 for gasoline). Fuel with high octane number is essential for SI engines in order to avoid engine knocking, which can lead to engine damage if severe. In most applications to date, the method adopted in introducing NG to the engine is through port fuel injection into the intake manifold (Korakianitis et al. 2011). However, the engine suffers a loss in volumetric efficiency due to the low density of natural gas as discussed earlier. Direct injection of natural gas into the combustion chamber after the air induction avoids the loss in volumetric efficiency associated with port fuel injection as there is no air displacement occurs in the intake manifold (Sevik et al. 2016). Moreover, the fuel-lean operating limit of natural gas engines can be extended with the adoption of direct injection with lower cycle-to-cycle variations resulted as compared to port fuel injection (coefficient of variation in indicated mean effective pressure is about 5% lower) (Korakianitis et al. 2011). This is due to an increase in charged motion as a result of the higher in-cylinder pressures caused by direct injection of natural gas, in addition to the locally fuel-rich mixtures near the spark plug which accelerates flame propagation. However, this results in an increase in combustion temperatures which favours NO_x formation.

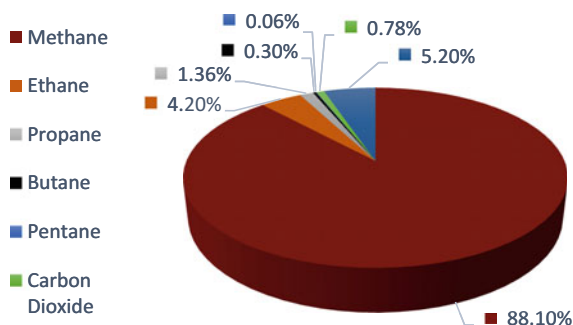
13.2.2 Exhaust Emissions from Natural Gas SI Engines

Natural gas is regarded as a cleaner form of energy compared to liquid fossil fuels as it emits comparatively lower CO_2 levels per unit energy during combustion (by

20–30%) than coal or petroleum fuels (Kakaee and Paykani 2013; Bielaczyc et al. 2016; Semin and Bakar 2008). This is mainly due to the composition of natural gas with methane being its main constituent (typically 70–90%), leading to a low C/H ratio (1/4). A detailed composition of natural gas is given in Fig. 13.3. In addition, CO and non-methane hydrocarbon emissions produced from natural gas engines are generally lower than naturally aspirated gasoline engines (Kakaee and Paykani 2013; Korakianitis et al. 2011). The majority of CO emissions from gasoline engines are produced during cold start due to poor air–fuel mixing and incomplete atomisation and vaporisation of the liquid fuel (Jahirul et al. 2010). Conversely, the gaseous state of NG leads to a more homogenous air–fuel mixture inside the engine’s cylinder especially during cold start conditions, resulting in a more efficient combustion and significantly lower CO emissions (between 50 and 90% depending on engine calibration) (Sevik et al. 2016). The lower equivalence ratio adopted by natural gas engines results in a further reduction in CO concentrations and unburned non-methane hydrocarbon levels (by up to 55% less HC) (Semin and Bakar 2008). An opposite trend is seen at extremely low equivalence ratios because of deterioration in combustion quality. Moreover, the wall-wetting effect on intake manifold and cylinder liner is avoided due to the gaseous state of natural gas which further reduces non-methane hydrocarbon levels and reduces fuel consumption (Cho and He 2007). The comparatively higher compression ratios and advanced ignition timing adopted by natural gas-fuelled engines lead to higher NO_x emissions (by around 33%) than that of conventional gasoline engines (Aslam et al. 2006). This is due to the relatively higher in-cylinder pressure and temperature resulted which favours the formation of NO_x . The increase in NO_x emissions can be mitigated by retarding the spark timing; however, it will be at the expense of higher brake-specific fuel consumption. Therefore, a compromise among engine performance, exhaust emissions and fuel consumption have to be considered when deciding on the optimal engine operating parameters.

A major concern regarding NG engines is their methane emission as they produce large concentrations of methane gas. Hydrocarbon emissions in the USA are regulated in terms of their reactivity in the photochemical smog cycle, and although methane gas has no role in photochemistry or smog formation, it is considered a powerful greenhouse gas (global warming potential of methane is more than 20

Fig. 13.3 Detailed composition of natural gas
Reproduced from Kakaee and Paykani (2013)



times higher than CO₂ over 100 years) (US 2018). This is primarily caused by the slow flame propagation of natural gas which induces incomplete combustion and hence large amounts of unburnt natural gas escape through the combustion chamber (Ehsan 2006). This phenomenon is typical of engines converted to run on natural gas but is not optimally modified in terms of engine calibration (e.g. spark timing, injection timing) (Chen et al. 2018; Reynolds and Evans 2004). In addition, methane's reactivity is comparatively slower than most other longer-chain hydrocarbons, which makes it difficult to be removed in a typical three-way catalyst. With regard to PM, NG engines produce very low levels compared to gasoline and diesel engines (up to 95% less) as it does not contain any aromatic compounds such as benzene and has less dissolved impurities that contribute to the formation of PM (Semin and Bakar 2008). Hence, vehicles running on natural gas fuel should fulfil the emission limits of PM set out in the Euro 6 regulations. However, a new study has found that exhaust particles emitted from natural gas engines were observed to have peak diameters below 10 nm (2–5 nm range) and they were higher in number than particles with a peak diameters larger than 23 (Alanen et al. 2015). Therefore, it is important to take into consideration the peak diameter size range of 1–5 nm in order to get the full picture of natural gas emitted PM.

13.3 Current NG Emission Control Technologies in SI Engines

13.3.1 *Lean-Burn Versus Stoichiometric Natural Gas Engines*

The control of exhaust gases emitted from natural gas internal combustion engines can be achieved through the careful control of the relative air–fuel ratio, lambda (λ). Engines that run on natural gas as fuel are generally of two types, lean-burn ($\lambda > 1$) and the more common stoichiometric ($\lambda = 1$) combustion engines. Combustion of lean-burn NG engines can achieve lower concentrations of NO_x pollutants and a better fuel economy than stoichiometric engines, but this is achieved at the expense of higher HC and CO emissions (Karavalakis et al. 2016). The control of air–fuel ratio is very important as it immensely influences engine performance and subsequently exhausts gas emissions. While running on fuel-rich mixtures results in lower NO_x concentrations, significantly higher CO and unburnt HC emissions are produced due to the insufficient amount of oxygen available to oxidise the fuel. Moreover, rich engine running condition is also undesirable due to the significant fuel penalty it imposes. On the other hand, stoichiometric NG engines operate with $\lambda = 1$ or slightly less than 1. These engines produce significantly low levels of non-methane hydrocarbons and CO emissions with some cost in fuel economy and relatively high NO_x emissions. A combination of exhaust gas recirculation (EGR) and a three-way catalytic converter is used to mitigate and control exhaust

emissions from stoichiometric NG engines (Karavalakis et al. 2016; Hajbabaei et al. 2013; Einewall et al. 2005; Saanum et al. 2007).

In a lean-burn engine, the air–fuel ratio is increased beyond $\lambda = 1.2$ in order to suppress NO_x emissions (Saanum et al. 2007). However, there is a lean operating limit beyond which acceptable engine performance can be maintained as the cycle-to-cycle variations increase significantly with leaner mixtures. Conversely, the optimal air–fuel ratio for HC emissions is reportedly between $\lambda = 1.05$ – 1.2 as sufficient oxygen concentration is available to oxidise the unburnt HCs, but NO_x emissions at this range (1.0–1.1) are at its highest (Einewall et al. 2005; Saanum et al. 2007; Cho and He 2008). Still, HC emissions are easier to treat in the exhaust of a lean-burn natural gas as opposed to NO_x emissions by using an oxidation catalyst. The excess of oxygen available with increasing lambda can enhance the combustion of the air–fuel mixture leading to a complete combustion of unburned HC and CO emissions. At the same time, increasing the air–fuel ratio increases the time required for the initial flame development and hinders flame propagation through the cylinder charge, causing longer ignition delay (Cho and He 2007). This results in slower heat release rate, slow combustion velocity and deterioration in combustion quality compared to that under stoichiometric conditions, thereby increasing heat transfer losses to the cylinder walls. This has an adverse effect on HC and CO emissions, as the combustion temperature in the cylinder drops hence the improvement in oxidation of HC and CO with excess of oxygen is unrealised. Even though the lean-burn engines are successful at reducing NO_x emissions, the technology is not practicable in real-life conditions as it is difficult to maintain a high air–fuel ratio at transient situations (like acceleration and low engine speed). In addition, as exhaust emissions are very sensitive to small changes in lambda value, the accuracy of the air–fuel control system is critical. The control of air–fuel ratio in a natural gas engine can be achieved using a wideband oxygen sensor. Due to its precise determination of residual oxygen content, the engine control unit can efficiently optimise fuel delivery and ignition timing for better fuel economy and emission concentrations (Heck and Farrauto 2001; Alkemade and Schumann 2006).

13.3.2 Exhaust Gas Recirculation with Hydrogen Enrichment

Exhaust gas recirculation (EGR) is an engine strategy commonly adopted by gasoline and diesel engines for the reduction of NO_x emissions. By employing EGR, a portion of the engine's exhaust gas is recirculated back to the cylinder which decreases the amount of unburned fuel and oxygen concentration in the combustion chamber, thus resulting in better fuel economy. The recirculated gas displaces some of the inlet air resulting in a dilution of the inlet charge and an increase in heat capacity which lowers the combustion temperature (Abdelaal and Hegab 2012). The use of EGR in lean-burn natural gas engines can therefore

achieve very low levels of NO_x emissions, as along with the slow flame propagation of natural gas, reduction in oxygen concentration and in-cylinder temperatures slow down the combustion of the charge mixture even further. This, however, results in higher HC, CO and PM emissions due to the colder combustion and the insufficient oxygen available to oxidise these species. The deterioration in combustion quality resulted from the EGR strategy can be ameliorated by the addition of H_2 . The high flame speed of H_2 has an opposite effect as it speeds up combustion of the mixture charge resulting in increased combustion temperature and more complete oxidation of HC and CO emissions. The combination of moderate EGR substitution with hydrogen in NG engines can achieve significantly lower engine-out emissions. For a 15% H_2 –85% NG fuel mixture, increasing EGR substitution reduced NO_x emissions significantly as compared to the baseline NG combustion. On the other hand, HC emissions reduced with increasing EGR up to an EGR substitution of 14% but remained higher than baseline NG engine emissions (Dimopoulos et al. 2008).

13.3.3 Spark Timing

Modifying the spark timing can greatly influence the combustion process and engine-out emissions. In a natural gas-fuelled engine, the fuel mixture does not completely burn due to the slow flame speed of natural gas and therefore a spark advance strategy must be implemented. The advance in spark timing employed in NG engines can be between 2 and 10 CAD earlier BTDC compared to stoichiometric gasoline-fuelled engines (Evans and Blaszczyk 1997; Ji and Wang 2009). For leaner air–fuel mixtures, the spark energy transmitted to the cylinder charge in the vicinity of the spark plug is reduced at spark discharge which increases the time required for initial flame development (Cho and He 2009). In addition, the slow burning velocity of natural gas especially at lean mixtures results in an increase in combustion duration due to the low in-cylinder temperature causing a delay in ignition timing. Therefore, lean-burn NG engines require much-advanced spark timing BTDC in order to offset the ignition delay resulted with lean mixtures; however, this can also lead to knock (Cho and He 2007). The optimal MBT spark advance for better fuel economy and exhaust emissions depends on the variation of natural gas composition and the air–fuel ratio where more spark advance is needed with leaner mixtures due to the slower flame speeds (Evans and Blaszczyk 1997; Cho and He 2007). Early spark timing increases THC emissions as the fuel mixture is ignited earlier and the combustion duration is decreased. As the combustion duration is reduced, the temperature of the burned gas is lowered during the expansion stroke which further impedes the oxidation of the unburned fuel. Similarly, CO emissions follow the same trend with advancing the spark timing as the homogeneity of the air–fuel mixture is decreased due to the less mixing time. This induces incomplete combustion of the fuel in the fuel-rich or fuel-lean regions, and thus, CO emissions increase. On the other hand, NO_x emissions have a decreasing trend with early spark timings due to the lower combustion temperatures and lower burned gas temperatures resulted.

13.3.4 Hydrogen-Enriched Natural Gas Engines

The exhaust emissions of CO, unburned HC and CH₄ resulted from the slow burning rate of natural gas can be further mitigated by the addition of another fuel with a higher flame speed velocity. The combustion characteristics of natural gas engines can be enhanced by the addition of hydrogen in the intake charge (Alrazen and Ahmad 2018). The addition of small amounts of hydrogen concentrations in natural gas-fuelled combustion engines can lead to significant improvements in term of combustion stability, engine performance and levels of exhaust emissions. Table 13.3 details the combustion properties of hydrogen.

The higher burning rate of hydrogen as compared to natural gas leads to an increase in cylinder temperatures as the air–fuel mixture can be burnt more rapidly speeding up the combustion process (Açıkgöz et al. 2015). This is partially due to the increase in concentrations of H and OH radicals that increase combustion reactivity and lead to a faster flame propagation through the cylinder charge and hence more fuel is burnt (Chen et al. 2018; Korakianitis et al. 2011). This improves engine in-cylinder conditions which reduces emissions of HC and CO due to the more complete combustion. Compared to baseline natural gas engines, hydrogen-fuelled engines can have lower CO emissions depending on engine running conditions. With stoichiometric air–fuel ratio, the addition of H₂ leads to an increase in CO emissions while lean operating engines are expected to produce zero CO concentrations (Alrazen and Ahmad 2018; Açıkgöz et al. 2015). The higher in-cylinder temperatures resulted from the faster burn rate of the fuel mixture with the addition of hydrogen lead to a reduction in unburnt THC, although methane emissions remain high due to a big valve overlap angle (Alrazen and Ahmad 2018). The low overall carbon content of hydrogen-enriched natural gas along with the shorter quenching distance (distance between the position of flame extinguishment and the cylinder wall) induced by hydrogen addition is another reason for the reduction in HC emissions (Alrazen and Ahmad 2018; Açıkgöz et al. 2015). However, hydrogen-enriched natural gas engines produce higher NO_x emissions due to increase in combustion temperature (Chen et al. 2018). The combination of hydrogen addition with lean combustion and optimal spark timing in a natural gas engine can reduce NO_x exhaust emissions significantly without compromise in engine performance. Ultra-lean combustion can be attained with the addition of H₂

Table 13.3 Combustion properties of hydrogen (Mehra et al. 2017)

Fuel	H ₂
Flammability limit in air (%vol.)	4–75
Flammability limits (λ)	0.14–10
Auto-ignition temperature (°C)	585
Octane number	140
Stoichiometric air–fuel ratio	34.2
Laminar burning velocity (m/s)	2.9
Diffusivity in air cm ³ /s	0.63

in lean-burn NG engines due to the favourable combustion characteristics of H_2 , such as its wide lean flammability limit and fast flame propagation (Lee et al. 2014). Hydrogen enrichment enhances the lean-burn capability of the NG engine and allows for more retarded ignition timing due to the shorter combustion duration, hence reducing the work done on the charge by the piston during compression (Chen et al. 2018). In addition, the deterioration in coefficient of variation (COV) of indicated mean effective pressure (IMEP) resulted from lean-burn operation is improved with H_2 addition because of the more volatile fuel mixture and enhancement in combustion stability.

13.3.5 Aftertreatment System

As mentioned previously, lean-burn and stoichiometric combustion are the most common technologies used for the best engine performance and emission control in NG engines. However, these technologies alone cannot effectively reduce emissions to the levels acceptable to the Euro 6 emission standard, and thus, natural gas vehicles are equipped with exhaust aftertreatment technologies. In a stoichiometric NG engine (air/fuel ratio, $\lambda = 1$), the abatement of methane (CH_4) and other engine exhaust emissions (CO, NMHC, NO_x) is achieved through a three-way catalyst (TWC) technology adapted from a gasoline TWC (Karavalakis et al. 2016). Currently, TWC technologies are very efficient in reducing exhaust emissions; however, they require a stoichiometric mixture in order to work effectively which induces drawbacks such as higher heat losses and pumping work at low-to-medium engine loads. Thus, most stoichiometric NG engines are equipped with a water-cooled EGR in order to dilute the stoichiometric mixture, allowing for a better fuel economy (i.e. lower pumping losses) and reduced emissions with combination of a TWC as compared to the lean-burn engines (Karavalakis et al. 2016; Einewall et al. 2005). The emission level of NO_x and CO can be reduced by 10–30 and 360–700 times, respectively, with the use of the combined technology as compared to lean-burn combustion (Mehra et al. 2017). Careful control of the air–fuel ratio is, however, critical for the efficient operation of the TWC as the lambda window for an acceptable trade-off between CO oxidation and NO_x reduction is very narrow (± 0.01) (Einewall et al. 2005).

In addition, despite the very low HC concentrations emitted from natural gas engines as compared to gasoline engines, methane emissions remain a considerable issue. The majority of HC emissions produced by NG engines are composed of methane. As methane presents high stability of the C–H bond, it is one of the most unreactive hydrocarbons and is difficult to oxidise having a higher light-off temperature as compared to the longer-chain hydrocarbons. Therefore, platinum-group metals (PGMs), in particular palladium (Pd) and rhodium (Rh), are added to the TWC composition in order to enhance the efficiency of CH_4 oxidation and meet end of life THC regulations (Raj 2016). When operating in stoichiometric conditions, a Pd–Rh catalyst with high total PGM loadings ($>200 \text{ g ft}^{-3}$) can effectively remove

methane emissions. A stoichiometric air–fuel ratio is required for the TWC to simultaneously remove CO, NO and THC emissions. The performance of a bimetallic Pd–Rh catalyst on the exhaust of a conventional gasoline engine and a stoichiometric NG engine is illustrated in Fig. 13.4 as a function of engine lambda. The catalyst exhibits a similar trend overall for NO_x and CO conversions in both engine cases. At stoichiometric conditions, the conversion efficiency of CO is close to 100% while higher NO_x conversions can be achieved with the NG engine as they produce much lower engine-output NO_x than their gasoline counterpart. In addition, HC conversion is significantly improved (95% efficiency) at stoichiometric conditions. The low HC conversion efficiency in the NG engine case in the lean condition is attributed to the poor combustion of NG at excess air, and therefore, the catalyst is exposed to high amounts of unburnt CH₄ which is difficult to oxidise (Karavalakis et al. 2016).

In a lean-burn NG engine, while the control of non-methane HC and CO emissions can be achieved with the use of an oxidation catalyst, NO_x emissions and methane are more difficult to remove in lean conditions. Therefore, catalytic aftertreatment systems such as selective catalytic reduction (SCR) are necessary for lean-burn natural gas engines in order to comply with the Euro 6 emission standards. However, this is a rather complex and costly system and hence vehicle manufacturers could potentially favour the stoichiometric engine with TWC despite its inferior engine performance (Cho and He 2007). The coupling of an NH₃–SCR (selective catalytic reduction with ammonia as reducing agent) with an oxidation catalyst based on palladium and platinum oxides has shown a great potential in the abatement of exhaust emissions produced from lean-burn NG heavy-duty vehicles (Adouane et al. 2013). The combined catalytic performance was able to achieve 40% CH₄ conversion at 415 °C while CO and NO_x conversions reached 99 and 70%, respectively (Adouane et al. 2013). No aftertreatment systems are required for PM emissions for both lean-burn and stoichiometric NG engines due to the almost homogeneous combustion of the air–gas mixture and the absence of large hydrocarbon chains and aromatics in the fuel (Karavalakis et al. 2016).

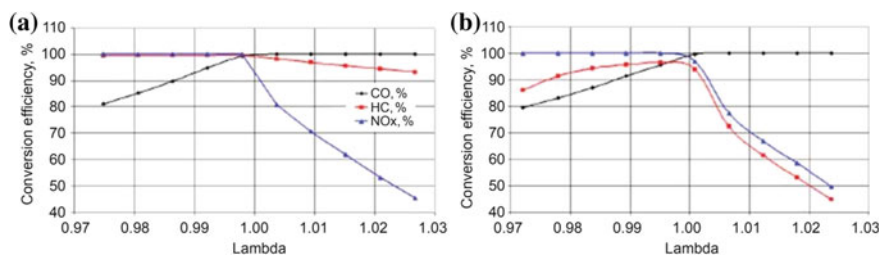


Fig. 13.4 Performance of an aged Pd:Rh TWC at 450 °C as a function of lambda on: **a** Stoichiometric Gasoline engine, **b** Stoichiometric NG engine (Raj 2016)

13.4 Natural Gas in Compression-Ignition (CI) Engines

13.4.1 *Combustion and Performance of Dual-Fuel CI Engines*

The increasing concern regarding exhaust emissions produced from diesel engines has led to advancements in the utilisation of alternative fuels in CI engines. Natural gas has proved to be a very promising and attractive alternative fuel for both environmental and economical reasons. As compression-ignition engines employ high compression ratios, the high octane number of methane warrants its use in CI engines without experiencing the knock phenomenon (Abdelaal and Hegab 2012). However, the high auto-ignition temperature of natural gas limits its use as a 100% feasible replacement for diesel fuel in compression-ignition engines. An important fuel property for CI engines is the cetane number, which is a measure of a fuel ignition delay period; the higher the cetane number, the shorter time required for the fuel combustion process to be started. Methane, which is the main component of natural gas, has a very low cetane number compared to diesel fuel (40–55 for diesel while negligible for methane) as shown in Table 13.2, which significantly affects its ignition quality. Thus, the employment of NG fuel in CI engines requires a source of controlled ignition which aids in initiating natural gas combustion in the cylinder. This is provided by injecting small amounts of ‘pilot’ fuel with a high cetane number into the cylinder, where it blends with a premixed natural gas/air charge. This mode of operating natural gas with a pilot fuel (typically diesel or biodiesel) is commonly known as dual-fuelling in compression-ignition engines.

In the dual-fuel mode, direct injection of diesel fuel into the combustion chamber is employed late in the compression stroke, while natural gas is introduced into the intake manifold to mix uniformly with air before being introduced into the cylinder (Gogolev and Wallace 2018; Khan et al. 2015; Bhandari et al. 2005; Wei and Geng 2016). In SI engines, the low flame speed of natural gas leads to increased combustion duration as there is only one source of ignition (spark plug) and hence the flame propagates from a single point outwards through the charge (Korakianitis et al. 2011). In dual-fuel CI engines, the problem is less apparent. Dual-fuel mode combustion is characterised by two different combustion stages: non-premixed combustion of the pilot diesel fuel followed by combustion of natural gas–air mixture (Abdelaal and Hegab 2012). After an initial ignition delay, combustion of the pilot diesel fuel takes place first which then ignites the natural gas, producing multiple ignition points throughout the chamber. This instigates flame propagation, resulting in a relatively faster burn rate producing most of the energy released during combustion. It is possible to achieve more than 80% reduction of diesel fuel with the dual-fuel mode as compared to conventional diesel engines with the pilot diesel fuel accounting for 2–3% of the total injected fuel energy in some studies (Wei and Geng 2016). A schematic diagram of the dual-fuel mode is illustrated in Fig. 13.5.

With regard to combustion performance of dual-fuel natural gas CI engines, peak in-cylinder pressure and pressure rise rate for the dual-fuel are lower than

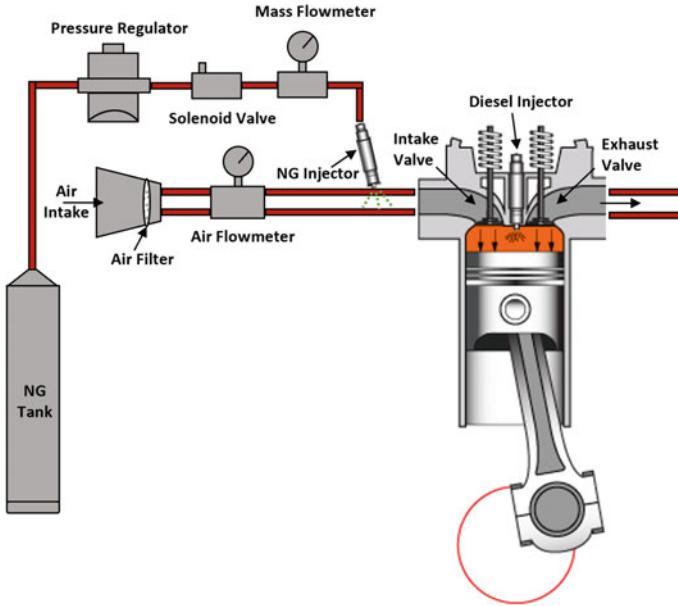


Fig. 13.5 Natural gas/diesel dual-fuel system schematic diagram

conventional diesel engines during the initial combustion period (Sun et al. 2015), while cycle-to-cycle variations are of similar tendencies (COV of IMEP of 1%) (Korakianitis et al. 2011). This is attributed to the slower rate of natural gas combustion and longer ignition delay of the dual-fuel which shifts the combustion phase further into the expansion stroke, thus reducing peak in-cylinder pressure and pressure rise rate. As natural gas is port-injected, the dual-fuel mode suffers from significantly lower engine power output as opposed to conventional diesel engines (Gogolev and Wallace 2018). Moreover, combustion efficiency of premixed flame is very sensitive to the air–fuel ratio where it is optimal around stoichiometric conditions. However, in dual-fuel mode, premixed combustion of natural gas–air mixture suffers from very lean mixture which deteriorates combustion efficiency reducing peak value of in-cylinder pressure (Abdelaal and Hegab 2012). Increasing the quantity of the pilot diesel fuel and advancing the injection timing can help in enhancing combustion of the dual-fuel due to the higher ignition source supplied to the engine cylinder and the increase in energy released during compression stroke with advanced injection. This results in an increase in heat release rate and consequently higher peak in-cylinder temperature and pressure. An alternative method of injecting natural gas into the engine cylinder is through the High-Pressure Direct Injection (HPDI) technology. In the HPDI mode, both the pilot diesel and natural gas fuels are directly injected into the combustion chamber, thus avoiding knock limitations and subsequent power losses resulted from the port injection in the dual-fuel mode (Gogolev and Wallace 2018; Wei and Geng 2016). A small quantity

of pilot diesel is initially injected into the combustion chamber which then auto-ignites under compression providing the ignition source for NG combustion. This is shortly followed by direct injection of natural gas which is then ignited by the diesel fuel's diffusion flame and burns in a predominantly non-premixed combustion event (Gogolev and Wallace 2018; Wei and Geng 2016). This mode of injecting natural gas achieves similar thermal efficiencies and power output to that of an equivalently sized diesel engine while providing better fuel economy. However, the dual-fuel injector system is more complicated as it requires a special concentric needle operating at high pressures in order to inject the two fuels. As such, combustion and emission characteristics of the dual-fuel mode will be the point of focus in this chapter.

13.4.2 Exhaust Emissions from Dual-Fuel Combustion

Depending on engine running conditions, dual-fuelling in CI engines can result in significant reduction in exhaust NO_x emissions with respect to conventional diesel engines (Korakianitis et al. 2011). In a dual-fuel engine, the production of NO_x emissions is mainly due to the combustion of the non-premixed pilot diesel fuel. As the quantity of the pilot diesel fuel is considerably small, NO_x levels are significantly lower than those of conventional diesel engines. Hence, as the combustion of natural gas occurs late in the expansion stroke, the amount of NO_x emitted from dual-fuel CI engines greatly depends on the quality and quantity of the pilot fuel (Korakianitis et al. 2011). In addition, the low flame speed of natural gas combined with the very lean mixture in the dual-fuel mode reduces in-cylinder combustion temperatures and suppresses NO_x formation. Alternatively, hydrocarbon emissions resulted from incomplete combustion of the dual-fuel engine are substantially higher than in conventional diesel engines especially at low engine loads due to low charge temperatures. While at high engine loads unburned HC concentrations decrease due to the higher in-cylinder temperatures induced by the more complete combustion, concentrations remain much higher than that of normal diesel engines. This is primarily due to the very lean air-fuel ratios adopted in CI engines which, along with the slow flame speed of NG, hinder flame propagation through the mixture charge (Korakianitis et al. 2011; Sun et al. 2015). The bulk of the HC emissions consist of unburned natural gas that might have got trapped in the crevices, survived the combustion process and escaped to the exhaust. Decreasing the percentage of natural gas substitution leads to a rapid decrease in HC concentrations. As the pilot diesel fuel quantity increases, spray atomisation characteristic is enhanced and a higher proportion of diesel fuel is ignited, leading to a more complete combustion of the air-fuel mixture. CO emissions from dual-fuel CI engines follow a similar trend to HC emissions. Remarkably higher concentrations of CO are emitted from dual-fuel combustion as compared to diesel engines. The development of flame extinct regions caused by deterioration in flame propagation favours the CO formation mechanism due to the incomplete oxidation of the

premixed natural gas–air mixture (Sun et al. 2015). Particulate matter emissions are one of the major concerns of diesel engines and the use of natural gas with pilot fuel injection may well contribute in meeting PM regulations for diesel engines. Natural gas has lower carbon atoms than diesel and does not contain aromatic compounds such as benzene which contributes to the formation of PM. Hence, most of the PM emissions formed from dual-fuel engines resulted from the combustion of the pilot diesel fuel. However, the quantity of the pilot fuel is very small, which in addition to the more homogenous air–fuel mixture caused by the longer ignition delay results in lower soot formation (Sun et al. 2015). Therefore, dual-fuel mode produces very low levels of PM emissions compared to diesel engines (up to 95% less) (Semin and Bakar 2008).

13.5 Current NG Emission Control Technologies in CI Engines

13.5.1 Exhaust Gas Recirculation (EGR)

The use of EGR in dual-fuel engines can partially enhance the lower thermal efficiency and reduce the comparatively higher CO and unburned HC emissions depending on engine running conditions while resulting in even lower NO_x emissions (Abdelaal and Hegab 2012). By using EGR, the inlet charge is diluted as part of the exhaust replaces some of the inlet air which reduces oxygen levels while combustion temperature is reduced due to an increase in the heat capacity. These combined effects lead to reductions in NO_x levels. In addition, with the adoption of EGR, the unburned exhaust gas is recirculated back into the engine cylinder where it is expected to reburn in the following cycle. This results in lower levels of unburned HC and a subsequent reduction in CO emissions particularly at low engine loads, while higher thermal efficiencies are also realised. Increasing EGR percentages will lead to further reductions in HC emissions as larger amounts of unburned HCs are recirculated and reburned in the mixture. The slight increase in the intake charge temperature and the reburning of the HCs resulted with EGR application induces a more complete combustion of the fuel which results in CO emission reductions. At high engine loads, HC reduction with EGR is negligible due to the reduced oxygen levels in the combustion chamber which hinders the reburning of the unburned HCs. This also has an adverse effect on CO and PM emissions due to the insufficient O₂ available for CO oxidation and hence an increase in these emissions is seen at high loads (Abdelaal and Hegab 2012). Moreover, the in-cylinder peak pressure reduces substantially with higher EGR percentages as more O₂ is replaced by carbon dioxide and water vapour which hinders the combustion of the dual-fuel and increases ignition delay.

13.5.2 Pilot Fuel Quantity and Type

Evidently, the pilot fuel is the main source of ignition in a dual-fuel NG engine and hence the quality and type of pilot fuel used will greatly affect engine combustion performance. In the dual-fuel natural gas engines, the bulk of the exhaust emissions are produced from the ignition of the pilot fuel. As mentioned in Sect. 13.4.2, when the pilot fuel quantity is small, unburned HC emissions as well as CO emissions are comparatively higher than that of conventional diesel engines as the flame cannot propagate throughout the whole cylinder charge in the excessively lean mixture. Increasing the quantity of the pilot fuel increases the envelope size of the pilot fuel mixture and provides a greater multitude of ignition centres that require shorter flame travel which shortens ignition delay; hence, a larger volume of the charge is ignited (Imran et al. 2014; Namasivayam et al. 2010). Moreover, the unburned fuel is compressed to a higher temperature with larger pilot energy release which increases in-cylinder temperatures and enhances the oxidation of the fuel leading to a reduction in HC and CO concentrations (Liu et al. 2013). This effect is more evident at low engine loads, whereas at high loads pilot fuel quantity has little effect as the gaseous fuel concentration in the air charge is above the lean combustion limit which leads to faster flame propagation through the cylinder charge. On the other hand, NO_x emissions increase with increasing pilot fuel quantity due to the higher charge temperatures resulted (Abd Alla et al. 2000). Similarly, increasing the NG fuel concentration in the cylinder charge leads to higher NO_x concentrations as the size of the combustion zone increases significantly (Abd Alla et al. 2000). In addition, as PM emissions from dual-fuel NG engines are mainly formed during the diffusion combustion process of the pilot fuel, an increase in pilot fuel quantity will result in a subsequent increase in PM concentrations (Liu et al. 2013).

Several alternative fuels have been investigated as potential replacement to the conventional pilot diesel fuel in dual NG engines in order to reduce exhaust emissions of HC, CO and NO_x. Biodiesel fuels such as rapeseed oil methyl esters (RME) performance as a pilot fuel is reportedly like that of diesel with both engine performance and exhaust emissions showing very comparable trends (Imran et al. 2014; Nwafor 2000). Still, the use of RME as a pilot fuel for natural gas CI engines produced lower NO_x levels compared to diesel which is attributed to the higher cetane number of RME. The higher cetane number of RME as compared to diesel results in shorter ignition delay and thus less time available for premixed combustion leading to lower in-cylinder temperature and resulted NO_x emissions (Imran et al. 2014). Other biodiesel fuels have been well researched in the literature and have also shown similar trends in terms of their performance and emissions. This is due to the similar physical and combustion properties of biodiesel as compared to diesel fuel (Abd Alla et al. 2000). On the other hand, the use of dimethyl ethers (DME) as an alternative pilot fuel showed positive reductions in NO_x emissions due to the lower combustion temperatures resulted from the cooling effect upon injection of the gaseous DME fuel. In addition, the slower flame propagation coupled with the longer ignition delay of the DME pilot fuel as compared to liquid

fuel slows down the rate of combustion and thus produce lower NO_x levels. However, this also leads to higher HC and CO levels (Namasivayam et al. 2010). These results indicate that natural gas combustion is responsible for most of the combustion enthalpy in the dual-fuel mode and the pilot fuel only acts as an ignition source to initiate combustion.

13.5.3 Varying Pilot Fuel Injection Timing

The injection timing of the pilot fuel plays a major role in defining the combustion and emission characteristics of dual-fuel NG engines. Retarding the injection timing means that the combustion of the fuel mixture occurs later in the cycle and more fuel burns after TDC which decreases the peak cylinder pressure. As the pilot fuel combustion is delayed with retarding the injection timing, incomplete combustion of the fuel mixture occurs as the in-cylinder temperature is too low for the flame to propagate throughout the combustion chamber. This leads to the production of higher HC and CO emissions (Abd Alla et al. 2002). On the other hand, slightly advancing the injection timing leads to an earlier start of the combustion process and increases the peak cylinder pressure resulting in higher peak charge temperatures as more fuel is burned before TDC (Abd Alla et al. 2002). In addition, advance in the start of injection (SOI) timing leads to a longer ignition delay as the pilot diesel fuel is injected at lower cylinder temperatures which result in a reduction in unburned hydrocarbons. This is attributed to the fact that the longer ignition delay provided more time for diesel to mix with the surrounding natural gas–air mixture which results in a more homogenous charge in the cylinder. In addition, it allowed for a fuller spray penetration and development while creating a larger amount of air–fuel mixture prior to ignition which results in multiple ignition regions throughout the cylinder (Sahoo et al. 2009; Zhou et al. 2013). These multiple ignition regions lead to an increase in flame propagation resulting in higher burning rates and shorter combustion duration. As the burning rate of the larger premixed air–fuel region increased, CO unburned HC emission levels were reduced. However, an increase in NO_x emissions is resulted with advancing the injection timing due to the higher maximum charge temperature. When the injection timing is too advanced, misfire and partial oxidation may occur as the in-cylinder temperature is not sufficiently high enough to ignite the injected fuel. In addition, excessive ignition delay will cause the diesel–air mixture to be too lean due to over-mixing of the spray which deteriorates flame propagation and prolongs the start of combustion (Zhou et al. 2013). This results in lower in-cylinder temperature and heat release rate which induces incomplete combustion of the fuel, hence increasing HC and CO emissions while reducing NO_x emissions. The effect of injection timing on the characteristics of PM emissions is apparent with a significant increase in the number of particles with advancing the injection timing while the particle mass concentration exhibits a decreasing trend. The longer ignition delay period and the more homogenous air–fuel mixture formed with advancing the

injection timing increase the formation of smaller particles while the higher in-cylinder temperatures resulted enhance the oxidation process. Thus, this leads to a reduction in the particle mass concentration but an increase in the number of particles (Zhou et al. 2013).

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