



BRNO UNIVERSITY OF TECHNOLOGY

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

FACULTY OF MECHANICAL ENGINEERING

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ÚSTAV AUTOMOBILNÍHO A DOPRAVNÍHO INŽENÝRSTVÍ

CATALYTIC CONVERTER AND PARTICULATE FILTER FUNCTIONS ON DIESEL VEHICLES

FUNKCE KATALYZÁTORU A FILTRU PEVNÝCH ČÁSTIC U NAFTOVÝCH VOZIDEL

BACHELOR'S THESIS

BAKALÁŘSKÁ PRÁCE

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BRNO 2021

Assignment Bachelor's Thesis

Institut: Institute of Automotive Engineering
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Degree programm: Engineering
Branch: Fundamentals of Mechanical Engineering
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Academic year: 2020/21

As provided for by the Act No. 111/98 Coll. on higher education institutions and the BUT Study and Examination Regulations, the director of the Institute hereby assigns the following topic of Bachelor's Thesis:

Catalytic converter and particulate filter functions on diesel vehicles

Brief Description:

With increasing legislative requirements for emission control, ways are being sought to further eliminate these emissions. From the nature of the function of the catalyst, it is clear that it needs to be at operating temperature as soon as possible. The student first introduces the function and individual architectures and possibilities of catalysts and then introduces the possibilities of how the temperature can reach the working temperature as soon as possible.

Bachelor's Thesis goals:

Analysis of existing solutions, types and architecture
Heating and its requirements in relation to the size of the car / engine
Evaluation of various heating systems, pros and cons
Other potential solution concepts
Future outlook
The work will be in English

Recommended bibliography:

STONE, Richard. Introduction to internal combustion engines. 3rd edition. Warrendale, Pa.: Society of Automotive Engineers, 1999. 641 s. ISBN 0768004950.

Deadline for submission Bachelor's Thesis is given by the Schedule of the Academic year 2020/21

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ABSTRACT

This bachelor's thesis aims to present diesel emission-reduction systems to a broader public, uncovering the basic principles of diesel engine and mechanisms of emission-creation. Catalytic reduction and diesel particulate filter functions are then described, explaining the importance of operating temperature and methods it can be controlled. Finally, it discusses the possibilities of reducing the carbon footprint and complying with the upcoming EURO VII standard.

KEYWORDS

Diesel, emissions, treatment, diesel oxidation catalyst, diesel particulate filter, selective catalytic reduction, nitrous oxide trap, catalyst heating, phase change energy storage, chemical energy storage, DOC, DPF, SCR, NO_x trap.

ABSTRAKT

Tato bakalářská práce se zabývá představením dieselových emisně-redukčních systémů široké veřejnosti, odkrývá základní principy funkce dieselova motoru, mechanismy vzniku emisí a následně se věnuje jejich regulaci za pomoci katalytické redukce a filtru pevných částic. Odhaluje, proč je provozní teplota pro funkčnost těchto systémů klíčová a prezentuje možnosti, jak ji regulovat. V závěru pojednává o možnostech snížení uhlíkové stopy a vyhovění nadcházející emisní normě EURO VII.

KLÍČOVÁ SLOVA

Diesel, emise, úprava, dieselový oxidační katalyzátor, dieselový filtr pevných částic, selektivní katalytická redukce, zachytávač NO_x, výhřev katalyzátoru, úložiště energie se změnou skupenství, chemické úložiště energie, DOC, DPF, SCR, NO_x trap.

BIBLIOGRAPHIC CITATION

ŠIŠPERA, Adam. *Catalytic converter and particulate filter functions on diesel vehicles*. Brno, 2021. Available at: <https://www.vutbr.cz/studenti/zav-prace/detail/132878>. Bachelor's thesis. Brno University of Technology, Faculty of Mechanical Engineering, Institute of Automotive Engineering. 80 p. Supervisor Jiří Bazala.



AFFIDAVIT

I declare that this bachelor's thesis is my original work, created under the supervision of Ing. Jiří Bazala and using the literature listed in sources at the end of this thesis.

In Brno 21st of May 2021

.....

Adam Šišpera



ACKNOWLEDGEMENTS

I would like to thank my supervisor Ing. Jiří Bazala, for valuable notices and friendly behaviour throughout my work on this thesis. Also, I would like to thank my family for an outstanding level of support during my study efforts.

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INTRODUCTION

Despite the ever more growing share of alternatively powered vehicles, the successor for diesel internal combustion engine that could fulfil all society's requirements is distant. With the recent break out of battery technology, a non-trivial part of today's population is convinced that internal combustion engines are on their last stand. However, this is a very shallow statement, and even though the future is most probably electric, it might not come as soon as some may think.

"The European Green Deal is a response to these challenges. It is a new growth strategy that aims to transform the EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use." (The European Green Deal, 2019 [1])

As stated in this communication from the EU commission, the emphasis on reducing emissions is high and crucial for the future. However, even under these conditions, continuing the internal combustion engine development is essential to ensure that humanity has a viable propulsion system for fulfilling its transportation needs while alternative emission-free solutions are being developed.

Even though today's diesel engine is a very complex piece of machinery, the two most impactful components on its emissions are catalytic converter and diesel particulate filter (also known as DPF). This thesis will focus on describing their modern evolutions by providing insight into the detail of their function while also assessing their flaws.

These imperfections will then be used to discuss possible solutions for the next generation of diesel-powered vehicles.

1 DIESEL COMBUSTION PROCESS

For understanding the emission-reducing systems' function, it is essential to be familiar with the basics of the diesel internal combustion process and its products.

1.1 FUNDAMENTALS

Diesel fuel is commonly defined as a liquid petroleum hydrocarbon mixture with a boiling point between 150 and 360 °C with chemical summation formula $C_{11-14} H_{22-28}$. It is further specified by the EN 590 standard [3].

The process takes place in a cylindrical combustion chamber and operates on a two or four-stroke cycle. A Two-stroke cycle can usually be found in heavy-duty army or navy applications. This thesis will focus on the four-stroke cycle. Hence its more frequent use.

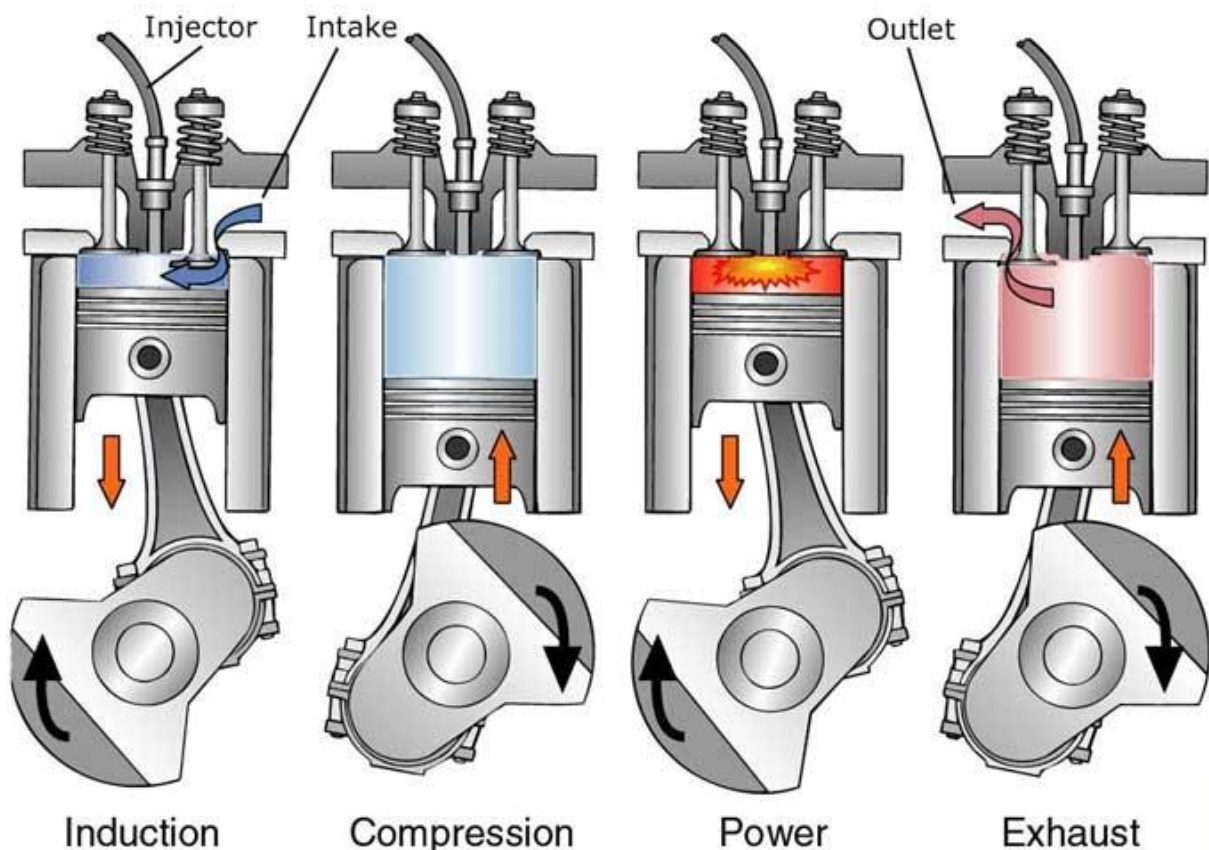


Figure 1. Crosssection of diesel engine [5]

1.2 INTAKE STROKE

Most of the designs in production use forced air induction, realized by a turbocharger. In specific applications, a supercharger or combination of both turbo and supercharger can be found. For this thesis, if not declared otherwise, a turbocharged diesel engine is considered to be standard.

Here, it would be advisable to note that as opposed to gasoline ICE, diesel ICE does not have any means of restricting airflow. Forced induction aside, the energy generated is regulated mainly by the amount of diesel fuel injected. Thanks to this, diesel engines tend to have a lean mixture, leading to eliminating CO (Carbon-Monoxide) emissions to low levels unless the engine is under heavy load.

The stroke begins by opening intake valves. The turbocharger then forces in the air. At the end of the stroke, intake valves are closed.

1.3 COMPRESSION STROKE

The typical compression ratio ranges from 14:1 to 22:1. For diesel engines, it is crucial to have a relatively high compression ratio as opposed to other ICE designs because the heat generated by air compression is used to ignite the air-fuel mixture on the next stroke. Since the reliance on compression heat, diesel engines are usually equipped with glow-plugs to assist with cold-starts.

In this stroke, the air is compressed to a pressure of 30 to 50 bar with both valves closed. This compression leads to a temperature increase [4].

1.4 POWER STROKE

Ignition is initiated by injecting fuel into the combustion chamber using a direct injection method. In modern common rail systems, the injection timing is controlled by the ECU (Electronic control unit).

Atomization and dispersion of the fuel in the cylinder play a critical role in the resulting emission and power characteristics. The prominence of unwanted secondary forces is affected as well, impacting the perceived smoothness of the engine by the end-user.

Atomization is achieved by both higher injection pressures and better injector design. Dispersion is defined by the piston and air-intake design, which causes the air-fuel mixture to swirl in the combustion chamber.

The direct effects of atomization and dispersion will be discussed later in this thesis.

In this stroke, fuel is injected into the combustion chamber with high timing precision. Ignition occurs spontaneously upon injection due to the higher cylinder (air) temperature than diesel fuel's flashpoint.

Dependent on engine design, this cylinder temperature is found in the vicinity of 550 °C, while the diesel auto-ignition temperature is 260 °C according to EN 590 [3].

The mixture of air and fuel is defined as λ .

If $\lambda = 1$, the mixture is called stoichiometric. At this ratio, all of the present fuel will chemically oxidise with all of the present oxygen, with no excess remaining after the combustion ended. For diesel engines, it is equivalent to 14,6:1.

If $\lambda < 1$, the mixture is called to be rich – containing more fuel than stoichiometric.

If $\lambda > 1$, the mixture is called to be lean – containing less fuel than stoichiometric.

Due to emission and fuel efficiency optimisation, diesel air:fuel ratio can usually be found around 25:1 at peak load, or up to 160:1 at idle for turbocharged engines. It can be concluded that the general operation of a diesel engine is lean.

1.5 EXHAUST STROKE

The result of the combustion process is a mixture of exhaust gasses, unburnt oxygen, soot (particulate matter) and unburnt fuel. These gasses consist mainly of NO_x , CO_2 , C_xH_x , CO .

During the exhaust stroke, this mixture is pushed out of the cylinder through exhaust valves. In this thesis, the mixture pushed out of the exhaust valves will be referred to as pre-cat emissions.

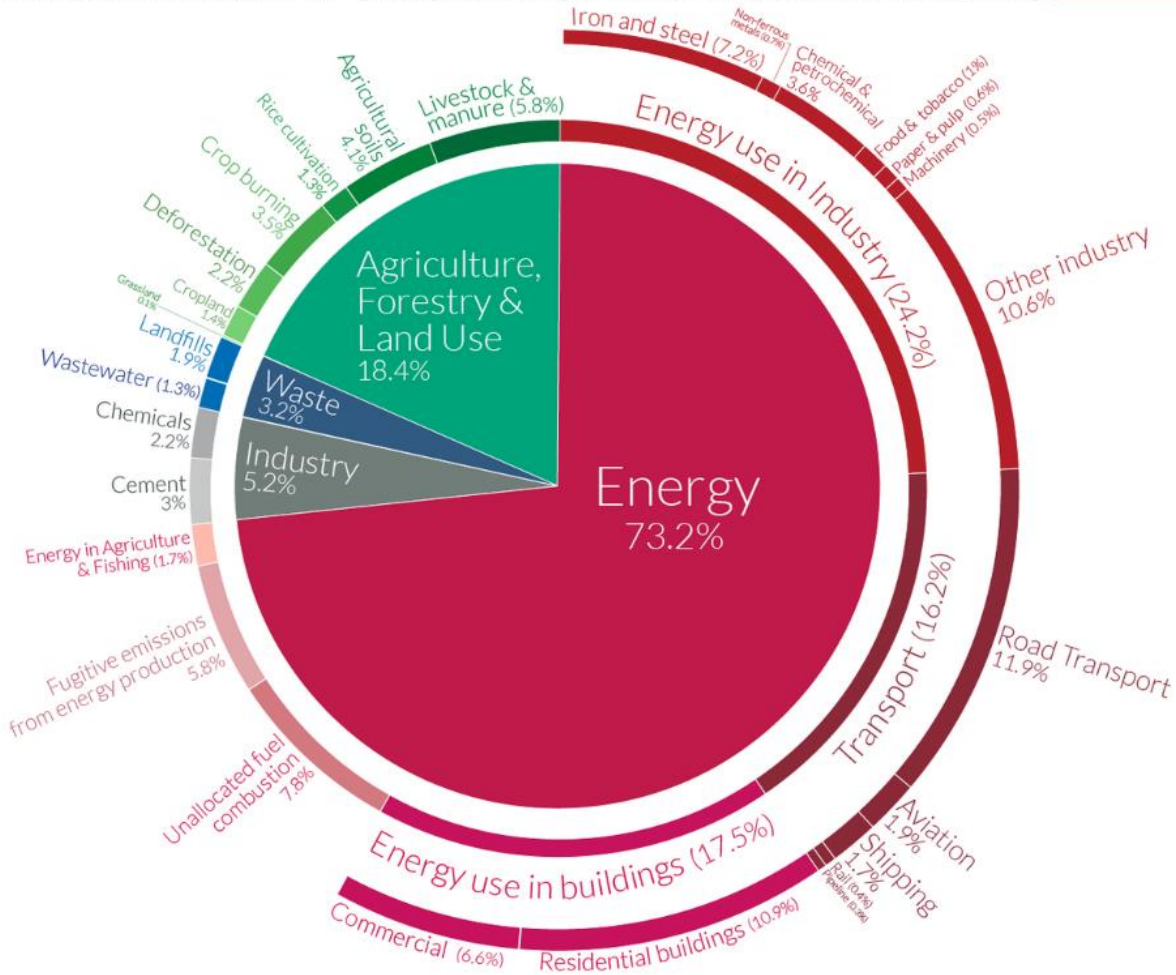
2 EMISSIONS

Emissions characteristics have become an essential parameter during engine development.

Global greenhouse gas emissions by sector



This is shown for the year 2016 – global greenhouse gas emissions were 49.4 billion tonnes CO₂eq.



OurWorldinData.org – Research and data to make progress against the world's largest problems.

Source: Climate Watch, the World Resources Institute (2020).

Licensed under CC-BY by the author Hannah Ritchie (2020).

Figure 2. Global greenhouse gas emissions by sector [9]

As figure 2 shows, the 11,9 % impact of road transportation on global greenhouse gas emissions makes it the single biggest impactor on the environment out of all sectors.

Internal combustion engines will always negatively impact the environment. However, through thoughtful design, the extent of the impact can be reduced significantly.

2.1 COMBUSTION PRODUCTS

As it will be discussed in the next chapter, the specific composition of combustion gasses is directly affected by a particular engine design. This chapter summarises the primary gasses and their impacts on the environment.

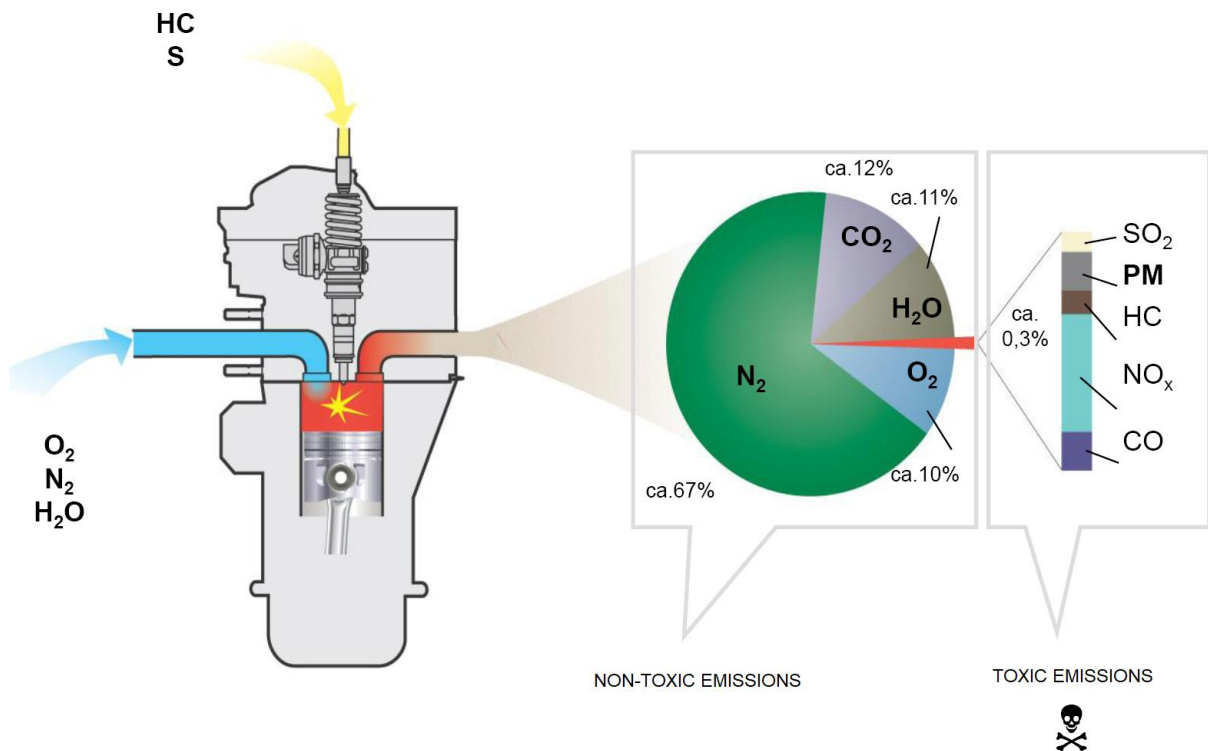


Figure 3. Products of diesel combustion [43]

2.1.1 CO₂

Carbon dioxide is a gaseous product of every combustion process. Since it is a naturally occurring component of the earth's atmosphere (in the concentration of 0,04 %), it is not considered to harm life directly. Even though it is highly probable that increasing CO₂ concentration in the atmosphere leads to global warming, direct evidence had not yet been discovered. Research on this topic is still in progress, with no definitive answer.

The amount of carbon dioxide produced by internal combustion engines directly correlates with their fuel consumption.

2.1.2 CO

Carbon monoxide is odour-less gas, which poses an immediate danger to human beings and other living creatures.

It creates a powerful chemical bond with a critical component of blood – haemoglobin. Haemoglobin usually bonds with oxygen and carbon dioxide to provide their transportation among the body. However, its bond with carbon monoxide is 200 times stronger compared to CO₂ and O₂. Breathing in an atmosphere with raised CO level leads to a severe and often lethal condition of CO poisoning [10].

CO presence in higher quantities is an indicator of incorrect combustion. Factors leading to its formation are a rich air-fuel mixture, poor fuel atomization, or high engine load.

CO reduction is performed by an oxidation-reduction catalyst. The exact process will be discussed in chapter 4 of this thesis.

2.1.3 NO_x

Nitrogen oxides are indirect products of combustion. They form in the combustion chamber through a reaction of nitrogen with unburnt oxygen at high temperatures. These gasses have a negative direct impact on health, causing respiratory problems upon prolonged exposure.

Factors supporting NO_x formation are high in-cylinder combustion temperature, inlet temperature and advanced injection timing. The typical cylinder temperature of diesel ICE is 1900 K with an inlet temperature of 293 K. Increase of just 100 K in inlet temperature leads to an increase by 700 K in cylinder temperature [11].

NO_x formation is reduced by implementing EGR (exhaust gas recirculation) system. The NO_x formed is further processed by SCR (selective catalytic reduction) system.

EGR and SCR systems will be discussed in chapters 3 and 4 of this thesis, respectively.

2.1.4 H₂O

Water is formed when hydrogen from hydrocarbons (diesel fuel) reacts with oxygen.

It is released into the atmosphere in the form of steam. It is not uncommon for this steam to condensate inside the exhaust system and exit in its liquid form.

2.1.5 O₂

Due to the usually lean air-fuel mixture of diesel combustion, oxygen can be present in exhaust gasses.

2.1.6 H_xC_x

Hydrocarbons - unburnt fuel - are usually found in the exhaust due to incomplete combustion. However, there are operating conditions when the ECU artificially increases the share of unburnt fuel in exhaust gasses to initiate regeneration of DPF (diesel particulate filter).

They are further processed by the oxidation-reduction catalyst.

2.1.7 PM

Particulate matter is a solid-state material that can be divided by the particle diameter into categories:

PM₁₀ Diameter of 10 μm and less - visible by the naked eye

PM_{2,5} diameter of 2,5 μm and less - filterable by the human respiratory system

PM₁ Diameter of 1 μm and less

PM_{0,1} diameter of 100 nm and less

2.2 EURO NORMS

The first Euro norm – EURO 1 was introduced in 1992, becoming effective in 1993. Since then, more strict limitations of exhaust gasses composition had been enforced periodically.

Table 1. Euro norm requirements for diesel vehicles of different sizes [43]

| Tier | First valid in | CO | NOx | HC+NOx | PM |
|---|----------------|---------------|------------------|------------------|-----------------|
| Euro 1 | 1993 | 2,72/5,17/6,9 | N/A | 0,97/1,4/1,7 | 0,14/0,19/0,25 |
| Euro 2 | 1997 | 1/1,25/1,5 | N/A | 0,7/1/1,2 | 0,08/0,12/0,17 |
| Euro 3 | 2001 | 0,66/0,8/0,95 | 0,5/0,65/0,78 | 0,56/0,72/0,86 | 0,05/0,07/0,1 |
| Euro 4 | 2006 | 0,5/0,63/0,74 | 0,25/0,33/0,39 | 0,30,39/0,46 | 0,025/0,04/0,06 |
| Euro 5 | 2011 | 0,5/0,63/0,75 | 0,18/0,235/0,28 | 0,23/0,295/0,35 | 0,005 |
| Euro 6 | 2020 | 0,5/0,63/0,76 | 0,08/0,105/0,125 | 0,17/0,195/0,215 | 0,0045 |
| | | g/km | g/km | g/km | g/km |
| m < 1305 / (1305 – 1760) / > (1760 – 3500) kg | | | | | |

3 REDUCTION OF PRE-CAT EMISSIONS

PRE-CAT emissions are direct products of oxidation reaction (combustion process) inside the combustion chamber. The exhaust system then processes them before becoming the exhaust gasses that are vented to the atmosphere.

While catalysts and particulate filters significantly affect emission reduction, it is crucial to focus on pre-cat emissions in the diesel engine design process too. With rising requirements for lower emissions and material advancement, the operating pressures inside the fuel injection system and combustion chamber are ever more increasing. While this is having primarily positive effects, it does not come without sacrifice.

3.1 EMISSION FORMATION

Diesel engines are the most efficient, non-stationary, fossil-fuel-powered machines of today. Their deficiencies lie primarily in the NO_x and particulate matter (soot) emissions.

As figure 4a projects, theoretical, optimal combustion occurs at the low-temperature combustion (LTC) zone, where virtually no soot nor NO_x emissions are being created. Figure 4b illustrates the real-world example of fuel injection, resulting in creating different zones in which emissions can form.

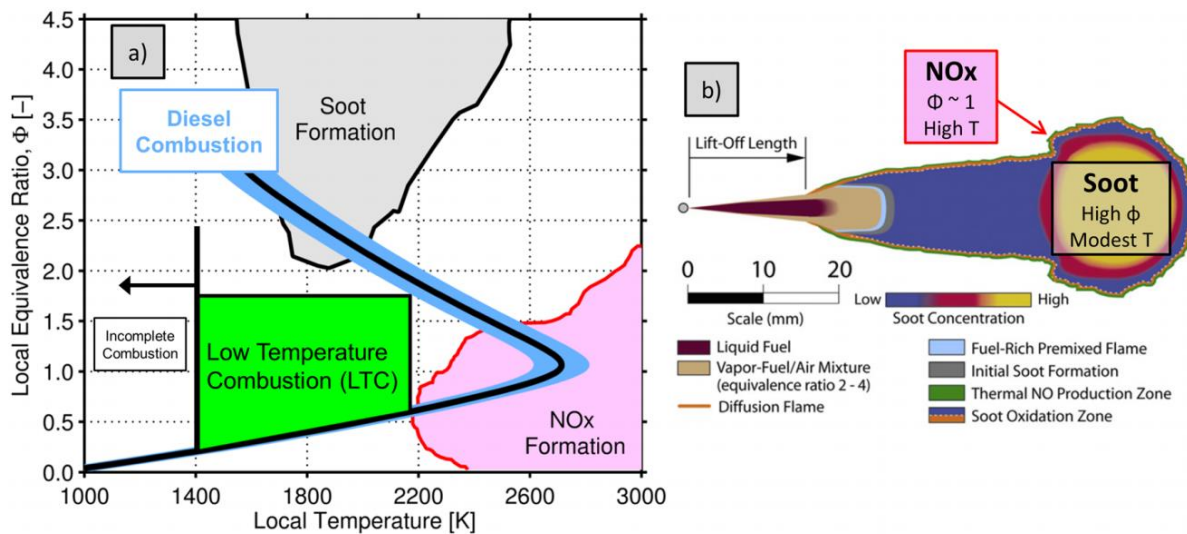


Figure 4. NO_x and soot formation characteristics [37]

3.1.1 NO_x FORMATION

NO_x emissions form in high temperatures. Thanks to the diesel combustion process reaching most of the time lean air-fuel ratios, there is a significant amount of extra oxygen (O_2) in the combustion chamber. If a high temperature occurs, nitrogen (N) reacts with O_2 , and NO or NO_2 is created. As shown in Figure 4b, the area at which this process occurs lies on the border of fuel spray with air in the cylinder. Therefore, this area has optimal air-fuel mixture $\lambda \sim 1$, resulting in the highest combustion temperature.

3.1.2 SOOT FORMATION

As it is also demonstrated in figure 2b, soot is created in spots with rich air:fuel ratio. These spots can be found in the centre of the spray pattern.

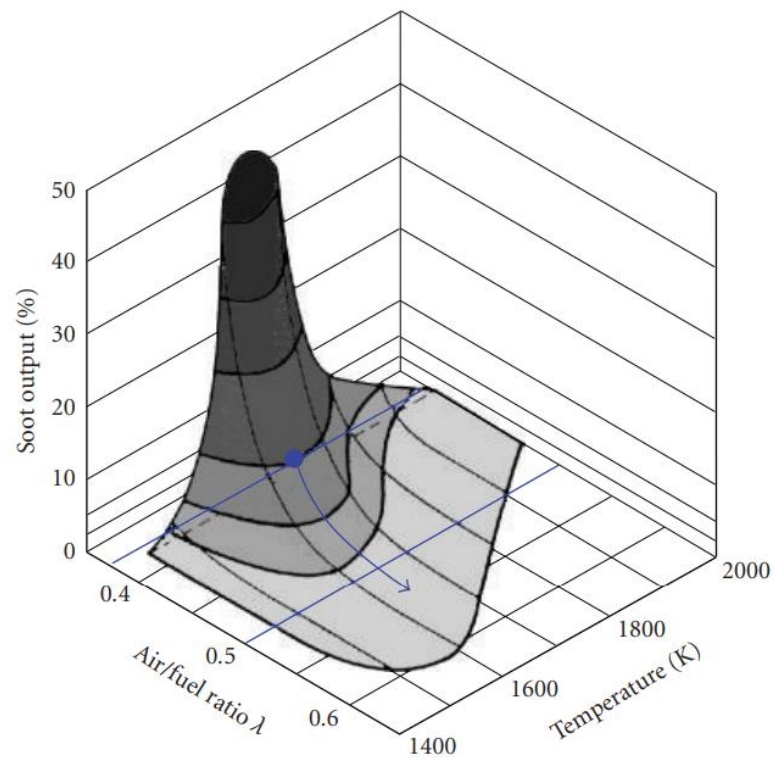


Figure 5. λ and temperature effect on soot creation [34]

3.2 FUEL INJECTION PRESSURE AND TIMING

Fuel injection pressure is the pressure at which fuel is injected into the cylinder. The industry standard for today's diesel engines is a direct injection common-rail system, reaching injection pressure higher than 200 MPa (or 2000 bar). This system is responsible for pressurizing the fuel to the desired level and timing fuel injection according to the ECU.

Since fuel is ignited spontaneously upon injection, the injection timing essentially times the start of the combustion.

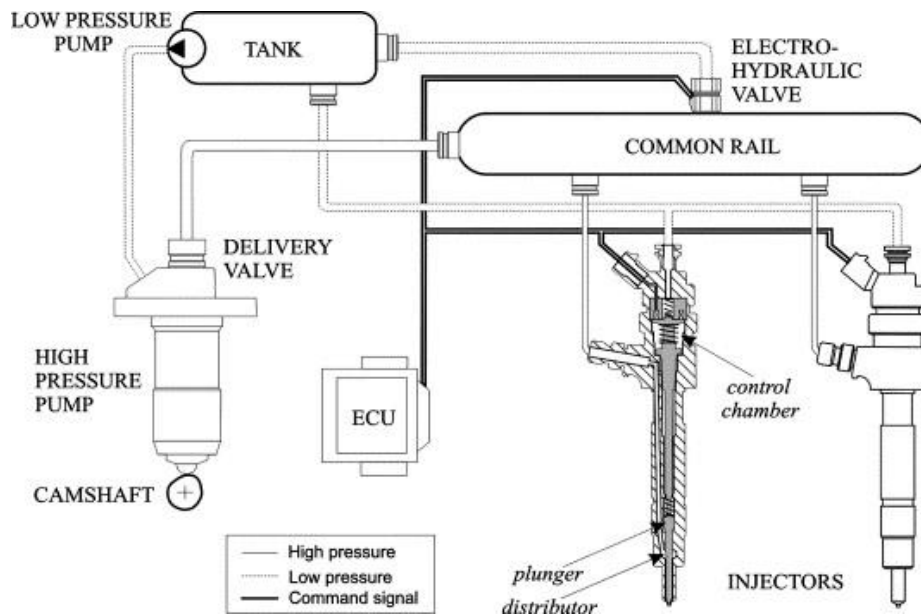


Figure 6. Common rail injection system [12]

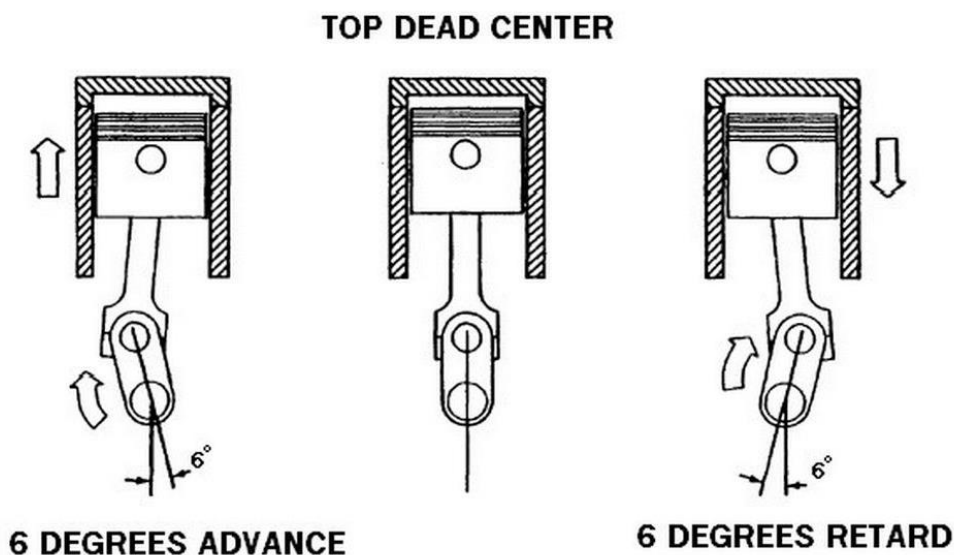


Figure 7. Advanced and retarded timing visualisation [33]

3.2.1 FUEL CONSUMPTION

Historically, direct injection pressure has been rising thanks to a positive impact on efficiency and emissions.

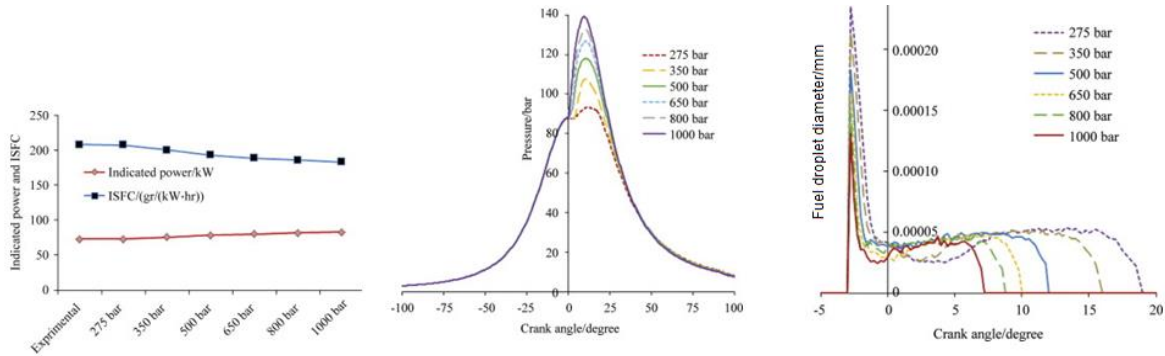


Figure 8. Injection pressure, Indicated power and indicated specific fuel consumption (ISFC) [38]

As figure 8 states, indicated power of the engine increases, while the engine's total fuel consumption decreases with higher fuel injection pressure. This fuel consumption decrease originates in the increase of the overall in-cylinder pressure, leading to better thermal efficiency of the work-cycle and better combustion characteristics thanks to decreased fuel droplet diameter.

3.2.2 EMISSION CHARACTERISTICS OF INJECTION PRESSURE

Apart from requiring advanced construction techniques to increase fuel injection pressure and engine efficiency, its impact on emissions needs to be considered.

With higher fuel injection pressure, the fuel atomization increases along with cylinder penetration. Increased fuel atomization is defined as exposing a greater surface area of the fuel droplets to air. Higher atomization means a higher amount of smaller droplets is injected into the cylinder. The so-called NO_x / soot ratio problem becomes apparent with the combination of upper mentioned observation, illustrated in figure 9.

If injection (rail) pressure is lowered, burn-temperature is lower and NO_x formation is reduced. On the other hand, slower burning process with worse dispersion initiates larger amount of soot formation. In the opposite situation, higher injection pressure eliminates soot, however increases temperature, inducing NO_x formation.

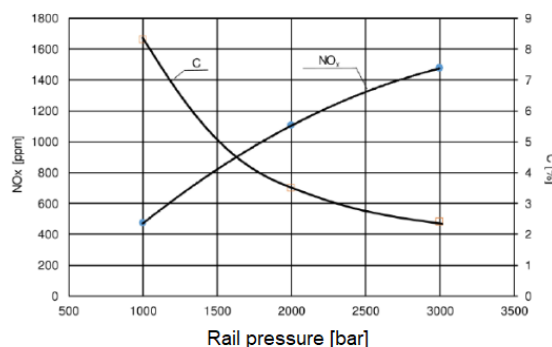


Figure 9. Injection pressure impact on NO_x and soot (C) emissions [47]

By increasing the fuel injection pressure, combustion conditions inside the cylinder improve. More fuel is able to burn completely, which increases CO₂ emissions considerably, as figure 10 shows.

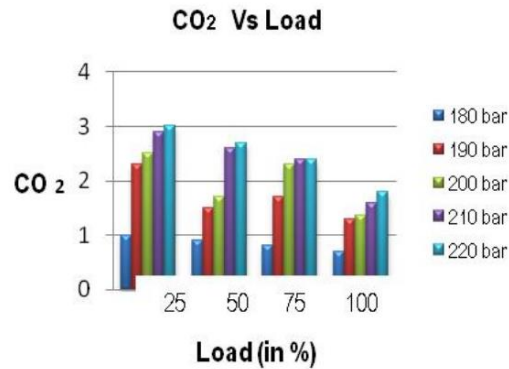


Figure 10. CO₂ load dependency [13]

3.2.3 EMISSION CHARACTERISTICS OF INJECTION TIMING

Advancing the injection timing alters the emission characteristics in both positive and negative ways.

CO concentration decreased due to an improvement of the combustion quality. This same effect, however, increased the level of CO₂. In addition, thanks to the advanced timing, combustion occurs earlier, relative to the top dead centre. This results in higher compression of the charge, higher temperature, higher NO_x emissions, and lower HC emissions.

Appendix 1 demonstrates experimentally measured data on a 7,4 kW Super Star 7710 engine. Experiments were conducted with loads of 15 and 30 Nm and with multiple fuels. E0 being diesel according to EN 590 and E5, E10 and E15 being blends of diesel and ethanol in volumetric concentrations of 5, 10 and 15 % of ethanol, respectively. For understanding the impact of injection timing, the E0 values are of the most importance.

3.3 COMPRESSION RATIO

Compression ratio is defined as a fraction of maximal and minimal combustion chamber volumes. Maximum volume is measured in the bottom dead centre (BDC) of a piston, while minimum volume is determined while the piston is in the top dead centre (TDC). As discussed above, the typical compression ratio for modern diesel ICE is expected to be found in the range of 14:1 up to 22:1.

3.3.1 EFFECTS ON EMISSIONS

Measured on a scaled-down 0,5 l single-cylinder model, it is clear that a higher compression ratio positively affects almost all parameters of the engine. It leads to better thermal efficiency, lowering indicated specific fuel consumption (ISFC) and CO₂ emissions. However, due to increased pressures and temperatures, results also in a noticeable NO_x increase.

When the engine is experiencing low load, injection pressure and cylinder wall temperature decrease, which leads to worse fuel atomization, resulting in higher ignition delay.

As Figure 11 shows, the soot particulate matter weight is dramatically reduced by up to 50 % if increasing the compression ratio from 13,3 to 15 and higher. Also confirming, that higher load and thus higher injection pressures do have a significant impact too.

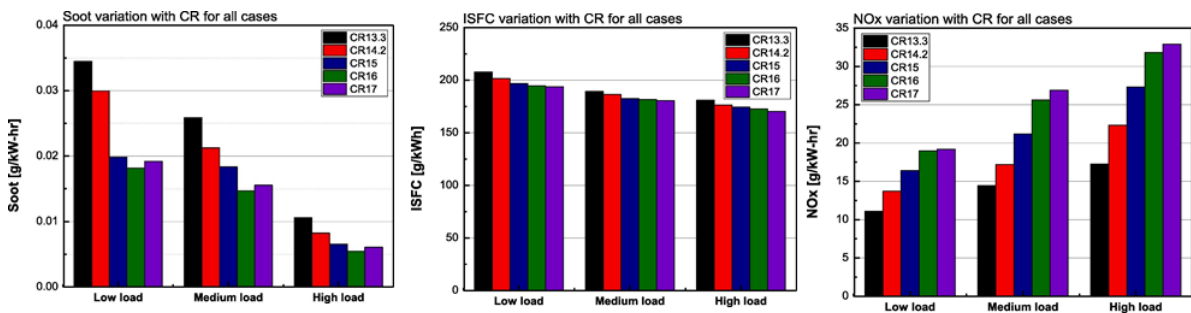


Figure 11. Soot, ISFC and NO_x dependence on compression ratio and load [7]

Indicated specific fuel consumption - ISFC also benefits from a higher compression ratio, directly resulting in lower CO₂ emissions. However, there is a trade-off made on NO_x emissions, increasing by up to 60 %.

3.4 HIGH-PRESSURE EGR

Exhaust gas recirculation (EGR) is a valve located between the exhaust and intake manifolds. Its purpose is to allow a precisely adjustable amount of exhaust gasses to enter the engine's intake. As its name suggests, this allows the exhaust gasses to participate in the combustion process again.

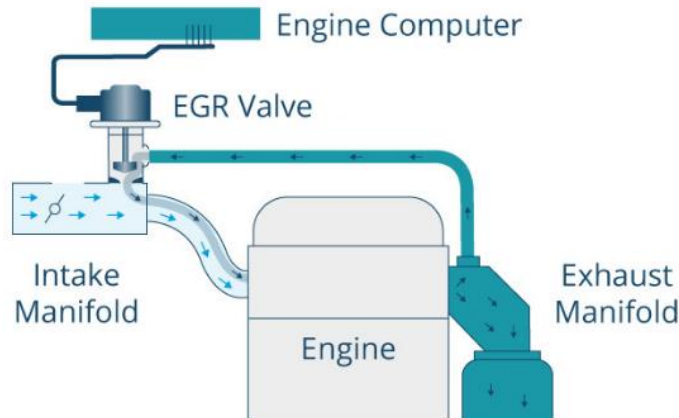


Figure 12. EGR valve position [23]

3.4.1 OPERATION

The main reason for the EGR valve to be fitted to a diesel engine is NO_x emissions reduction. If the valve is opened, less oxygen can reach the cylinder, resulting in lower combustion temperature and a lower level of unburnt oxygen. In diesel vehicles, the EGR valve is supplemented by an air-intake pressure regulation valve. Like a throttle valve in a gasoline engine, this valve can regulate intake air pressure, allowing more exhaust gas to enter the cylinder if needed. Since high temperature and available unburnt oxygen are the most critical conditions that enable NO_x emissions to be created, incorporating an EGR valve in engine design can reduce NO_x emissions by up to 80 % [25].

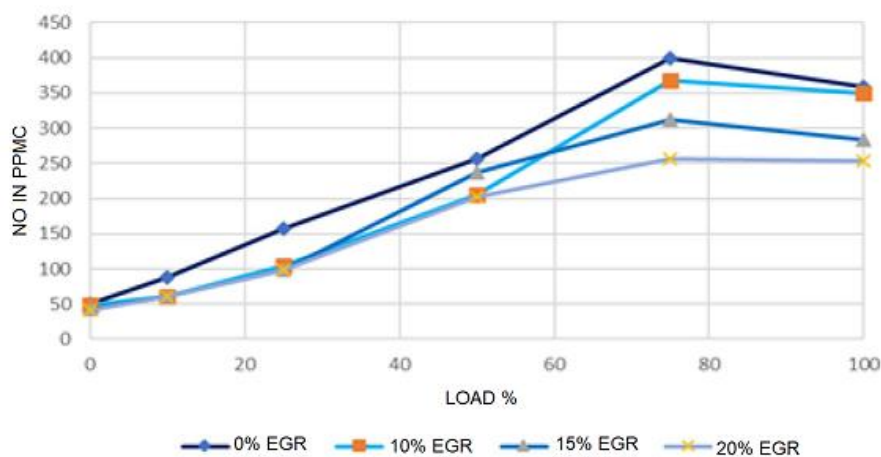


Figure 13. NO emissions characteristics depending on EGR recirculation [24]

3.4.2 DESIGN

Designs can vary by the diameter of the valve, electronic or vacuum valve position control, but the most critical design difference is additional cooling of exhaust gasses by a water-based heat exchanger. Cooling of the gas before entering the combustion chamber makes a significant impact on the resulting temperatures. A difference in the intake temperature of just 100 K results in an increase of up to 700 K in the peak cylinder temperature, which is beneficial for NO_x reduction. The heat exchanger can also be bypassed by an integrated flap, which is helpful for cold starts and fast heat-up of the engine and DOC.

3.4.3 BENEFITS

Apart from lowering the emissions, entering the exhaust after-treatment system, a noticeable increase in thermal efficiency under low load by 2 % and medium load by 3,5 % can be observed due to re-burning hydrocarbons. Effects on brake specific fuel consumption (BSFC) are even more substantial, reaching its decrease by 4 to 10 % under medium load and 3 to 5 % under heavy load [24]. A reduction in BSFC also directly contributes to lowering CO₂ emissions since less HC is being burned in the system as a whole. Some experiments show that a reduction of up to 30 % in fuel consumption are possible [25]. However, typical applications show that a 5 to 10 % improvement is usually achieved.

3.4.4 SHORTCOMINGS

Under heavy load, a high EGR rate can not be applied without considerably decreasing engines performance and worsening emission characteristics.

Recirculation of exhaust gasses into the clean air intake results in carbon deposits forming on the intake valves and along the whole air intake, potentially shortening the engines lifespan.

3.5 LOW-PRESSURE EGR

The purpose of the low-pressure EGR valve is much the same as its high-pressure counterpart. This system was introduced when high-pressure EGR did not fulfil the emissions requirements needed to comply with Euro 6 emission standards. Euro 5 allowed 180 mg/km of NO_x gasses, while Euro 6 decreased this limit to only 80 mg/km for standard size road-going cars [56].

3.5.1 OPERATION

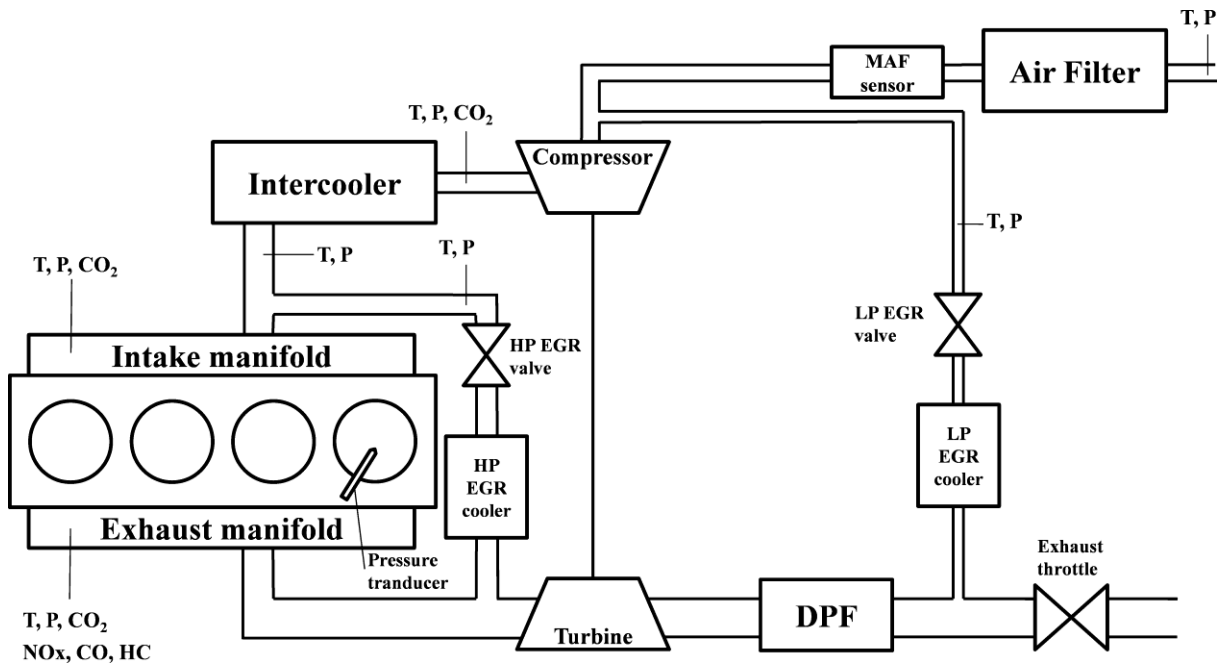


Figure 14. Combination of low LP and high HP pressure EGR [57]

As figure 14 demonstrates, the low-pressure EGR is introduced after the turbocharger and DPF filter. The benefit of this solution is that exhaust gasses, re-entering intake manifold are cleaner compared to high-pressure EGR, eliminating one of its most significant drawbacks.

3.5.2 DESIGN

In order for the exhaust gasses to be routed back into the intake manifold, exhaust backpressure has to be regulated. This is done by the exhaust throttle valve, which partially closes upon opening the EGR, restricting the exhaust flow and resulting in higher backpressure. The whole system is now much trickier to incorporate into vehicle design due to long piping from after the DPF back to the engine intake, fitting another EGR cooler along with coolant piping and controlling the exhaust throttle valve.

3.5.3 EMISSION CONTROL

Since low-pressure EGR allows slower air speeds, the cooling of the gasses in the EGR cooler is much more efficient. Thanks to its location, gasses are also enabled to pass through the intercooler, further reducing temperature and thus NO_x emissions compared to the high-pressure EGR.

Other benefits of this design allow higher boost pressures and better mixing of the exhaust gas/fresh air mixture since they travel for much longer distances together.

Thanks to a lower temperature and more homogenous mixture, NO_x and particulate matter emissions are further reduced.

Thanks to reintroducing the gas from the exhaust to the intake, pumping losses are also reduced, leading to better brake specific fuel consumption [57].

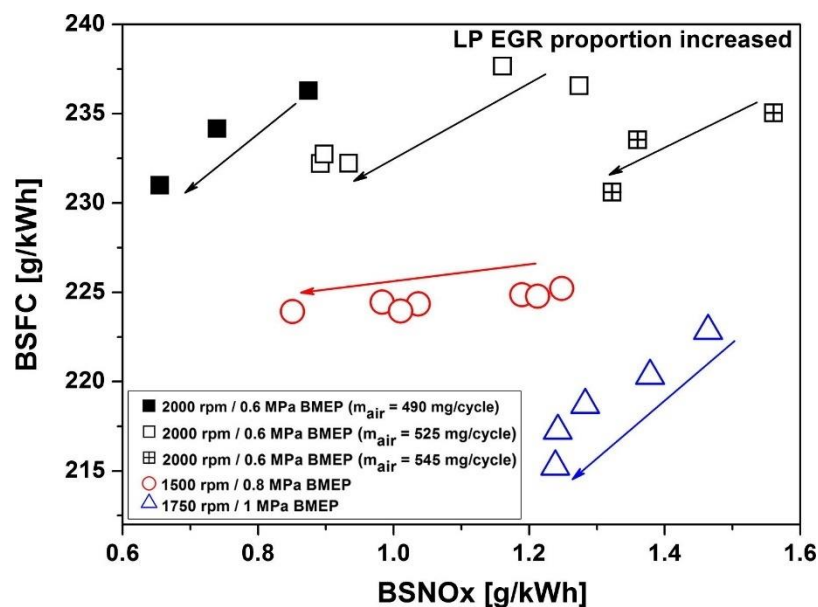


Figure 15. NO_x and brake specific fuel consumption BSFC [57]

As figure 15 shows, upon increasing the EGR recirculation rate, NO_x and brake specific consumption are lowered among all of the tested operating conditions.

3.5.4 SHORTCOMINGS

The system has a much greater volume than high-pressure EGR, leading to significant delays in supply times.

Even though the low-pressure EGR intakes exhaust gasses after the DPF, they are passed again through a turbo-charger. The inclusion of microparticles, water vapour, and corrosive gasses might negatively impact the turbo-charger lifespan.

Challenging application due to the size and complexity of the system.

4 AFTER TREATMENT OF EXHAUST GASSES

4.1 DIESEL OXIDATION CATALYST (DOC)

Catalytic convertor had been used on both – diesel and gasoline internal combustion engines (ICE) for decades. They have been developed at the end of the 19th century in France. Eugene J. Houdry first patented this device in 1952 [2]. While the diesel oxidation catalyst (DOC) had been used since 1967. These devices became mandatory by the year 1970, defined by clean air act resolution in the US [15] and 70/220/EEC directive in the EU [16].

4.1.1 HARDWARE ANALYSIS

4.1.1.1 STRUCTURE

The basic principle of oxidation-reduction catalyst is to initiate a chemical reaction, transforming the most harmful gasses to more tolerable forms while not being consumed itself. Usually, the so-called catalytic convertor has a lifespan greater than the rest of the vehicle.

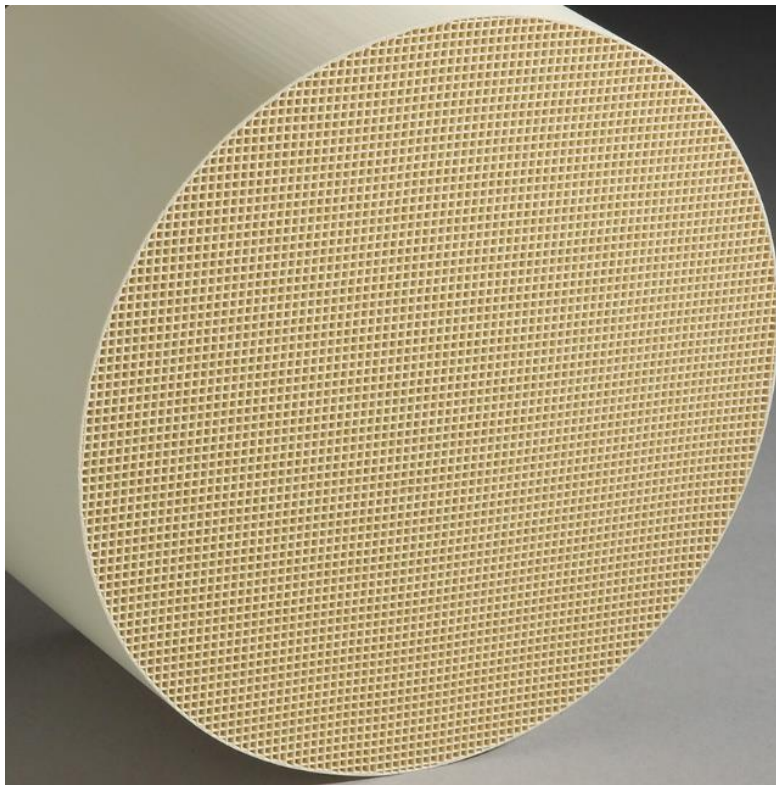


Figure 16. A render of oxidation catalyst pattern [8]

DOC structures have circular or stadium cross-section. The central mass of the catalyst, also called substrate, consists of a cordierite (ceramic) grid coated with a washcoat and precious metals. This grid with a combination of washcoat is optimized to provide the largest surface area for chemical reactions whilst maintaining the lowest backpressure possible to keep the engine's efficiency unharmed.

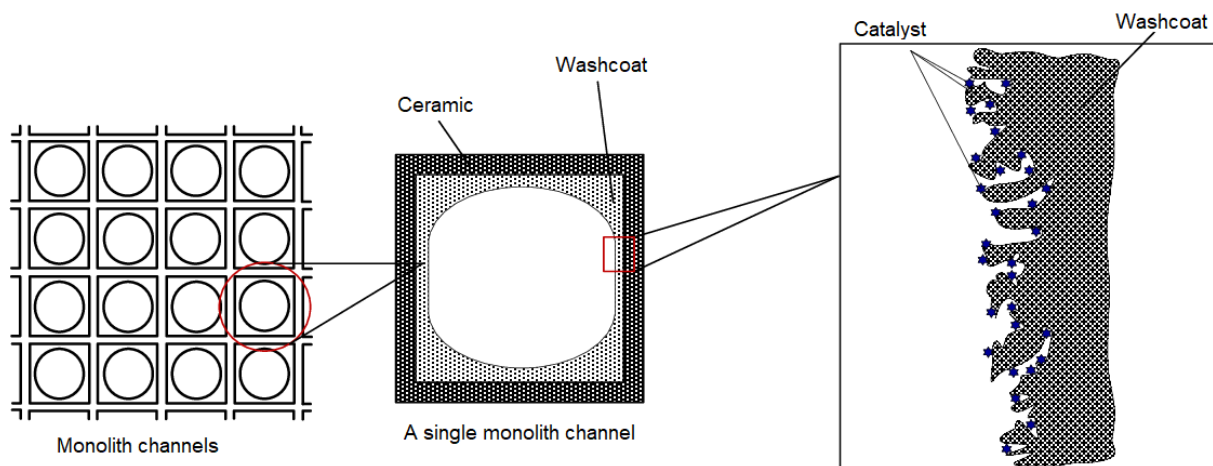


Figure 17. Detail of DOC surface [20]

4.1.1.2 WASHCOAT

As figure 17 demonstrates, washcoat directly affects the surface area on which chemical reactions can occur. Aluminium Oxide (Al_2O_3) is a primarily used material [14].

4.1.1.3 CATALYSTS

In other words, materials that are actively participating in the catalytic reaction. Industry-standard elements that are used as catalysts are platinum (Pt), palladium (Pd) and Rhodium (Rh). However, Pd and Rh are mainly used in gasoline three-way catalytic converters (TWC), whilst Pt is the most prominent choice for DOC.

DOC tends to operate at a lower temperature compared to TWC. Thus platinum superior oxidation activity in lower temperatures is favoured. The same principle applies in terms of HC oxidation, thanks to the platinum ability to oxidize heavier HC present in diesel exhaust.

Even though Pt has more substantial oxidation capability in lower temperatures, its content in DOC is up to 3 times higher than the content of precious metals in TWC for achieving comparable results in emission oxidation [14].

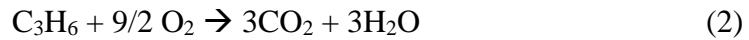
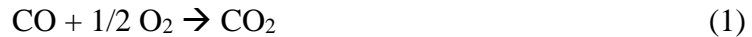
4.1.2 OPERATION

The DOC is located close to the engine's exhaust ports, following the exhaust manifold. Usually, this results in the converter being placed in the front of the undertrain. However, placement between the engine and passenger-cabin firewall is not uncommon. This placement is referred to as a close-coupled catalytic converter.

The primary use of this catalyst is to remove CO and HC emissions. Nevertheless, being the most upstream part of the exhaust system, DOC has important secondary usages too. These include initiating DPF regeneration and $\text{NO} > \text{NO}_2$ oxidation to increase the efficiency of NO_x reduction systems.

The process of oxidation starts with CO, HC (hydrocarbons – mostly unburnt fuel), particulate matter (PM), a soluble organic fraction (SOF), NO_x and O_2 coming to the DOC from the exhaust manifold of the engine [21].

The main chemical processes include:



These processes take place only if the light-off temperature of the catalyst had been reached. This temperature is usually found in the vicinity of 200 °C.

4.1.3 TEMPERATURE MANAGEMENT

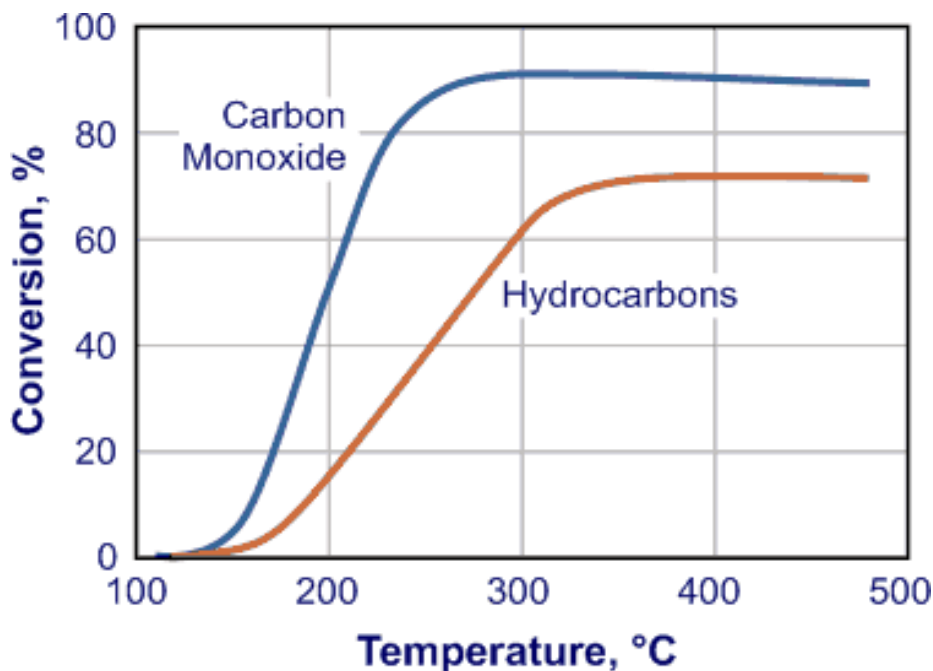


Figure 18. CO and total hydrocarbons THC conversion efficiency dependency on temperature [69]

Figure 18 shows that the amount of CO and hydrocarbons is dramatically reduced with increasing temperature, mainly above 250 and 300 °C, respectively. Effects of preheating are going to be discussed in chapter 6 of this thesis.

4.1.4 SHORTCOMINGS OF DOC

DOC operation relies heavily on its temperature. It can only carry the chemical reactions if the light-off temperature had been met.

4.2 DIESEL PARTICULATE FILTER

Diesel particulate filter is a device designed to reduce particulate matter emissions via their capture, storage and subsequent burn by up to 99 % [36].

4.2.1 HARDWARE ANALYSIS

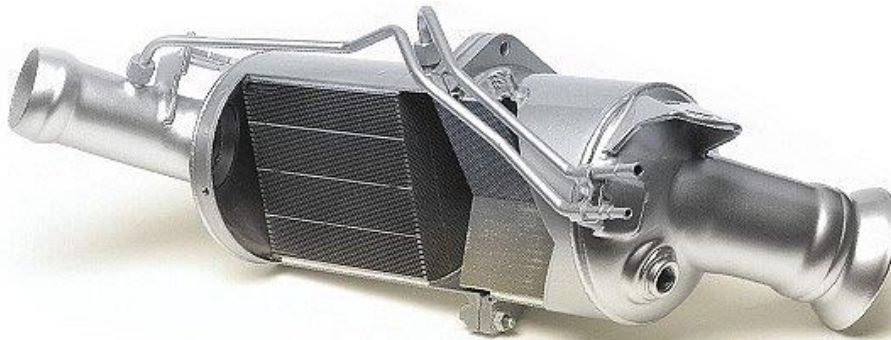


Figure 19. Diesel particulate filter [29]

The hardware consists of usually a ceramic grid, similar to the one found in DOC, however with larger channels. Same materials are used. The walls of these channels are coated with inorganic non-noble metal oxides. This coating also contains catalytic metals – Pt, Pd and Rh.

The size of filtered particles depends on multiple factors, while the most prominent being fuel injection pressure and timing. Usually, with today's engine designs, DPF is designed to filter particles of 50 nm in diameter by incorporating 10 to 20 nm pores in its walls [31].

A pair of pressure sensors is installed so that ECU can monitor a pressure difference. This information is then used along other parameters to initiate active regeneration.

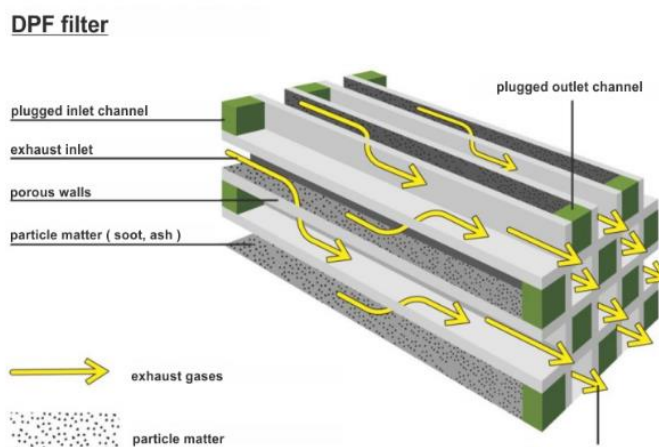


Figure 20. Diesel particulate filter channels illustration [30]

4.2.2 OPERATION

Most of the time, DPF operates in a passive mode. Soot particles are being captured in the pores, created by outlet plugs – as figure 20 shows – whilst exhaust gasses are escaping through the porous walls and out of the DPF.

It is clear that the volume of the channels is finite and they would become clogged up over time. Regeneration is a process, which ensures that captured particulate matter gets burned, and exits the DPF in gaseous or smaller particles form.

4.2.2.1 PASSIVE REGENERATION

Passive regeneration, sometimes called continuous regeneration, occurs while the engine experiences long-term light to medium load. This includes highway or smooth backroad driving of a typical vehicle – car.

Passive regeneration can be split into NO₂ oxidation and O₂ oxidation.

$C + O_2 \rightarrow CO_2$ requires a temperature around 600 °C, which are rarely met during typical driving.

$2C + 2NO_2 \rightarrow N_2 + 2CO_2$ thanks to NO₂ being a stronger oxidizer than O₂, temperature requirement of this oxidation reaction is only around 260 to 300 °C which is commonly exceeded during a regular operation of a vehicle [36].

DPF with passive regeneration capability is fitted with Pt/Pd layer at the inner surface of the channels, catalyzing this reaction. This regeneration is entirely independent of ECU management and happens spontaneously when optimal conditions are reached.

4.2.2.2 ACTIVE REGENERATION

If the vehicle experiences sub-optimal conditions, passive regeneration can not keep up with a newly incoming particulate matter rate. These conditions include prolonged low-load or high-load operation. The ECU detects the filter occupancy through a couple of installed pressure sensors, one upstream and one downstream of the DPF. If the pressure difference between these two sensors reaches a critical level, active regeneration is initiated by the ECU.

Diesel particulate filters can be divided into three main designs regarding their active regeneration initiation:

- a) Standard design > Additional diesel fuel is injected into the cylinder before the top dead centre of an exhaust stroke. This fuel is expelled into the exhaust system. Upon its entry into DOC, it oxidizes, resulting in 600 to 650 °C in temperature, incinerating the particulate matter in the DPF. Additionally, ECU closes the EGR valve, so the unburnt fuel can not re-enter the cylinder.
- b) Exhaust injection > One injector with glow plug is installed directly into the exhaust system, upstream of DOC. When active regeneration is initiated, fuel is injected directly into the exhaust, causing the same effects as described in standard design
- c) Additive design > A vehicle is equipped with an additive tank. The additive is injected into the fuel tank in automatically weighed ratios upon each fuel tank fill-up. These

additives combust along with fuel and get deposited onto the DPF. During the Active regeneration, they lower the temperature needed to just 400 to 500 °C, while also shortening its duration. This design is beneficial mainly for vehicles with separate DOC and DPF, where the DPF is located further downstream in the exhaust system.

4.2.3 REGENERATION EMISSIONS

During the regeneration of DPF, additional emissions are created and particulate matter exiting exhaust the exhaust system temporarily increases.

The typical capacity of DPF is to store around 1000 km of driving worth of particulate matter. Of course, this heavily depends on the driving style the vehicle is experiencing.

Figure 21 represents a driving cycle of a test vehicle that had been continuously repeated until the ECU automatically initiated active regeneration.

At the start of the cycle, cold engine emissions can be observed, gradually decreasing with engine and catalysts heating up. Active DPF regeneration is automatically initiated by the ECU at approximately 9000 seconds mark, while the immediate increase of CO, NO_x, CO₂ and THC (total hydrocarbons) is observed. Regeneration lasted for 9 minutes. A difference between emissions of CO₂ and NO_x before and after the DPF regeneration show that increased backpressure of DPF also negatively affects emission.

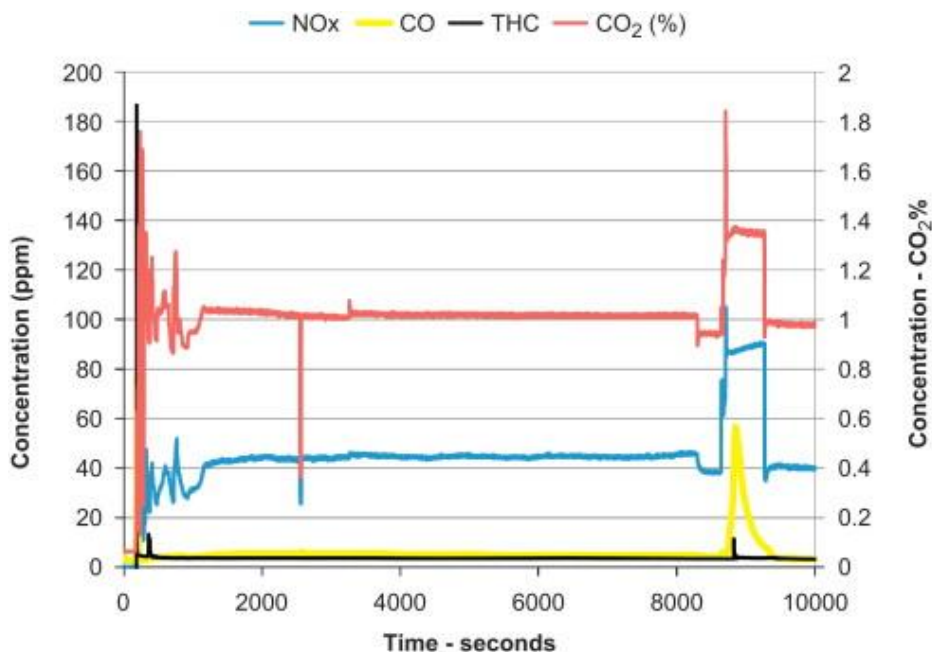


Figure 21. Emissions during DPF regeneration [40]

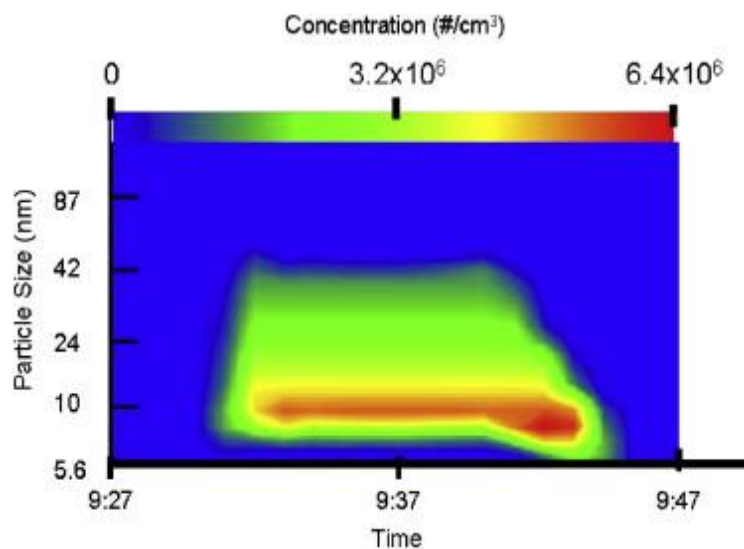


Figure 22. Particle size concentration during DPF regeneration [40]

Figure 22 represents a measurement of engine exhaust particle sizer and spectrometer (EEPS). This measurement was carried on the same regeneration cycle as in figure 21. Before the start of the regeneration, virtually no particles had been detected. Upon the start of regeneration at approximately 9:30, particles of 8 to 50 nm in diameter started exiting the DPF. The majority of concentration is located in the vicinity of 10 nm in diameter while decreasing to 5 nm near the end of the regeneration process.

It needs to be noted that the range of the equipment had been exceeded during this test, which leads to slight inaccuracy of the results. However, the measurement is still representative for the purpose of this thesis.

4.2.4 SHORTCOMINGS OF DPF

4.2.4.1 LIMITED LIFESPAN

The name itself suggests that DPF is a filter, while an inevitable part of every filter usage is its lifespan. DPF becomes clogged with particulate matter that can not be burned off by its regeneration and has to be cleaned or exchanged.

4.2.4.2 DRIVING STYLE ADJUSTMENT

In order for DPF to function correctly, driver awareness of the regeneration system is required. Primarily, diesel vehicles in low-load situations with short driving times (typically a city-driving) result in not meeting requirements for the active regeneration to be automatically initiated. If this situation persists and DPF reaches an extreme level of particles build-up, it becomes unable to perform active regeneration by itself and needs to be serviced or exchanged.

4.2.4.3 REGENERATION ADDITIVE

Systems with additive design DPF require extra maintenance, ensuring that the regeneration additive level in its storage tank is adequate.

Also incorporating fuel tank injector for dosing the additive into the fuel tank and more precise means of measuring fuel level due to reaching required ratios of additive to fuel.

4.2.4.4 LOW-DIAMETER PARTICLES

During the regeneration of the DPF, a substantial amount of particles sizing 5 to 15 nm in diameter was observed. However, the current testing cycle for diesel vehicles only measures particles with a diameter of 23 nm and higher. This might be a significant health concern that has to be evaluated [40].

As measurements show, the diameter of diesel particulate matter during standard engine operation and without DPF filter ranges from 60 to 120 nm [40], [65].

When these particles are filtered, the exiting particles range mainly from 5 to 15 nm in diameter, while most of them are expelled during the regeneration process. The difference in the distribution of these particles is described in figure 23.

This is where a health concern arises, and evaluation of whether particles of 60 to 120 nm aren't less harmful to the environment than 5 to 15 nm particles is needed.

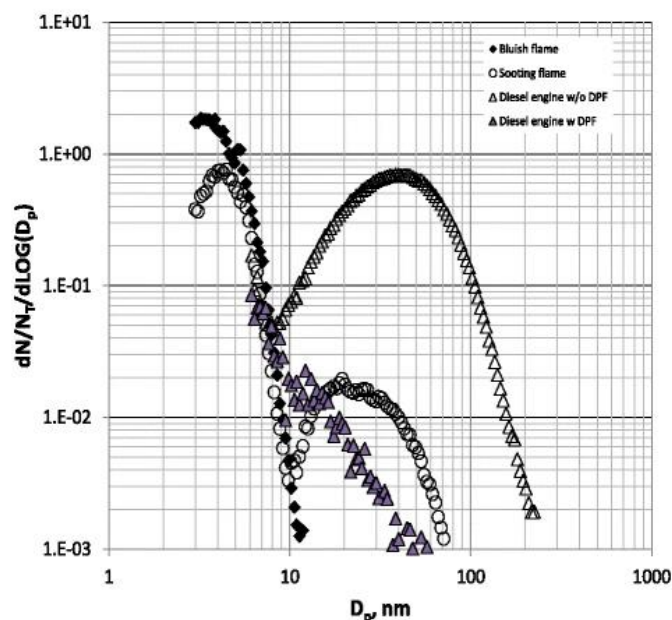


Figure 23. Particle distribution [66]

Studies do agree on the negative effects of diesel particulate matter on human health, documenting a higher risk of cardiovascular diseases and cancer development at workers exposed to the particulate matter in high quantities. Including professional drivers and people living in proximity of high traffic roads.

With decreasing particulate size, the chemical reactivity increases dramatically, independently of the total particulate matter mass. This intensifies the harmful effects of the particulate matter even further [66], [67].

This might imply that the inclusion of the DPF filter might pose a higher risk to the environment than the unfiltered diesel emissions in the first place.

Despite these slightly alarming results, long term health effects are very tricky to assess, and further independent investigation, including long term study of these issues, is certainly needed.

4.3 NO_x REDUCTION SYSTEMS

4.3.1 LEAN NO_x TRAP (LNT)

A typical LNT is based on two main components. Noble metal and alkaline compound. Typically for LNT, these are Platinum (Pt) and Barium Oxide (BaO). They are usually based on an aluminium oxide layer (Al₂O₃). This technology was first used by Toyota in 1990 [18].

Lean NO_x trap main objection is to transform NO_x emissions into N₂, CO₂ and H₂O. In this process, other combustion products are also altered.

The LNT is shaped very similarly to a DOC, also consisting of the layer of precious metal on top of the washcoat, which is being supported by the base cordierite grid. As figure 26 shows, the LNT consists of catalytic materials: Al₂O₃, BaO and Pt. The operation of the catalyst differs between lean and rich conditions, which has to be altered periodically to provide a desired catalytic effect.

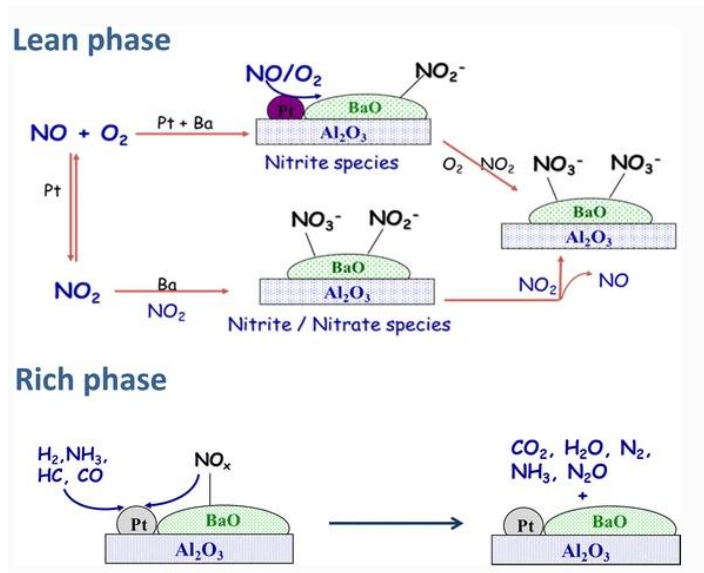


Figure 24. Schematic workflow of LNT [17]

4.3.1.1 LEAN OPERATION

Exhaust mass of NO, NO₂, and O₂ enters the LNT.

Using the oxidation ability of Platinum, NO and O₂ react to form NO₂.



NO₂ will react with BaO.



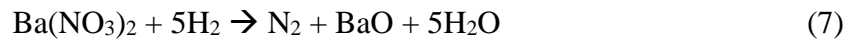
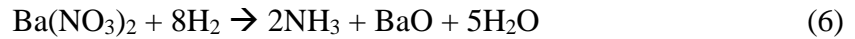
This reaction continues until all of the BaO is converted to Ba(NO₃)₂.

When the unit reaches its maximum capacity and has no more BaO to react, it must be regenerated.

4.3.1.2 RICH OPERATION

Exhaust mass of H₂, NH₃, HC and CO enters the LNT.

Stored nitrogen and oxygen in the bond with BaO reacts with rich combustion products, resulting in the following reactions.



Regarding L. Lietti study [19], at a temperature of around 100 °C, the majority (> 90 %) of the H₂ undergoes the path described in equation 6. Resulting in the formation of Ammonia (NH₃).

When the reaction reaches a higher temperature, the NH₃ reacts further.



4.3.1.3 TEMPERATURE MANAGEMENT

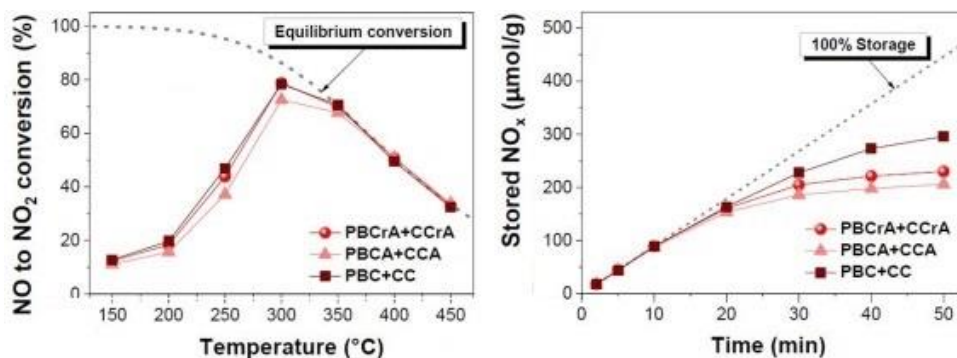


Figure 25. NO to NO₂ conversion and NO_x storage of LNT [41]

Figure 25 compares three major types of LNT, their ability to convert NO to NO₂ depending on temperature and the amount of NO_x that can be stored over time at 200 °C operational temperature.

4.3.1.4 SHORTCOMINGS

LNT are susceptible to poisoning by other reactants. The main problem is posed by SO₂, which reacts with BaO to form Ba(SO₃)₂. This substance requires higher temperatures of up to 800 °C to dissociate, which are achieved in regeneration mode. These high temperatures, however, limit LNTs lifespan. This problem is overcome by lowering sulfur content in diesel fuel.

4.3.2 SELECTIVE CATALYTIC REDUCTION (SCR)

SCR catalyst also shares many similarities with DOC and LNT. Its task is to transform NO_x emissions into N₂ and H₂O. It is an emission regulation system that utilizes a chemical reaction component that has to be added externally – diesel exhaust fluid (DEF) trademarked in the EU as AdBlue.

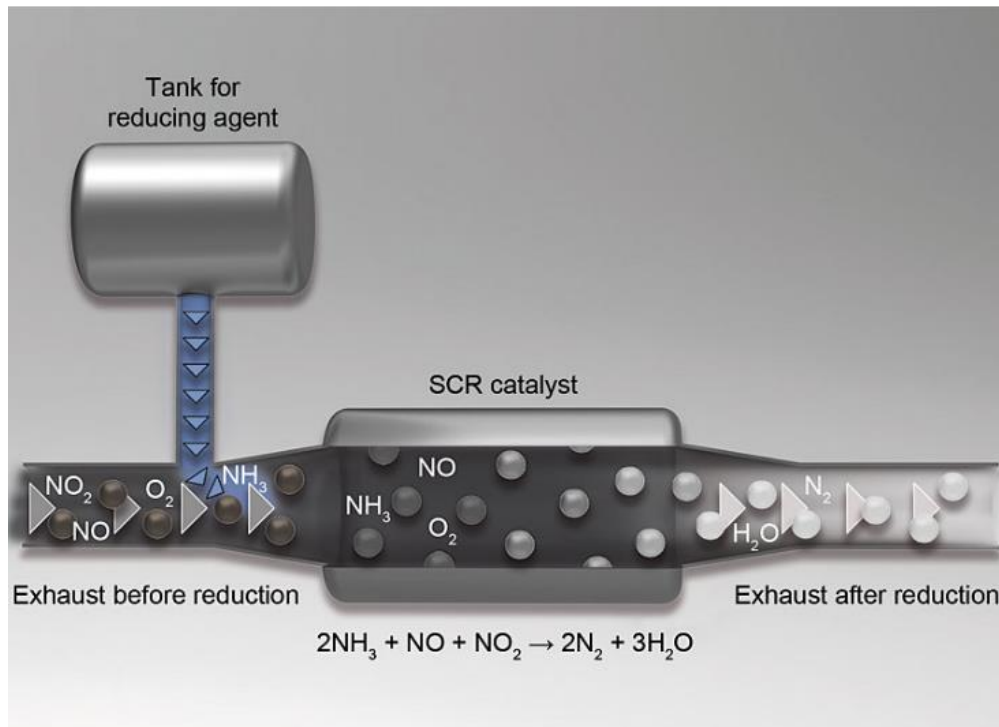


Figure 26. Selective catalytic reduction principle [26]

4.3.2.1 HARDWARE

The critical materials for SCR function are iron (Fe) and copper (Cu) based zeolites. Three main types of SCR exist, differentiated by the style of applying Fe/Cu zeolites onto the base grid. Every class can have multiple ratios and sequences of Fe and Cu zeolites. However, these had been established as the most efficient for NO_x conversion among a wide range of temperatures:

- A.) Sequential brick design with Fe-zeolite brick followed by a Cu-zeolite brick with a ratio of 33 % and 67 %, respectively.
- B.) Mixed washcoat design featuring Cu-zeolite and Fe-zeolite incorporated to an evenly applied washcoat layer while maintaining the ratio of 33 % Fe and 67 % Cu zeolite. This solution showed similar efficiency as an average of individual Fe and Co zeolites.
- C.) A dual-layer design, consisting of individual layers of different thicknesses and mass fractions of Fe and Cu zeolites. This design with 33 % Fe-zeolite on top of 67 % Cu-zeolite thicker base-layer proved to be very efficient in NO_x removal among a wide temperature range. This solution also demonstrated superior efficiency in a fast SCR reaction (NO + NO₂ + NH₃) [22].

4.3.2.2 OPERATION

SCRs main objective is to convert NO and NO₂ to N₂ and H₂O. It is achieved by reacting exhaust gasses with NH₃.

The process begins with injecting DEF to the exhaust system upstream of SCR through DEF injector.



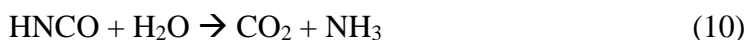
Figure 27. DEF injector – water-cooled [27]

DEF – chemically a 32,5 % solution of (NH₂)₂CO – urea and water is being heated up and mixed with gasses. In a temperature above 60 °C, decomposition of DEF to NH₃ + CO₂ is initiated. NH₃ then reacts with the gasses in the following reactions:

DEF decomposition

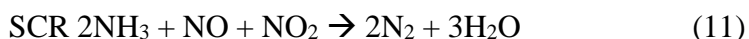


Hydrolysis of the created HNCO results in further NH₃ synthesis



NO_x emissions are reduced by these reactions with NH₃

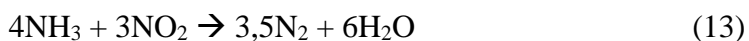
Fast



Standard



NO₂ only SCR



4.3.2.3 THERMAL MANAGEMENT

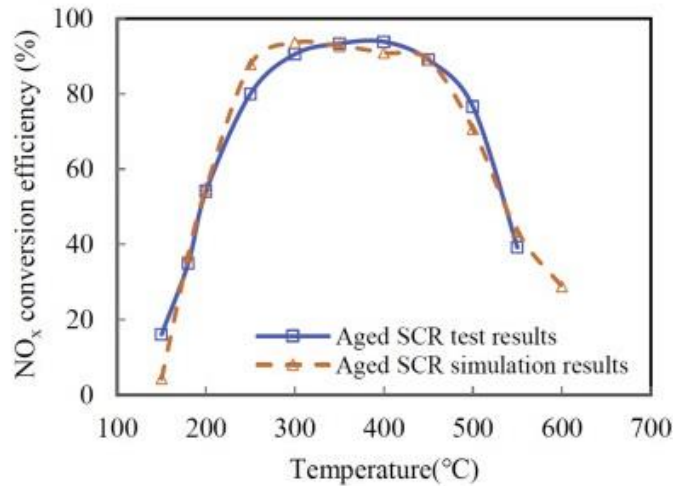


Figure 28. The efficiency of hydrothermally aged SCR catalyst [42]

The use of an aged SCR catalyst was chosen as it is more representative of its efficiency over the vehicle's lifespan. Fresh SCR catalyst can be expected to have 5 % improved efficiency through the whole temperature range.

4.3.2.4 SHORTCOMINGS

Both Fe and Cu zeolites catalyze NH_3 to N_2 oxidation, which poses an efficiency problem. Some of the NH_3 will react with O_2 without affecting NO_x emissions at all.



Fe zeolite starts oxidating NH_3 at 300 °C, while Cu zeolite is more problematic - oxidating NH_3 at 250 °C at a much faster rate [28]. With increasing temperature, this reaction accelerates, leading to a decrease in efficiency.

The freezing temperature of DEF is just -11 °C. To fight this, DEF tanks are equipped with electrical heating elements. To protect the tubing, after the engine shut-off, the ECU reverses the pump's flow to collect DEF from the tubing back into the tank.

Due to imperfection in NH_3 dosage, a situation where an excessive amount of NH_3 is left unreacted will occur. Due to NH_3 toxicity, it is crucial to address this problem by adding another device, called ammonia slip catalyst, into the emission system.

4.3.3 AMMONIA SLIP CATALYST

Usually, the last component of the exhaust emission-reduction system installed. Its sole purpose is to prevent any unreacted NH_3 originating in SCR from entering the atmosphere. NH_3 is a toxic gas with a very low threshold of human irritation. At concentrations above 15 ppm causes irritation of eyes and respiratory problems [44].

Ammonia slip catalysts facilitate the reaction of NH_3 to H_2O and N_2



4.4 CONCLUSION

It was established that all catalysts highly benefit from reaching operating temperature quickly. There are numerous ways to address this problem, which can be sorted mainly into two categories – internal engine parameters alteration and engine-independent thermal management. These solutions will be discussed in the following two chapters.

5 INTERNAL ENGINE PARAMETERS ALTERATION

5.1 CYLINDER DEACTIVATION

As it might seem counter-intuitive, cylinder deactivation is a viable option to increase exhaust gas temperature at cold-start conditions. To evaluate this possibility, a six-cylinder diesel engine was operated with three of the cylinders deactivated, supplemented by flexible valve actuation, enabling late intake valve closure.

This approach moved the load of 6 cylinders to 3. Since the same amount of energy had to be generated by the engine, the working cylinders were under essentially double the load, resulting in halving the exhaust flow rate [49]. Depending on the load state, the following scenarios were verified to be possible.

5.1.1 LIGHTLY LOADED IDLE

This condition was defined by 800RPM and 0,26 bar BMEP load. Compared to all six-cylinder operation, the possibility of these scenarios was defined:

- Turbine outlet temperature (TOT) increase from 120 to 196 °C with no measurable fuel consumption penalty, compared to all 6-cylinder operation
- Achieving a 50% reduction in fuel consumption, achieving the same 200 °C target
- A 36% reduction in fuel consumption achieving the same turbine outlet temperature of 260 °C when combined with EGR
- At a given BSFC heat-up speed of all after treatment catalysts was sped up by up to 300 % for reaching the same target [50].

5.1.2 LOADED IDLE

This condition was defined by 800RPM and 2,5 bar BMEP load. Compared to 6 cylinder operation, the possibility of these scenarios was defined:

- Turbine outlet temperature increased from 190 to 310 °C with a negligible 2% fuel consumption penalty, compared to the most efficient 6-cylinder operation
- Above 35% reduction in fuel consumption, when achieving temperatures of 300 to 400 °C
- 200 % faster heat-up of after-treatment catalysts [50].

5.2 EARLY EXHAUST VALVE OPENING (EEVO)

This system relies on flexible valve actuation. Advancement of the exhaust valve opening is initiated, leading to a substantial increase of turbine outlet temperature by 30 to 100 °C with the advancement of exhaust valve opening by 90° [51].

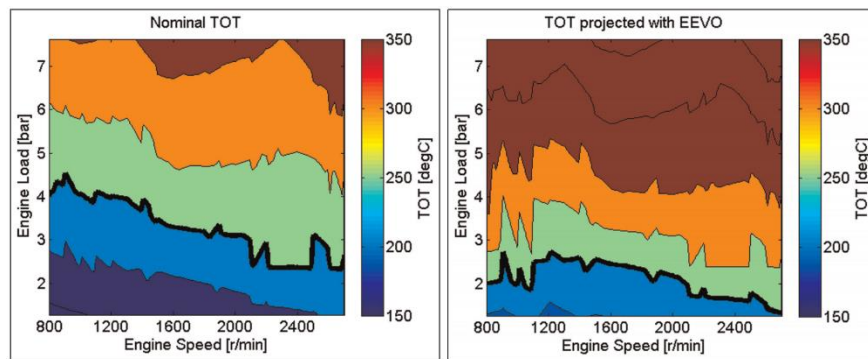


Figure 29. Turbine outlet temperature, nominal vs EEVO [51]

5.3 SECONDARY FUEL INJECTION

DOC can directly oxidise unburnt fuel, creating a significant portion of heat. This ability is commonly used, for example, to initiate DPF regeneration. Due to this usage, all of the instrumentation is already installed in the vehicle. While some emission systems can be equipped with an extra fuel injector, injecting directly into the exhaust. Usage of an in-cylinder injector is preferred due to its ability to cool the combustion chamber down and thus reduce NO_x emissions.

This method of emission reduction is based on initiating secondary injection after the combustion process has ended. The intended purpose of this fuel is to travel to the DOC, oxidise and create excessive heat to help reach a light-off temperature as soon as possible.

Timing of the post-injection is vital because it determines the ratio of the fuel injected that gets into the exhaust unburnt and the fuel, which ends up trapped in the cylinder and burns during the next combustion due to in-cylinder gas flow and vortices created during the exhaust stroke.

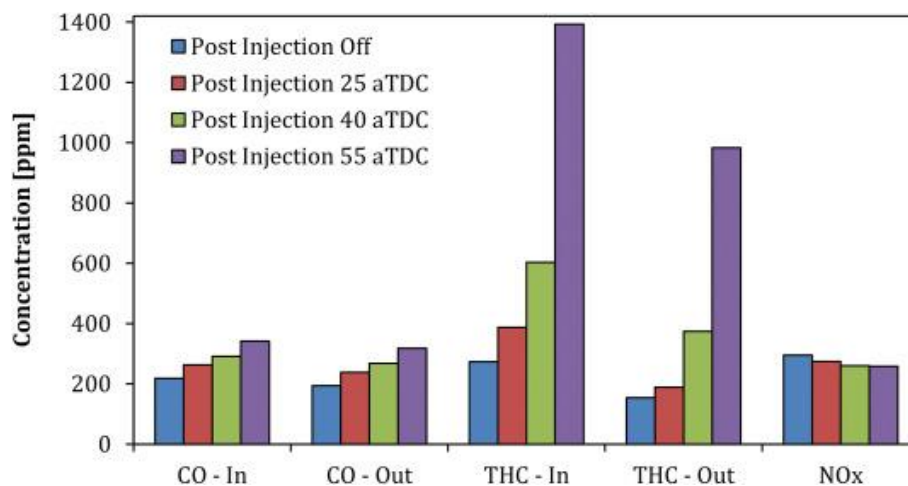


Figure 30. Post injection timing and resulting emissions [46]

This method resulted in an increase of exhaust gasses concentration across the board, which is expected due to the higher total quantity of fuel being oxidised. The exception was up to a 7% reduction of NO_x emissions.

6 ENGINE-INDEPENDENT THERMAL MANAGEMENT

As it may be concluded from efficiency diagrams in chapter 4, correct operating temperature is critical for the maximum effectivity of every emission-reduction device. All of them benefit from fast heat-up, while DPF and LNT require periodical regeneration phases initiated by increasing operating temperature. The arrangement of the emission system is then crucial to its function because it defines the ability to control temperatures precisely.

6.1 SYSTEM LAYOUT

The placement of the catalyst has a significant effect on its performance. Multiple strategies on the order of catalysts can be chosen.

6.1.1 DPF FRONT SYSTEM

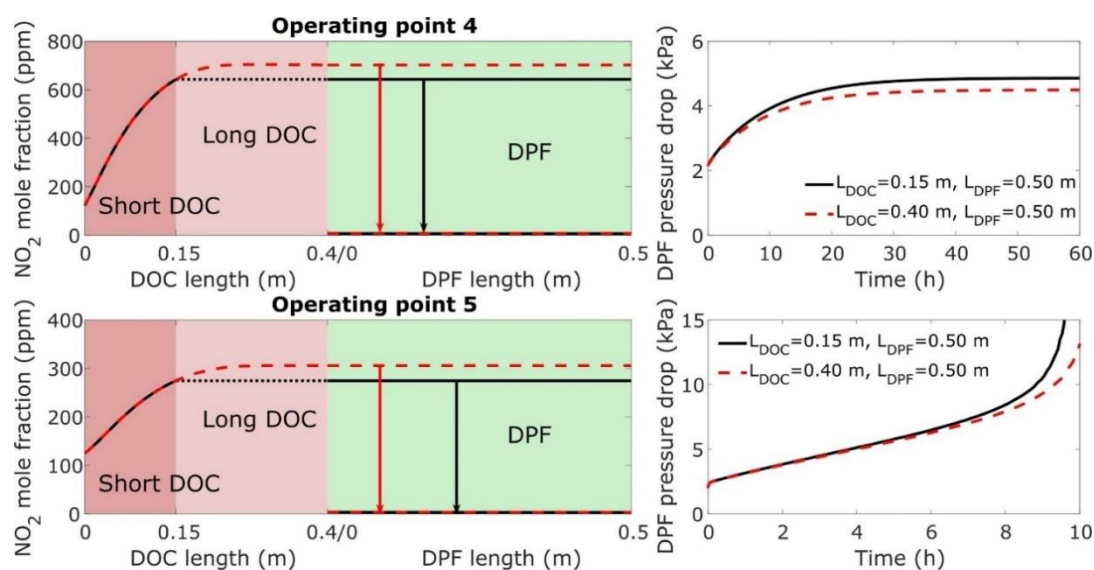


Figure 31. DPF front system [64]

As figure 31 shows, DPF front system had been tested under various conditions [64]. Operating point 4 has a smaller load than operating point 5. As it can be seen, the length of the front DOC does not impact the performance as a whole. The NO_2 did manage to oxidise completely in only the short DOC. Upon examination of the pressure graphs, it can be identified that after 8 hours at operating point 5, this setup does not passively regenerate fast enough, and active regeneration is needed.

6.1.2 SCR FRONT SYSTEM

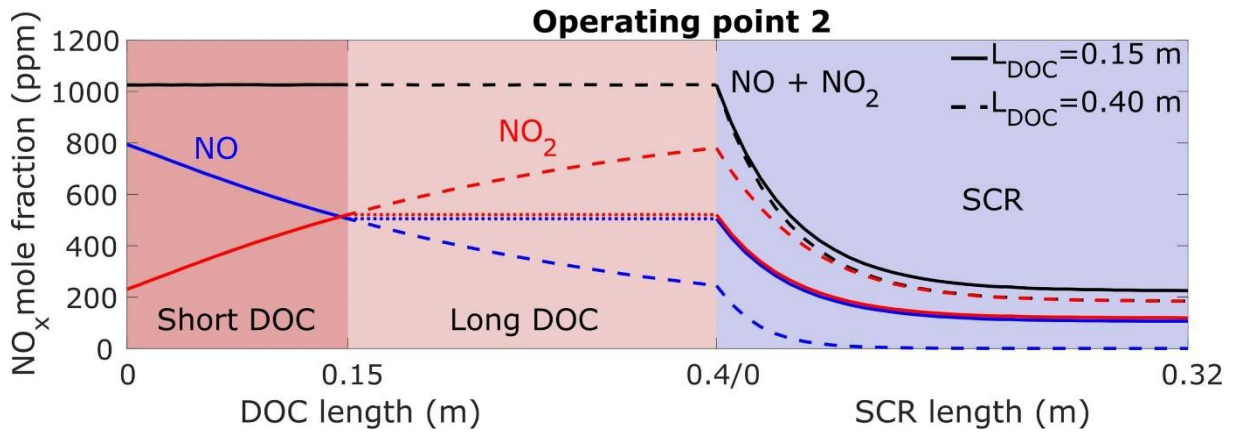


Figure 32. SCR front system [64]

Also operated under different conditions, the DOC oxidises NO to NO₂, allowing the fast SCR reaction to gain dominance in the SCR process. However, higher dosing of NH₃ is needed in this configuration, and a higher amount of NO_x overall is created.

6.1.3 CONCLUSION

The DPF front system showed superior performance because of its ability to regenerate in 6 out of 8 operating points passively. Also, when the DPF had triggered active regeneration, the SCR can further process the exhaust gasses and reduce the final amount of CO.

6.2 ELECTRICAL HEATING ELEMENT

In the past, electrical heating was not considered an option due to increased load on a vehicle's electrical system, leading to a potential increase of the overall emissions due to higher engine load.

With modern mild-hybrid vehicles, this problem is easily overcome by the incorporation of small to medium-sized battery into vehicles design in the first place. Furthermore, this solution is beneficial for hybrid vehicles, while they frequently stop and re-start the combustion engine in order to decrease emissions when stationary.

Heating both – DOC and SCR catalysts had been tested. However tests showed, that heating only DOC is beneficial from an energy standpoint. An experiment was conducted on a 4,5 l engine with a set goal to reach the light-off temperature of the SCR in 200 seconds after cold start. Electrically heated DOC consumed 6,9 kW while heated SRC needed 7,5 kW.

After DOC reaches light-off temperature, SRC is heated very quickly by DOC's waste heat. Heating only DOC had then shown to be beneficial [52].

6.2.1 POSITION

Three different positions of the electrical heating element are viable:

- (a) catalyst skin heating
- (b) substrate heating
- (c) upstream exhaust gas heating

The experiment was conducted by delivering 60 kJ of heat over a span of 30 seconds for each position individually.

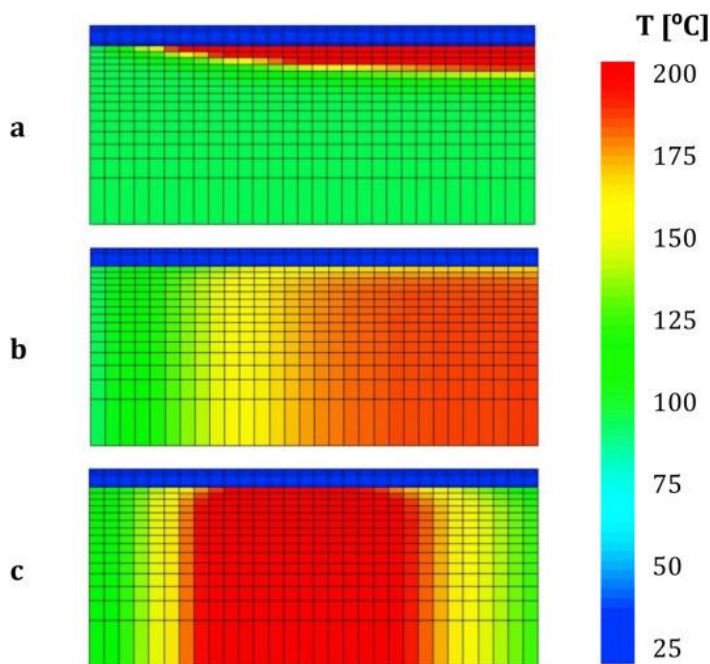


Figure 33. Model of heat distribution in the catalyst [46]

Figure 33 shows the deficiency of skin and substrate heating and superiority of upstream exhaust gas heating solution.

Skin heating fails on the prospect of a really hot but small-surfaced area, which is not able to transfer the heat to the exhaust gas efficiently.

Heating the substrate is a better option, providing sufficient surface area. However, the process of heating up the exhaust gas renders a significant part of the catalyst inactive due to the gas being still too cold to reach the light-off temperature at the entrance.

Finally, the heat distribution of the upstream exhaust gas heated catalyst illustrates its domination over other methods.

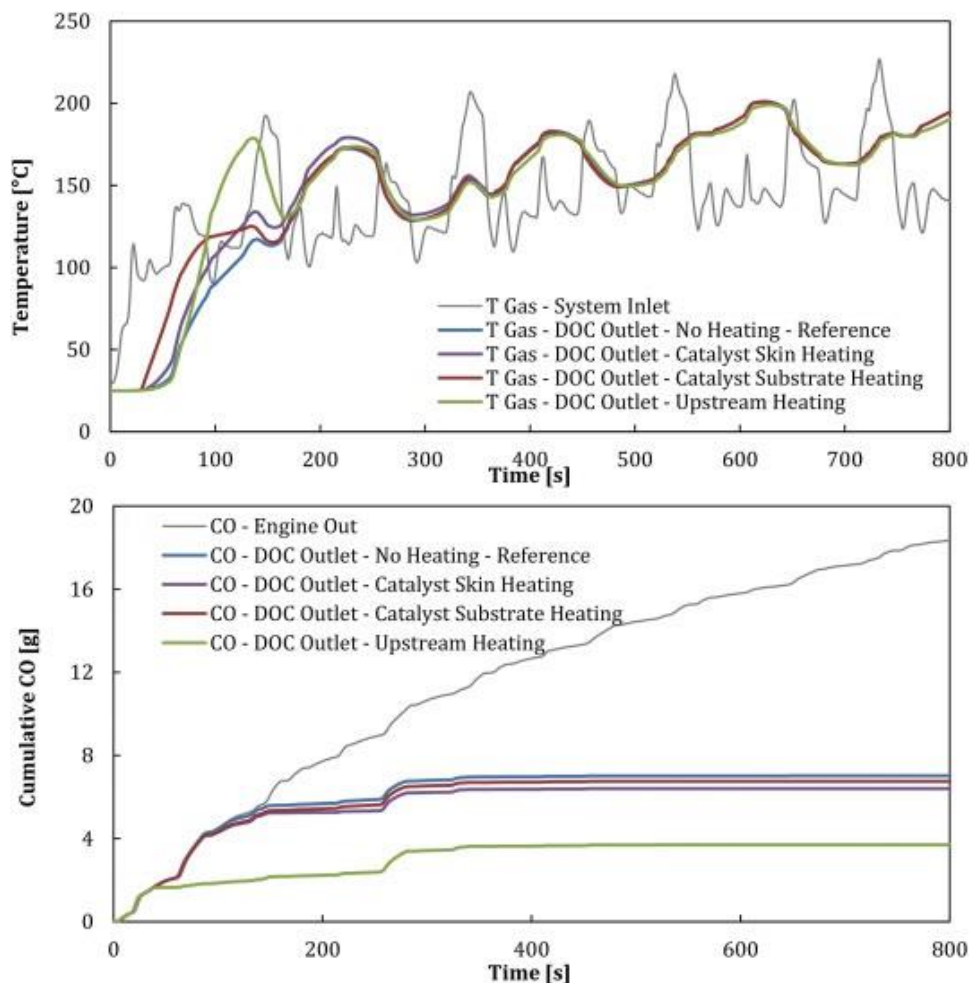


Figure 34. Model of catalyst temperature and CO emissions according to heating element position [46]

As Figure 34 illustrates, the upstream heated catalyst's peak temperature was measured at 137 seconds after cold-start, increasing 62 °C over the reference measurement. The time required for catalyst light-off after cold start decreased from 144 seconds to 42 seconds.

This brought a staggering 47% reduction of carbon-monoxide emissions along with an 18% reduction in emission of total hydrocarbons.

6.2.2 TIMING

It has been established that an upstream exhaust gas heater is the best way to address electrically heated catalyst. In figure 34, it can be seen, however, that there is still room for improvement. Around the 240 second mark, the temperature of the catalyst dropped to as low as 129 °C leading to catalyst deficiency and additional CO as well as total hydrocarbon emission increase. Exhaust gasses provided by the engine are still too cold to hold the light-off temperature of the catalyst, decreasing its temperature and efficiency.

Another heat-pulse, timed to occur between 210 and 230 seconds, resulted in the cancellation of this effect as can be observed in the Figure 35. This brought the total efficiency increase of this system to 70% reduction of cumulative CO and 24% reduction of cumulative total hydrocarbons. 2 kW heater, delivering 120 kJ of energy was used [46]

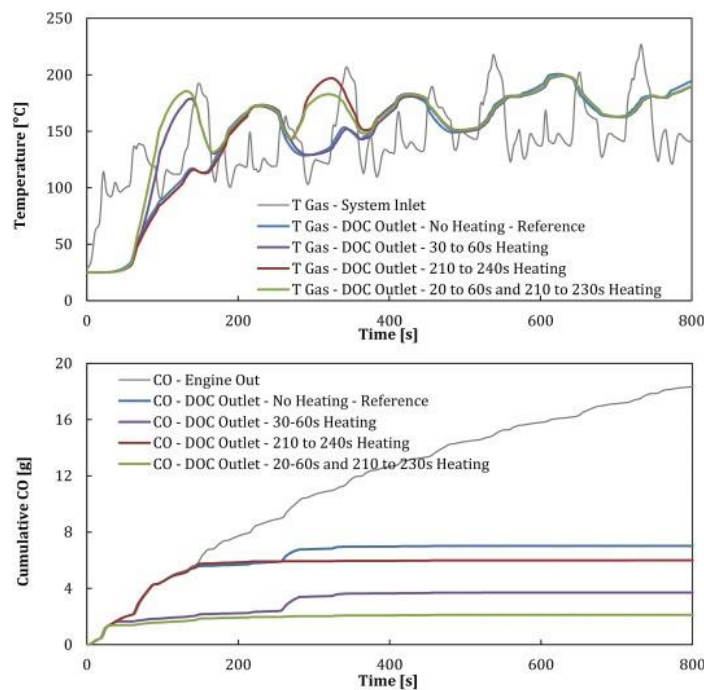


Figure 35. Model of dual preheat cycle of the upstream exhaust gasses [46]

6.2.3 EXPERIMENTAL STUDY

This experiment used 443, 603 and 885 W continuous upstream exhaust gas heaters.

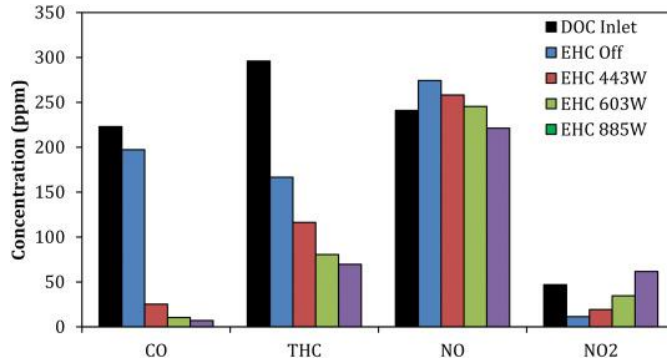


Figure 36. Measured concentration of emissions for multiple power of heating element [46]

Expected results had been measured. An increase in power results in an increase in temperature, leading to emission reduction.

6.2.4 EFFICIENCY

Taking the catalysts thermal inertia into account, pulsation of power yields better results. Continuous 443 W heating and pulsation heating of 885 W was compared, with varying pulsation period from 10 to 40 seconds. These two systems use the same amount of power over the heat-up cycle.

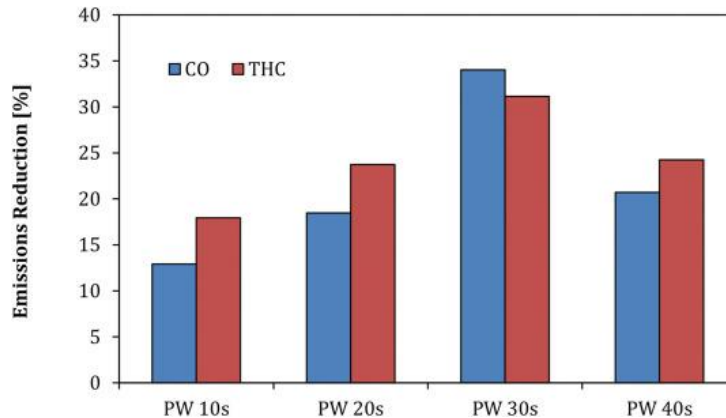


Figure 37. Emission reduction dependency on varying pulsation period [46]

Figure 37 shows the additional emission reduction achieved by pulsation of the 885 W heating element over the continuous 443 W heating element. A pulsation width of 30 seconds was determined to bring the best result.

6.2.5 COMBINATION WITH FUEL POST INJECTION

Referring to the upper-mentioned secondary fuel injection (5.3) combination of these systems had been tested:

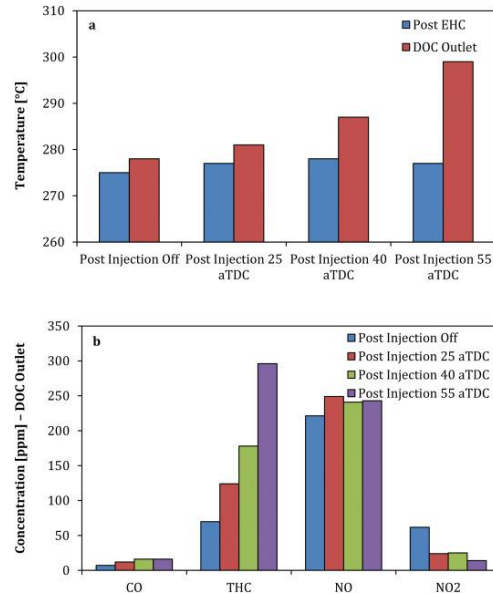


Figure 38. Emissions of post-injection and electrical heating element combination [46]

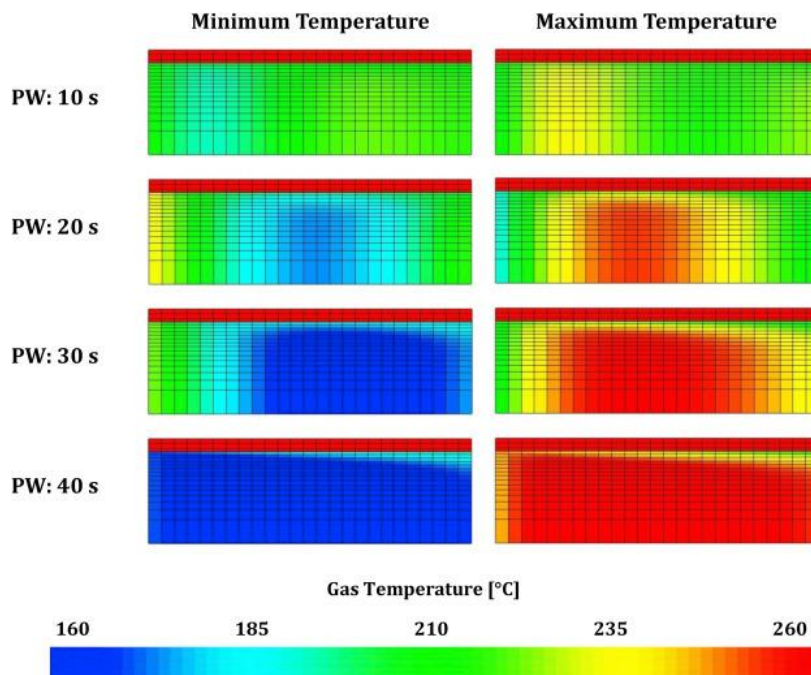


Figure 39. Catalyst temperature distribution with electrical heating and post-injection combined [46]

In combination with the electrical heating, fuel post-injection did increase total hydrocarbon emissions too. However significant decrease was observed in NO_2 reduction, mainly because of cooling of the cylinder upon post-injection. DOC outlet temperature has risen substantially to over 300 °C, which is beneficial for passive DPF regeneration and SCR efficiency downstream of DOC [46].

6.3 ENERGY STORAGE IN PHASE CHANGING MATERIALS

Instead of saving the engine-generated energy into batteries, direct chemical energy storage might be used.

Phase changing materials are great candidates since the change of material phase requires high energy transfer to occur. It results in storing a larger quantity of heat energy with the same temperature difference.

Optimal parameters for such material are appropriate operating temperature range, high latent heat of phase change, excellent heat capacity and high density – for volumetric and fitment reasons - while maintaining a reasonable cost. The temperature at which phase change occurs should also be taken into account, while optimally being higher, than catalyst light-off temperature. These materials include LiCl/KCl, NaNO₃, KNO₃, KOH [54].

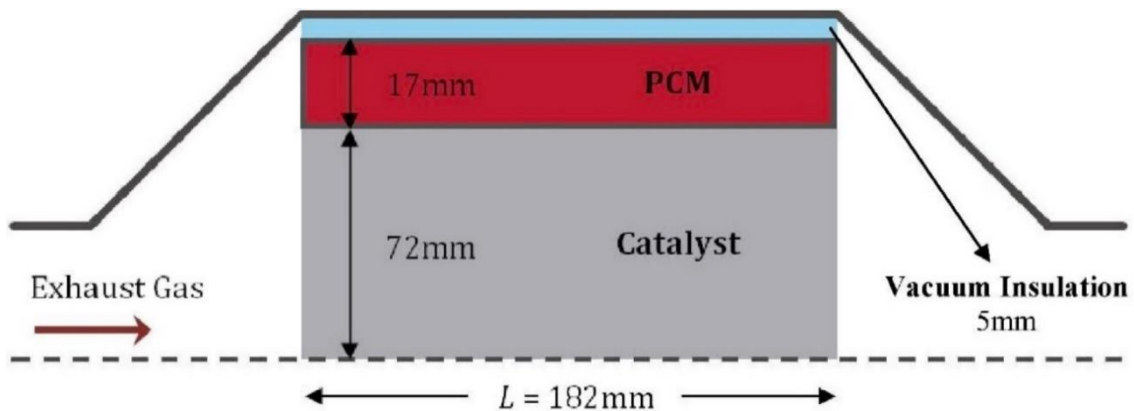


Figure 40. Catalyst design with phase change material (PCM) [53]

6.3.1 EFFECT ON EMISSIONS

As figures 40 and 41 show, the effect on emissions is clearly visible. Thanks to the DOC starting the cold-start cycle at above light-off temperature, the CO emissions were practically non-existent with a reduction of 93 % versus traditional DOC with no phase change material being achieved. Total hydrocarbon content (THC) was also reduced by up to 41 %.

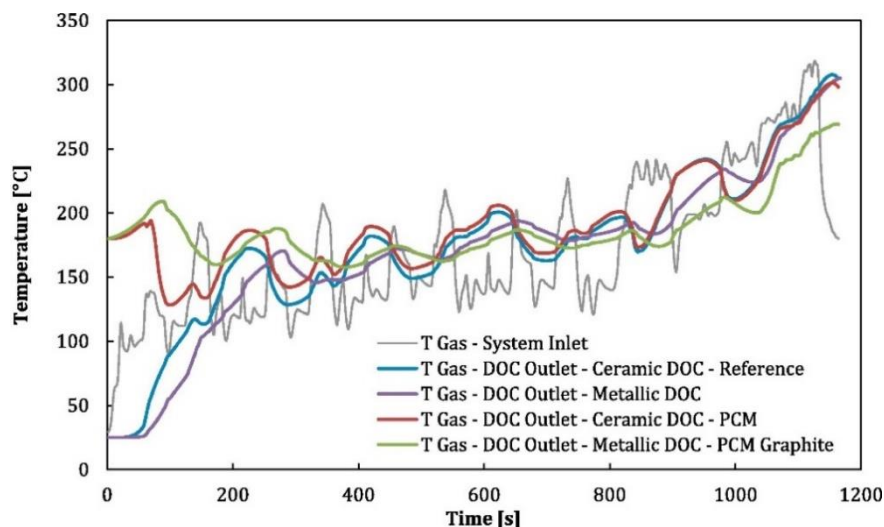


Figure 41. DOC temperature upon cold-start [53]

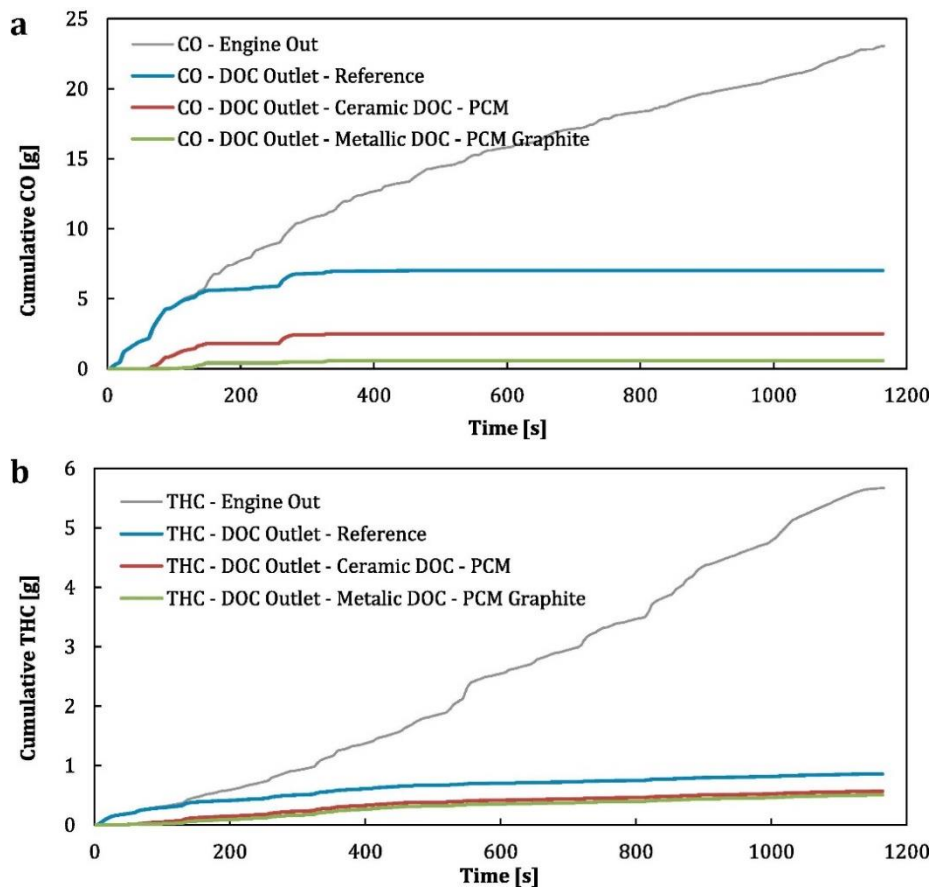


Figure 42. Cumulative emissions of different catalyst-phase change material configuration [53]

6.3.2 HEAT STORAGE

The principle of this device's operation is to store the heat energy and keep the catalyst above the light-off temperature. As figure 43 shows, the catalyst temperature is held at phase change temperature (180 °C) while the material gradually solidifies. After 100 % of the material solidified, DOC starts to cool down until reaching ambient temperature.

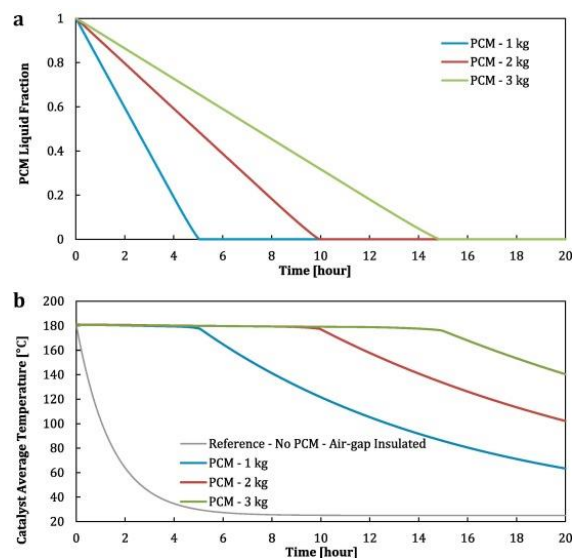


Figure 43. Temperature fade of the catalyst with phase change material [53]

6.3.3 ALTERNATIVE DESIGN

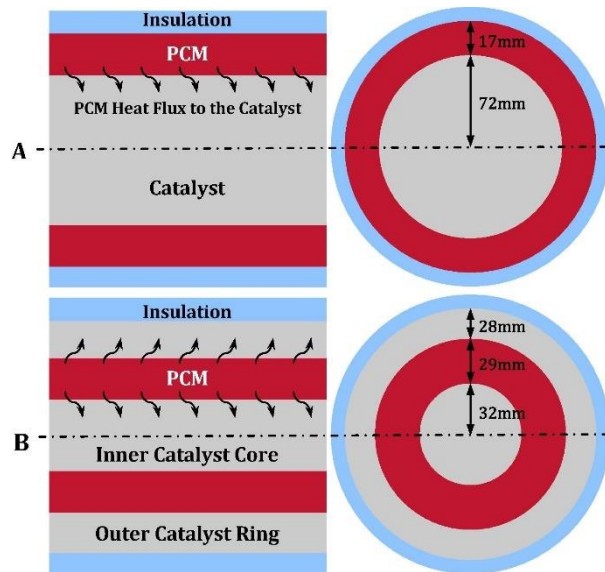


Figure 44. Design optimisation of phase change material [53]

Figure 44 shows different placements of the phase change material, viable in the DOC, while figure 45 confirms that the arrangement B (green – optimised design) is beneficial in the heat-up phase, delivering up to 37 % more energy to the after-treatment system in the first 200 s after engine start. [53]

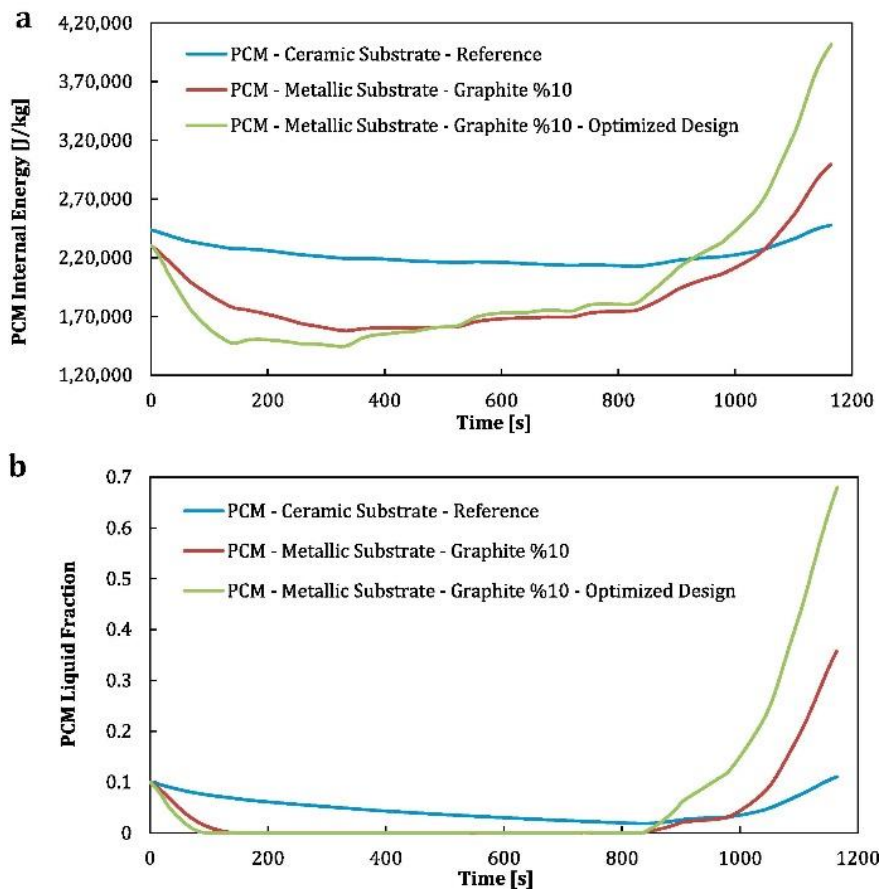


Figure 45. Design optimisation of phase change material [53]

6.3.4 SHORTCOMINGS

The phase change material can store energy only for a certain amount of time. This time will vary depending on ambient temperature, amount of the material and also with driving style. For example, if the vehicle was driven for very short periods of time, the phase change material did not fully liquefy and will hold the temperature for a shorter time.

As it was experimentally proven, the material solidifies with a rate of approximately 1 kg per 5 hours. After a fully solid state was reached, it continues to cool down by radiating heat. This is demonstrated in figure 43.

If the vehicle was stopped for a prolonged period of time and the material reached ambient temperature, the possibility of negatively affecting emissions upon the next cold start had been tested. When the exhaust gasses are heating the DOC, phase change material effectively acts as a heatsink, removing the heat energy from the catalyst, leading to a 26% increase of CO and 20% increase of total hydrocarbons emitted in the period of cold-start up to light-off temperature. [53]

Implementing the phase change material can be very beneficial for frequently used vehicles, while it might bring possibly an aggravating effect to vehicles that are used more sporadically.

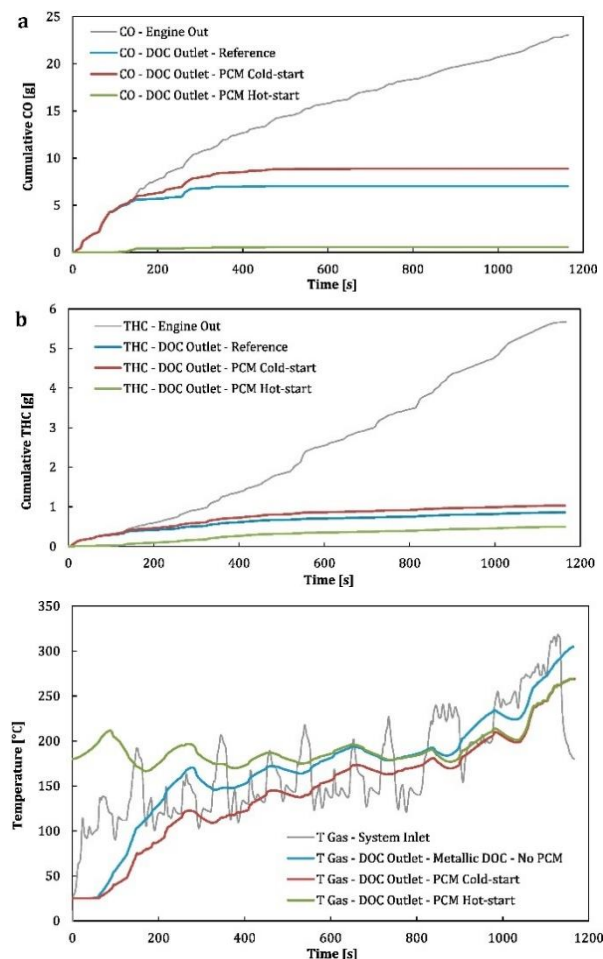


Figure 46. Phase change material at ambient temperature slowing down the heat-up of DOC [53]

6.4 CHEMICAL ENERGY STORAGE

This system of energy storage tries to battle the shortcomings of the phase change material energy storage.

This method does not involve heat transfer but rather chemical reactions. The goal is still the same – heat up the catalyst as fast as possible with the least negative effects.

6.4.1 CONFIGURATION

Generally, materials that create a chemical, exothermic reaction when exposed to water are used. A great example is magnesium hydroxide ($\text{Mg}(\text{OH})_2$). It is combined with expanded graphite in a mass ratio of 8:1 for better thermal conductivity. This compound is called an EM8block.

The system consists of 2 separate parts. One of them is the reactor, placed between the exhaust manifold and catalytic converter. The second one is the water tank.

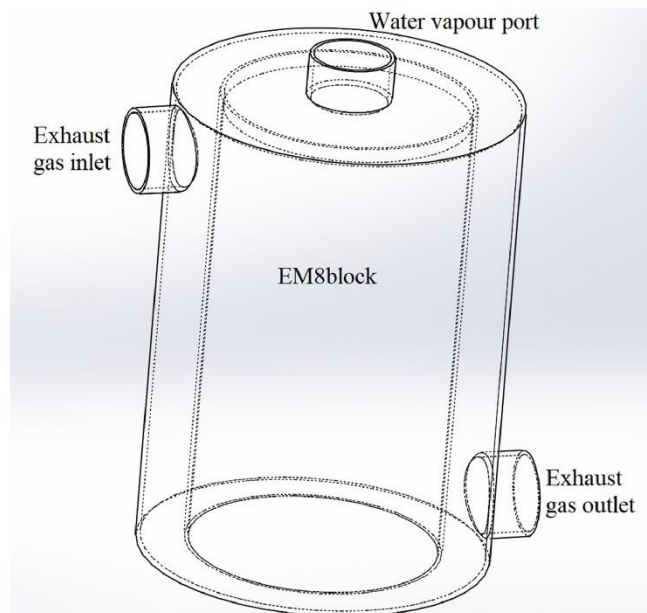


Figure 47. Chemical energy storage reactor [55]

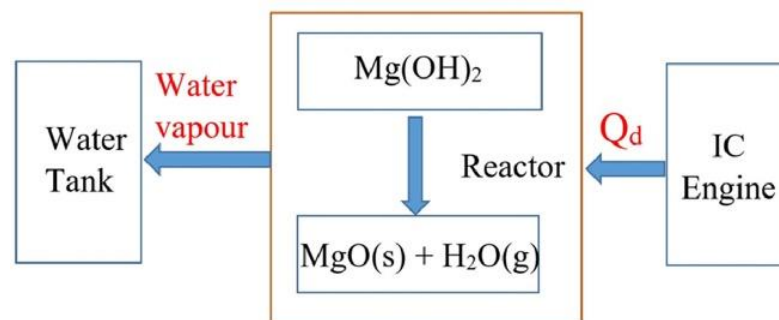
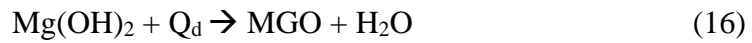


Figure 48. Configuration of chemical storage system during energy storage [55]

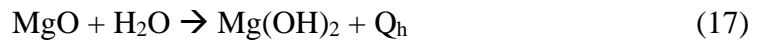
The storage system works on the basis of a simple combination of exo- and endothermic reactions. When the engine is at operating temperature, as figure 48 shows, heat from the engine is used to dehydrate the solution:



This reaction is endothermic and consumes heat. The MGO stays entrapped in the reactor while the H₂O is transferred to a water tank. This water tank can constantly be topped up by exhaust vapour condensation. Thus no refilling by the user is needed.

6.4.2 ENERGY RELEASE

When the new driving cycle begins – with a cooled-down engine – water from the water tank is evaporated by a small electrical resistance heater. This vapour enters the reactor and reacts with MgO in an exothermic reaction:



During this reaction, heat is released and can heat whatever medium necessary. In the study testing this method, the experiment was set up to heat the engine air intake [55].

The experiment started with an ambient temperature of 23 °C. The temperature of the reactor core reached up to 162 °C. However, the heat transfer through the shell in which the reactor is enclosed showed to be a significant limiting factor of this energy-storage method.

It took 11 minutes for the reactor wall to reach a temperature of 45 °C, which is very slow compared to other heat storage methods. The effective outer-shell temperature reached up to 90 °C over time.

The main benefit of this system remains in time. As had already been discussed, other methods retain the heat energy for a maximum of 24 hours. However, due to volumetric design restraints, reaching only 12 to 18 hours in a real-world application is common. Chemical energy can be stored almost indefinitely.

6.4.3 SHORTCOMINGS

The heat-up of the reactor is very slow, resulting in practically unusable application in emission-reduction efforts.

The energy storage also requires up to 60 minutes until the Mg(OH)₂ dehydrates, leaving the reactor ready for the next energy release.

6.5 EXTRA COMBUSTION DEVICE – AUXILIARY POWER UNIT

Applicable mainly to large-size transportation vehicles, the addition of an extra combustion device eliminates the need for prolonged idle operation of the main engine if the vehicle is stopped. This leads to significant improvements in overall vehicle emissions.

Installation of secondary, small combustion engine used for power and heat generation shows up to 70% reduction in NO_x emissions versus the main engine running at idle. The power is mainly used for the cabin comfort features, while the heat generated is partially used to maintain or preheat the main engine. This helps lower in-cylinder emission generation while also speeding up the catalyst heat-up process upon the next start.

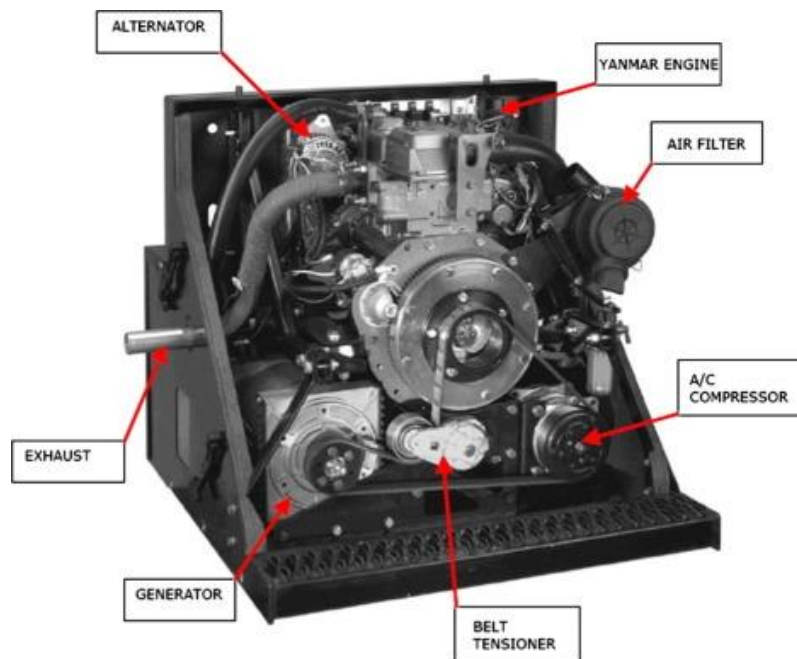


Figure 49. Auxiliary power unit [48]

7 EMISSION COMPLIANCE

7.1 HISTORICAL DEPLOYMENT OF TECHNOLOGIES

7.1.1 OXIDATION CATALYST

Catalytic convertor had been used on both – diesel and gasoline internal combustion engines (ICE) for decades. They have been developed at the end of the 19th century in France. Eugene J. Houdry first patented this device in 1952. [2] While the diesel oxidation catalyst (DOC) had been used since 1967. These devices became mandatory by the year 1970, defined by clean air act resolution in the US [15] and 70/220/EEC directive in the EU [16].

7.1.2 DIESEL PARTICULATE FILTER (DPF)

The first mentions of particulate matter reduction come from 1969, when Daimler-Benz carried out experiments with fine metal mesh. The first real-world tests were carried in 1985 on public transport vehicles. The first vehicle manufacturer to equip a mass-produced model with DPF was PSA group, who in the year 2000 equipped its new HDi engines with particulate filters as standard [58]. With the onset of Euro IV in 2005, almost every manufacturer was forced to implement DPF, while it was otherwise technically unviable to obey set limits.

7.1.3 SELECTIVE CATALYTIC REDUCTION

Engelhard Corporation, based in the USA, patented the SCR technology first in 1957. The first-ever documented use was on two Korean carrier ships. Made in 1989 and 1990, the system reached an efficiency of 92 %, however, was used only when sailing through waters with regulated NO_x emissions. The first production road-going vehicle using SCR was Nissan Quon heavy-duty truck, which started mass-production in November 2004. The SCR became mandatory with EURO VI in 2014 since no other way to obey the 80 mg/km of NO_x required existed [59].

7.1.4 EGR

The first applications of EGR started to appear in 1972. However, they were highly problematic. Low power, bad idling characteristics, poor cold-start performance, those were all the reasons why the early valves were more than sporadically blocked off by the vehicle owner. Volkswagen introduced the first variable system in 1973, which regulated the amount of gas recirculation by a valve. Beginning with EURO III in the year 2000, the amount of NO_x had been regulated, which lead to the EGR valve being basically mandatory on all vehicles.

7.1.5 LOW-PRESSURE EGR

The first vehicle to introduce low-pressure EGR was Volkswagen Jetta 2.0 TDI in 2008. While more widespread implementation is seen from the year 2011 when EURO V was proposed.

7.1.6 ELECTRICALLY HEATED CATALYST

The first electrically heated catalyst had not yet been put into mass production. However, a Vitesco technologies company with its Emicat catalyst had revealed that they are working on a multi-million contract related with a major manufacturer, leading to an electrified van that will start production in late 2022. Mandatory usage of this technology is to be expected in EURO VII compliant vehicles.

7.2 MEETING THE EURO VII LIMITS

Euro VII will become mandatory in 2025.

The main difference in oppose to today's Euro VI d will include 80 to 30 mg/km reduction in NO_x emissions along with 95 to 30 g/km in CO₂ reduction. Since CO₂ emissions are directly correlating with fuel consumption, it can be estimated that to reach 30 g/km in CO₂ emissions, the fuel consumption of the vehicle should not exceed 1,2 l/100km of diesel fuel.

Since today's diesel internal combustion engines work with an efficiency of at best 45 %, with real-world consumption reaching approximately 5 l/100km of diesel fuel, it is safe to say that this requirement will not be met since the engine would have to break the laws of thermodynamics and reach above 200% efficiency.

However, there are still multiple situations in which internal combustion engines won't become a technology of the past.

7.2.1 EURO VII LIMITS ARE NOT MANDATORY YET

Since the limits are still in the proposal stage, there is a chance that pressure on the EU from automotive manufacturers will have an effect. The final numbers might end up more realistically achievable.

7.2.2 ALTERNATIVE FUELS

Since the main objective is to limit the complete emissions of a vehicle, proposals for alternative fuels had been made. The leader in this space is a Canadian-based company Carbon Engineering, which since 2009 specialises in synthesizing hydro-carbon fuel from air.

The basic principle of their device is to capture CO₂ from the air and then use renewable energy (for example, solar) to split water into oxygen and hydrogen through electrolysis. CO₂ and H₂ are combined via chemical reaction to form hydrocarbons, while the leftover oxygen is released into the atmosphere.

On a large enough scale, this system could subsidise the CO₂ emissions made by internal combustion engine vehicles, effectively decreasing the global average under 30 g/km with ease.



Figure 50. Render of Carbon Engineering prototype [60]

7.2.3 CO₂ CREDIT TRADE

It had been accepted practice for the last few years that electric vehicles manufacturers – mainly Tesla – sells another car manufacturer "zero carbon footprint "that is then averaged with its line-up of cars, enabling him to fit into emission standards.

7.2.4 HYBRIDISATION

Adding reasonably-sized electrical battery into internal combustion vehicles, enabling them to travel a few tens of kilometres on solely electric power, can be hugely beneficial for reducing emissions. This trend had already begun, and a majority of vehicles offered today can be equipped with such system.

7.2.5 ELECTRICALLY HEATED CATALYSTS

As it had been described before, electrically heated catalyst shows superior cold-start operational properties to a traditional one. The recent development of hybrid vehicles with reasonably-sized battery is also a great starting point for electrical heating integration.

7.3 ELECTROMOBILITY

The first and most important thing that needs to be mentioned is that as of today, European Union considers the carbon footprint of electric vehicles to be 0 g/km.

Tesla Model 3 standard range – being one of the most efficient electric vehicles on the planet, reaches combined consumption under ADAC test of 15,3 kWh/100km. Real-world test [61] shows that this number might be too optimistic and might reach up to 19,5 kWh/100km. For the purpose of this calculation, both values will be used to showcase potential and real-world emissions.

The average emissions generated by power stations of the ČEZ group in the Czech Republic from the year 2019 are 361 g CO₂/kWh [62].

If the electric vehicle is given every benefit of the doubt, including 100% transmission efficiency and 100% charging efficiency (both of those being unrealistic), the total emission footprint of the Tesla Model 3 is 55,2g CO₂/km [61].

For the more realistic model, measured 19,5 kWh/km is used along with assumptions of 93% charging efficiency and 77,5% energy transmission efficiency [63]. This model results in the total emission footprint of the Tesla Model 3 being 97,67 g CO₂/kWh.

7.3.1 INITIAL EMISSIONS

It is commonly stated, that batteries are the biggest problem of electric vehicles. Their lifespan, toxic chemicals used throughout their production and other factors beyond the scope of this thesis need to be considered as well. For the purpose of this thesis, today's respected average of 75kg CO₂ per 1 kWh of battery capacity manufactured will be assumed [64].

The capacity of the Tesla Model 3 standard range battery is 54 kWh. This adds 4050 kg of CO₂ to the initial starting point. It can be observed in Figure 51 that this handicap returns only after 50 000 km of driving, considering optimistic diesel and electric vehicles. However, in a realistic scenario, the point of return moves to around 100 000 km. It is also important to note that more than one battery pack might be needed during the vehicle's lifespan.

The factor of the battery size also plays a big role. For example, Tesla Model 3 long-range, equipped with a 79 kWh battery, moves the point of return for the realistic scenario to 150 000 km.

7.3.2 LIFETIME EMISSIONS

For comparison, Škoda Octavia 2021 with 2.0 TDI 85 kW diesel engine and six-speed manual transmission had been chosen. Its emissions are 109 g CO₂/km [70].

For its realistic scenario, 140 g CO₂/km is expected. This assumption was made solely by comparing expected vs realistic fuel consumption, which highly correlates to CO₂ emissions. This comparison aims not to compare diesel and electric powertrains, but rather to show that even unrealistically optimistic usage of electric vehicles produces not negligible amount of CO₂ emissions compared to a similar diesel vehicle.

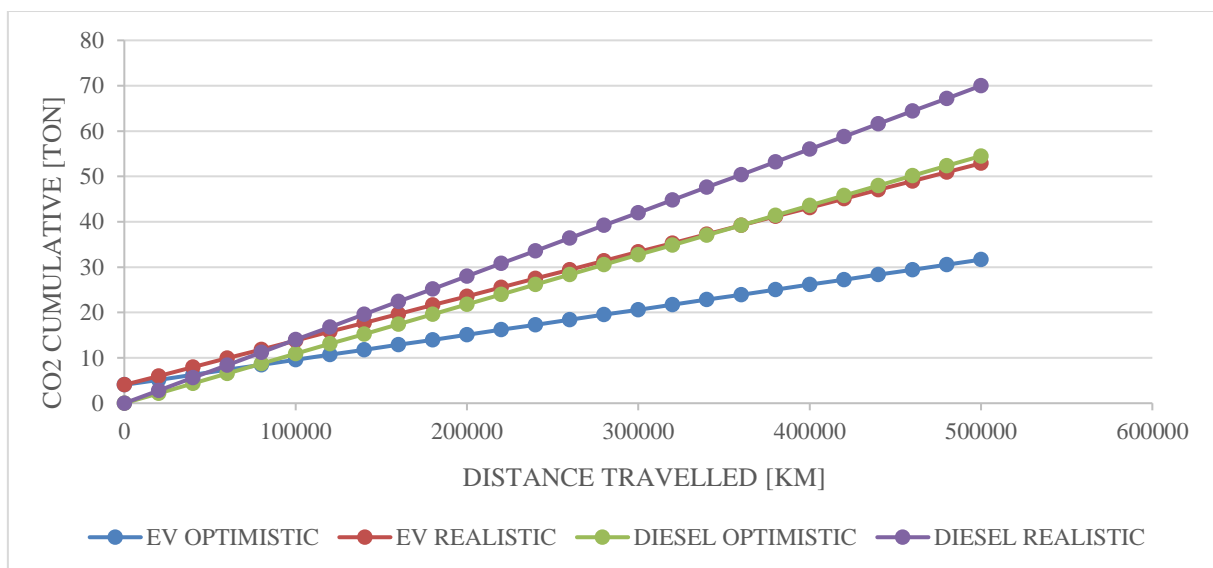


Figure 51. The carbon footprint of electric and diesel vehicles

Even though there are a lot of unknown variables that are out of the scope of this thesis, one conclusion can be made with certainty – emissions of electric vehicles are existent and need to be taken into consideration while suggesting regulation of the industry for the next decade.

EVALUATION

The beginning of this thesis focused on describing the diesel engine fundamentals and the conditions under which emissions are created. It was established that modern engines benefit from higher fuel injection pressure and compression ratio in almost every parameter. Resulting in reducing fuel consumption, CO₂ emissions, soot content and decreasing the particle size (typical particle size exiting the engine reaches 60 to 120 nm in diameter), with the only major drawback being a significant negative effect on NO_x emissions.

The body of this thesis aimed to introduce all of the serially produced emission reduction systems that are fitted to modern diesel vehicles, explain their principle of function and point out their negatives. It was concluded that a typical diesel vehicle of today's production is equipped with high and low-pressure EGR valves to reduce NO_x emissions. These systems take exhaust gasses, cool them down by water-cooled heat exchangers, and reintroduce them into the intake manifold. This operation leads to lowering peak in-cylinder temperature, which is a key factor for reducing NO_x emissions. Emissions are then further processed by a series of catalysts and diesel particulate filter, usually referred to as exhaust system.

The exhaust system usually consists of a diesel oxidation catalyst (DOC), followed by a diesel particulate filter (DPF). After reaching operation temperature, DOC reduces CO and unburnt hydrocarbons emissions with over 95% efficiency while having an observable effect on particulate matter and NO_x emission reduction as well.

DPF filters the particulate matter with up to 99% efficiency. Under perfect operation conditions, passive regeneration is expected to occur, burning off the accumulated particulate matter to a full extent. However, passive regeneration does not work perfectly during the majority of standard driving conditions, leading to the filter filling up. If the amount of particulate matter in the DPF filter reaches a critical limit, active regeneration is initiated by the electronic control unit (ECU), leading to incinerating the accumulated particles.

Upon reviewing the particulate matter emitted during the DPF regeneration, it was found out that a significant amount of particles reaching 5 to 15 nm in size was present. Studies suggest that this size of particles might be even more damaging to the environment than the size of particles in the unfiltered engine exhaust. The current standard states that only particles larger than 23nm are measured and calculated into the required limits. Further independent investigation of the small-diameter particles effect on the environment is undoubtedly needed.

It is not uncommon that DOC and DPF are combined into one enclosure. This brings significant efficiency gains, originating in DPF reaching higher temperature in this configuration, enabling its passive regeneration to occur sooner into the driving cycle while having a positive effect on active regeneration too. Multiple methods of initiating active regeneration are used, while the most frequently installed system relies on excessive heat-up of DOC resulting from unburnt fuel oxidation. This fuel is either injected directly into the exhaust system right before the DOC via a dedicated fuel injector or using a secondary injection of in-cylinder injectors.

Following the DOC and DPF, a selective catalytic reduction (SCR) system is installed. Its role is solely a reduction of NO_x emissions. It is achieved by injecting diesel exhaust fluid (DEF) solution, frequently referred to as AdBlue, into the exhaust system before the SCR catalyst. After the DEF is injected, it decomposes by heat into water and ammonia. When the mixture of exhaust gasses and urea reaches the SCR, the reaction is catalysed, and NO_x is reduced to CO₂, N₂ and water. A slightly excessive amount of the DEF is usually injected to ensure the highest possible efficiency of the SCR. Since ammonia itself is a harmful and highly irritating chemical to numerous living species, including humans, the SCR is followed by ammonia slip catalyst, ensuring that the remaining ammonia is converted to N₂ and water and prevented from entering the atmosphere.

These systems require a fairly high temperature reaching 200 to 350 °C to operate with peak efficiency. This results in most emissions, other than CO₂, are being created during the heat-up phase. Since compliance with EU standards is measured in a normalised driving test that begins with a cold-start, integrating additional heating systems is highly likely to be a requirement in vehicles complying with the upcoming EURO VII standard.

Multiple options of catalyst heating methods were discussed, while the electrical heating element appears to be the most promising one for future vehicles. This unit is located upstream of DOC and works by introducing additional heat into the exhaust system during cold-start. The application of this heater helped reduce emissions significantly thanks to shortening the heat-up time of DOC from 144 to 42 seconds.

Finally, the history of emission reduction efforts was briefly recapitulated, followed by other possible future solutions, including further hybridisation and alternative fuel synthesis from atmospheric CO₂. Furthermore, since a replacement of internal combustion engine by electrical powertrain is highly discussed in today's society, a short comparison of widely used modern diesel engine and the popular electric vehicle had been mentioned.

The measurement of real-world emissions of electric vehicles needs to be addressed mainly because today, they are entirely ignored, which seems at least inappropriate. Further development of electrical energy storage is also much needed to improve the viability of the electric powertrain, mainly by decreasing its weight and increasing charging speeds.

In conclusion, while the distant future is most likely electric, diesel engine development is crucial for providing a viable propulsion system for the upcoming decades until electric powertrains can at least match its properties.

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LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|-------------|-------------------------------------|
| <i>ICE</i> | INTERNAL COMBUSTION ENGINE |
| <i>ECU</i> | ELECTRONIC CONTROL UNIT |
| <i>DPF</i> | DIESEL PARTICULATE FILTER |
| <i>LTC</i> | LOW TEMPERATURE COMBUSTION |
| <i>BDC</i> | BOTTOM DEAD CENTER |
| <i>TDC</i> | TOP DEAD CENTER |
| <i>ISFC</i> | INDICATED SPECIFIC FUEL CONSUMPTION |
| <i>TWC</i> | THREE WAY CATALYTIC CONVERTER |
| <i>DOC</i> | DIESEL OXIDATION CATALYST |
| <i>HC</i> | HYDROCARBONS |
| <i>SOF</i> | SOLUBLE ORGANIC FORM |
| <i>LNT</i> | LEAN NO _x TRAP |
| <i>SCR</i> | SELECTIVE CATALYTIC REDUCTION |
| <i>DEF</i> | DIESEL EXHAUST FLUID |
| <i>TOT</i> | TURBINE OUTLET TEMPERATURE |
| <i>BMEP</i> | BREAK MEAN EFFECTIVE PRESSURE |
| <i>EGR</i> | EXHAUST GAS RECIRCULATION |

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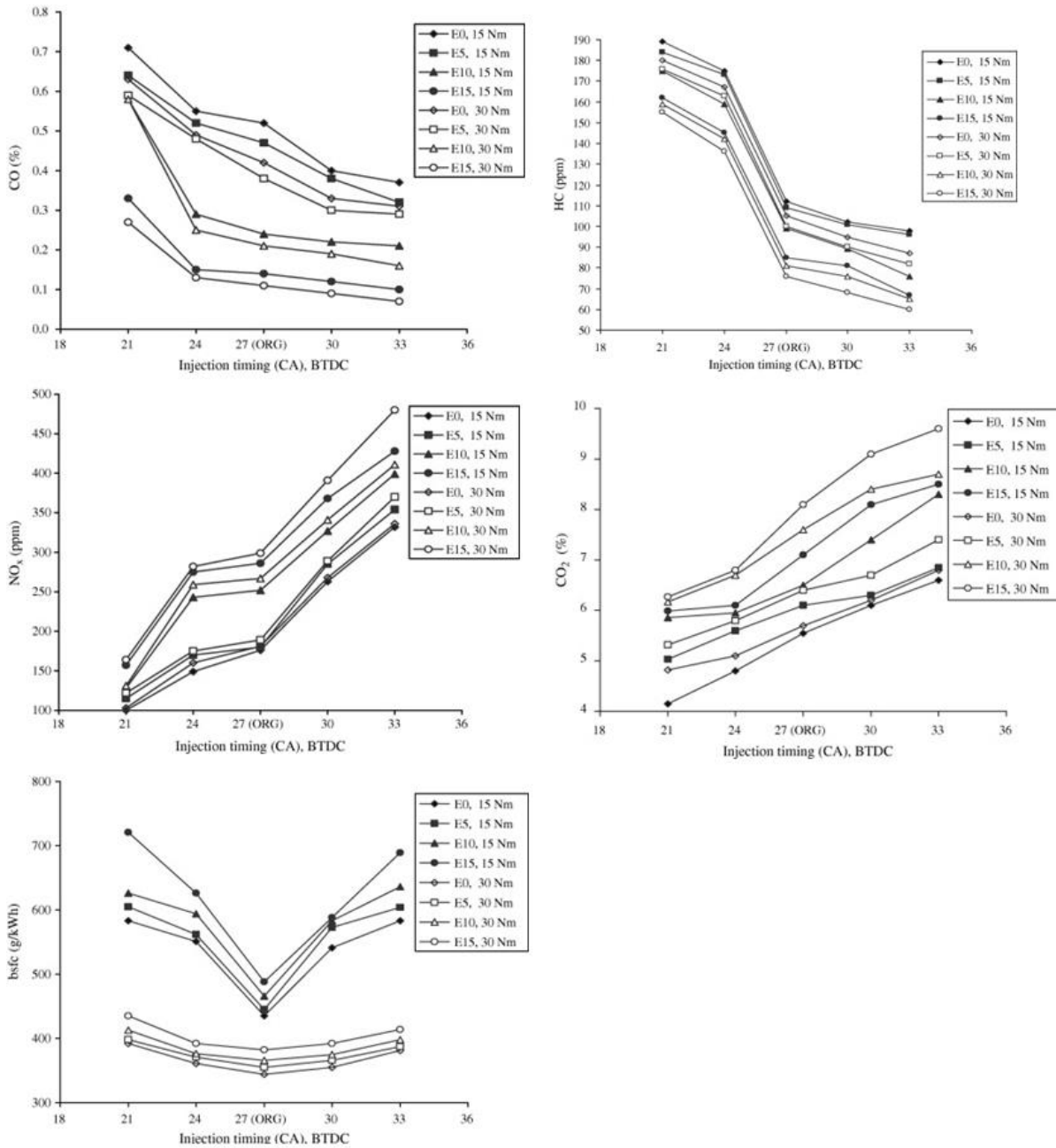
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LIST OF APPENDICES

Appendix 1 Injection timing impact on emissions and BSFC80



Appendix 1 – Injection timing impact on CO, HC, NO_x, CO₂ and break specific fuel consumption [32]