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Engine emissions with air pollutants and greenhouse gases and their control technologies

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ABSTRACT

Diesel and gasoline are the most used fossil fuels due to their high energy release and low cost for engines. However, the emission of air pollutants and greenhouse gases has caused severe environmental issues, and emission regulations are becoming stricter. Recently, several advances in emission control technologies for fossil fuel engines have been available, which need to be reviewed to manifest future research. Here, we reviewed the primary pollutants emitted from the diesel and gasoline-powered engines, their formation process, and the present technologies to control the emissions of greenhouse gases and air pollutants, especially during the COVID-19 pandemic. In this regard, this review concentrates on a particular matter ($PM_{2.5}$ and PM_{10}), carbon monoxide (CO), nitrogen oxides (NO_x), unburned hydrocarbons (UHC), and greenhouse gases (water vapor, CO_2, N_2O, etc.) as exhaust emissions, the difficulties they cause, and the strategies employed to reduce emissions. This review also provides a framework for understanding how to reduce air pollution and greenhouse gasses generated by diesel and gasoline-powered engines.

Keywords: Fossil fuels, diesel, gasoline, diesel- and gasoline-powered engines, environmental issues

1. Introduction

The immense use of gasoline and diesel fuels that started in the industrial period caused several benefits, especially in providing energy and spurring economic development; however, their environmental problems are also significant. Today, air pollution is one of the most critical problems that directly impact the environment and human health. Moreover, air pollution can increase electricity consumption (e. g., central air conditioning to avoid air pollution) and reduce the energy generated by solar cell panels (**Eom et al., 2020**; **He et al., 2020**). **Fig. 1** shows the major health problems caused by different air pollutants and greenhouse gases. Generally, air pollution's health problems are divided into short- and long-term effects. Short-term issues, which are temporary, include headache, skin irritation, irregular heartbeat, etc. On the other hand, permanent, long-term problems, such as blood cancer, decreased lung function, and heart disease (see **Table 3**).

Although there are several policies and legislations regarding energy usage worldwide, reductions in air pollution are not expected to be substantial (**Fig. 2**A). As can be seen, carbon monoxide, one of the most important air pollutants, plays a vital role in air pollution, and it is expected to enhance Air pollutant emissions worldwide from, 2020 after a sensible reduction from 2015 to 2020.

Additionally, unequal exposure to air pollution, and varied response to a given level of air pollution, lead to health inequities across and within nations, a phenomenon often referred to as environmental justice (**Rao et al., 2021**). Recently, the COVID-19 epidemic has been proved to affect energy demand and is projected to have a long-term influence (**Kikstra et al., 2021**). Viruses such as SARS-CoV-2, which is responsible for the current COVID-19 epidemic, may bind to other particles, altering their aerodynamic properties and causing airborne transmission. Research suggests that those who live in places with higher levels of air pollution have more COVID-19 cases (**Hoang et al., 2021a**, **2021b**; **Nguyen et al., 2021a**; **Prather et al., 2020**) and have been found almost in aerosols ranging in size from 0.25 to $>$4 pm (**Wang et al., 2021a**). Due to these problems, decision-makers have explored and enacted a variety of strategies to lower air pollution, such as regulation for emission control (i.e., limiting the emissions of CO_x, NO_x, and other pollutants emitted by vehicles (**Datye and Votsmeier, 2021**)), manufacturing green-energy cars and using of solar and wind energies (**Stokes and Warshaw, 2017**; **Kempa et al., 2021**). Although renewable energies have significant environmental benefits, their cost and performance and perceptions about cost and performance still limit their usage.

An active area of research is identifying which air pollution types and mixtures are most harmful to aid decision-makers in prioritizing air pollution control. One of the most significant anthropogenic contaminants is PM, with the main constituents of soot, a by-product of incomplete biomass and fossil fuel combustion, among other sources (**Lohmann et al., 2020**). Soot particles are mostly comprised of UHC and black and organic carbon and have a wide range of physicochemical characteristics depending on the combustion source (**Fayyazbakhsh and Pirouzfar, 2017**; **Ramanathan and Carmichael, 2008**).

Although PM_{10} are also harmful to health, $PM_{2.5}$ are reported as the most dangerous for human health as they penetrate deep into the respiratory system and further contribute to climate change (**Loh et al., 2012**). As a result, determining the influence of soot on atmospheric processes and their involvement in cloud formation and climate change is important (**Lohmann et al., 2020**). Another pollutant critically important to health and ecosystem damage is NO_x (**Peng et al., 2018**). On-road vehicles with diesel engines account for around a quarter of worldwide anthropogenic NO_x emissions. NO_x emissions are critical precursors for the formation of $PM_{2.5}$ and ozone. In most markets, NO_x emission standards have become gradually more stringent; however, modern diesel vehicles generate considerably more NO_x under real-world conditions than in laboratory settings (**Anenberg et al., 2017**).

SO_2 are another pollutant generated by internal combustion engines that are not discussed in depth in this review. SO_2 can be released from the burning of most types of fossil fuels that have a substantial adverse effect on human health. The release of sulfuric acid significantly influences atmosphere chemistry, air quality, climate, and ecosystem health, as well as causing adverse health outcomes such as cancer and cardiovascular issues (**McLinden et al., 2016**). The severe pollution haze in East Asia, in particular, results from exceptionally high amounts of sulfate emissions (**Su et al., 2020**; **Liu and Abbatt, 2021**). Moreover, SO_2 has ecological impacts on soil, forests, and freshwater. Also, they are the main content of sulfuric acid production (i.e., "acid rain") (**Smith et al., 2019**). SO_x emissions, aerosol sulfate production, and sulfate aerosol and dispersion of these components in the environment have all occurred at rates that greatly exceed the return of industrial S to more stable geologic elements (**Hinckley et al., 2020**).

Abbreviations

COP26	26th UN Climate Change Conference of the Parties
E10	A blend of 10% ethanol and 90% gasoline
ATCF	$Al_2O_3 - TiO_2/CeO_2/Fe_2O_3$
Al_2TiO_5	Aluminium titanate
ANCF	Al_2O_3-$Nb_2O_5/CeO_2/Fe_2O_3$
AFR	Air/fuel ratio
ASC	Ammonia slip catalyst
AOC	Ammonia oxidation layer catalyst
ACCT	Ammonia creation and conversion technology
NH_4NO_3	Ammonium nitrate
AB	Argemone Biodiesel
BC	Black Carbon
BSFC	Brake Specific Fuel Consumption
CARB	California Air Resources Board
CCS	Carbon capture and storage
CO_2	Carbon dioxides
CO	Carbon monoxide
CDPF	Catalysed diesel particulate filter
CAGR	Compound annual growth rate
COVID-19	Coronavirus Disease 2019
CRDi	Diesel common rail direct injection
EDI	Direct Ethanol Injection
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
DAC	Direct air capture
DF-PCCI	Dual fuel Premixed Charge Compression Ignition
EPA	Environmental Protection Agency
φ	Equivalence ratio
λ	Excess air ratio
EGR	Exhaust gas recirculation
GDI	Gasoline direct injection
GPF	Gasoline Particulate Filter
GHGs	Greenhouse gases
HSDF	High Speed Diesel Fuel
HCCI	Homogenous Charge Compression Ignition
HO_2	Hydroperoxyl
OH	Hydroxyl
IPCC AR6	Intergovernmental Panel on Climate Change Assessment Report 6
MARPOL	International Convention for the Prevention of Pollution from Ships
IMO	International Maritime Organization
LNT	Lean NO_x Trap
LTC	Low-Temperature Combustion
MOFs	Metal-organic frameworks
NRT	Near-Real-Time
NO	Nitric Oxide
NO_x	Nitrogen oxides
NO_2	Nitrogen dioxide
N_2O	Nitrous oxide
NTP	Non-thermal plasma
NSR	NO_x storage-reduction
OC	Organic carbons
O_3	Ozone
PGM	Pt, Pd, Rh
PM	Particulate matter
PM_{10}	Particulate matter with lower than 10μ in size
$PM_{2.5}$	Particulate matter with lower than 2.5μ in size
PNA	Passive NO_x adsorbers
Pt	Platinum
PGMs	Platinum group metals
PAHs	Polycyclic aromatic hydrocarbons
PFI	Port fuel injection
PCCI	Premixed Charge Compression Ignition
RON	Research Octane Number
Rh	Rhodium
SCR	Selective catalytic reduction
SARS-CoV-2	Severe acute respiratory syndrome coronavirus 2
SW	Shortwave
SiC	Silicon carbide
SACs	Single-atom catalysts
SI	Spark Ignition
SO_2	Sulfuric oxides
3DOM	Three-dimensionally ordered microporous
TWC	Three Ways Catalytic converter
UHC	Unburned hydrocarbons
UNFCC or COP21	United Nations Frameworks Conversion on Climate Change
VCR	Variable compression ratio
VOCs	Volatile organic compounds
WCO	Waste cooking oil
WHR	Water to hydrogen ratios
WHO	World Health Organization

CO produced during incomplete combustion is another important pollutant for human health (**Motterlini and Otterbein, 2010**; **Fujita et al., 2001**) as the human lungs absorb CO more than oxygen if there is the same amount of each in the environment. The emissions from China and the US are shown in **Fig. 2**B, which shows that CO has the highest air pollution emissions compared with other pollutants. Due to more stringent regulations, the amount of generated pollutants in the US was less than in China.

CO_2, which are the main product of complete combustion of fossil fuels, are critical GHGs, absorbing heat from the atmosphere and contributing to climate change. There are currently two methods to deal with the ever-increasing CO_2 levels in our biosphere: carbon seizing and storage or carbon seizing and usage (**Babacan et al., 2020**), which is due to their significant potential for CO_2 storage in natural areas such as depleted gas and oil fields, coal beds, and aquifers (**Aresta et al., 2014**). Carbon seizing and storage include the collection of CO_2, as well as its separation, compression, and transfer, in order to permanently deposit it, while carbon seizing and usage includes either biological/chemical conversions to fuels and products or direct CO_2 usage such as for fire extinguishers (**Navarro-Jaen et al., 2021**).

The increasingly strict emission regulations make a considerable number of researches about the emission of fossil fuel-powered engines springing up. It is urgent to review them to manifest the pollutants and their control technologies for future study and practice. This review discusses the air pollution and greenhouse gases generated by burning the two different types of fossil fuels, diesel and gasoline, the mechanisms of creating those pollutants, and the techniques used to control them in recent years. Finally, a short discussion on possible future techniques and recommendations is provided.

2. Diesel, gasoline, and engines

Diesel and gasoline emissions are affected by engine operating factors (load, speed, spark timing, AFR, and fuel compositions (specifically the C/H atom ratio) (**Wallington et al., 2006**)). Understanding the exhaust emission of these fuels needs a comprehensive view of both fuel and engine.

Substantial changes in global car sales of gasoline and diesel are anticipated over the next few years. In this case, cars with the gasoline engine are expected to reduce from 78% in 2019 to 44% in 2030, and diesel engines from 14% to 4% for the same period (Breakdown of global car sales, 2020). These reductions could result from regulations and policies enacted in the US and other western countries that facilitate the manufacture and use of hybrid cars (**Breakdown of global car sales, 2020**; **Borlaug et al., 2021**).

2.1. Diesel and gasoline

Diesel is the heavier portion of the distillation tower of the petroleum refinery, mainly composed of C_{10} to C_{22}, which are slightly branched paraffin and naphthene. It is denser than gasoline and has about 15% more energy by volume, while gasoline has better energy per unit mass. The main characteristics of diesel and gasoline are listed in **Table 1**. Diesel has a high content of aromatics (about 35%) that is usually slow in diesel combustion owing to their low cetane number. Diesel has a dimensionless cetane number to measure its ignition performance or quality. Cetane number of diesel ranges from 0 to 100, premium diesel has a cetane number between 47 and 52, and due to the standards of the USA and other countries, it should be higher than 45 (**Eagan et al., 2019**). Although the higher number of C_{10+} can make a poor cold-flow characteristic for low-temperature diesel uses, they can enhance the desired cetane number (as it has lower ignition delay) (**Chen et al., 2018a**). However, having a higher number of naphthene causes a lower cetane number but better cold-flow characteristics (see **Table 2**).

Gasoline is mainly composed of C_4 to C_{12} compounds, containing a blend of hydrocarbon families, including 30% aromatics, 8% naphthenes, 16% paraffin, 30% isoparaffins, and 16% olefins (**Shrivastav et al., 2017**). RON is an identifier of gasoline resistance to auto-ignition/knocking quality and is the most vital gasoline use parameter with values from 0 to 120. The lowest RON of gasoline is 87, the middle RON is usually 89-90, and the premium gasoline has RON between 95 and 96 (**Mabood et al., 2017**; **Gasoline explained, 2020**).

2.2. Diesel- and gasoline-powered engines

Diesel and gasoline-powered engines are internal combustion engines (an integral part of the climate problem (**Ueckerdt et al., 2021**)), a type of heat engine in which fuel is burned with an oxidizer, typically air, in a combustion chamber.

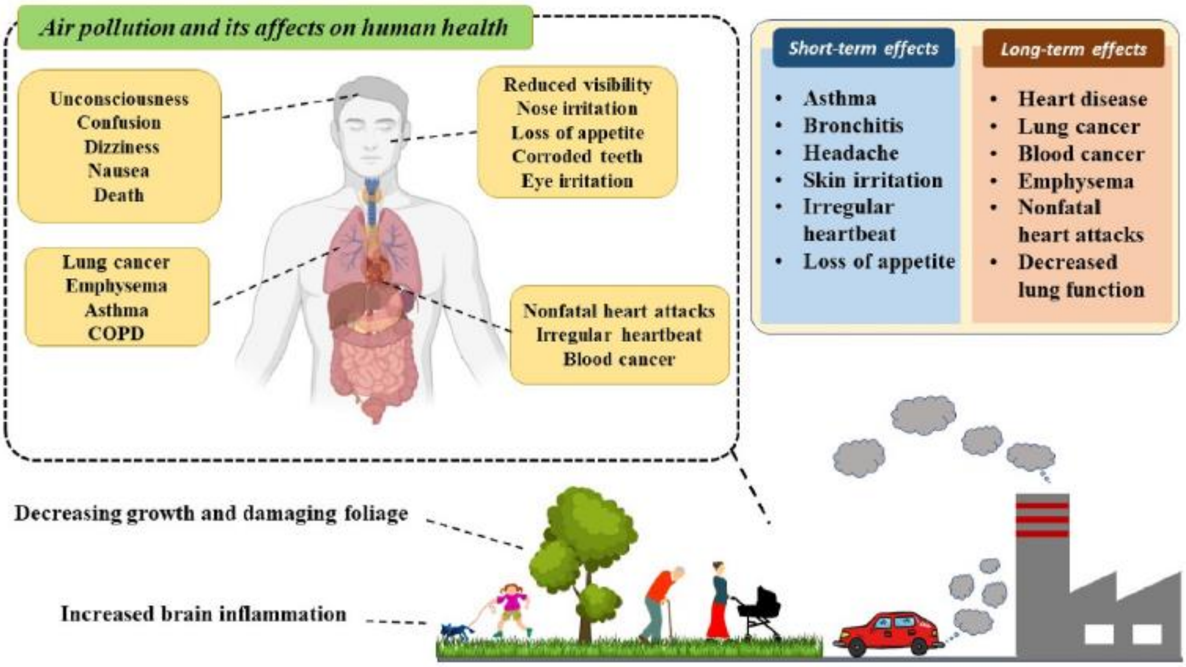

Fig. 1. Air pollution and its adverse effects on human health.

Because of the emissions created by this type of engine, many nations have declared plans to phase out internal combustion engine cars and promote electric vehicles (as the difference between hybrid electric vehicles and internal combustion engines is comparatively smaller (**Jenn, 2020**)) in response to the Paris Agreement (**Yang et al., 2021a**). However, it is expected that the internal combustion engine will continue to play a significant role in the following decades. Furthermore, internal combustion engine efficiency increases are possible since most spark-ignition engines' efficiency is generally 25-35%, but compression-ignition diesel engines are around 40-50% (**Chu and Majumdar, 2012**).

Diesel engines have also been used for maritime transportation in addition to the common. Therefore, the environmental issues triggered by the emission in coastal areas should also be considered (**Hoang and Pham, 2018**). IMO, the EU, EPA, the MARPOL (limits NOX and SOX), and the Ministry of Environmental Protection of China have fulfilled regulations to reduce the emitted pollution from marine diesel engines.

One of the main problems in diesel- and gasoline-powered engines is metallic alloy corrosion. In those engines' types, several factors, such as using biobased fuels (due to their water and free fatty acids) (**Hoang and Pham, 2019**; **Hoang et al., 2020**) and gasoline and diesel blended with alcohols (**Edwin Geo et al., 2019**), cause this problem. Compared with pure diesel, using alcohols in the fuel cause washing and removing the lubrication oil, which is a source of elements a metal, increasing the concentration of metal and elements in the PM (**Ghadikolaei et al., 2021**). Moreover, due to the higher oxygen contents of alcohols than petroleum-based fuels, using them as additives for diesel and gasoline can increase lubricating oil oxidation through combustion (higher oxygen content and fatty acid, more problematic regarding the corrosion) (**Hoang et al., 2019**).

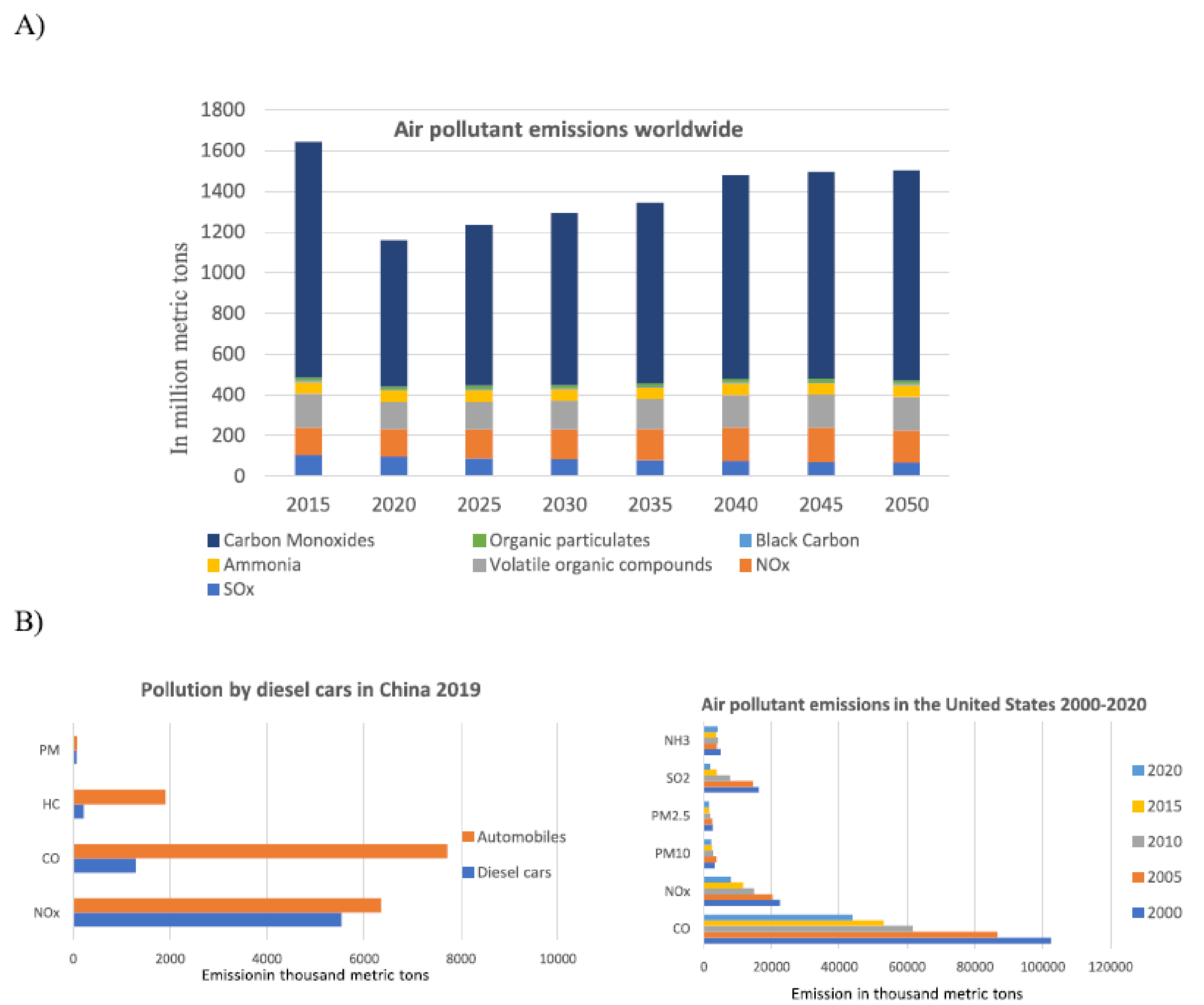

Fig. 2. Air pollution emissions worldwide (by all sectors) (A) and emitted in China and US (B) (Emissions in the U, 2019; Air pollutant emissions worldwide from, 2020)

3. Emission pollutants

3.1. Greenhouse gases

The emission of CO_2 that the main GHC emitted from the complete combustion of fossil fuel in engines is determined by theAFR, fuel consumption, and fuel composition (specifically the C/H atom ratio). Moreover, a higher oxygen level of fuel helps the reaction with carbon monoxides to create CO_2, which can be done by a catalyst or naturally (**Deutschmann and Grunwaldt, 2013**).

N_2O, another greenhouse gas, is often raised as a by-product in SCR systems (that are used to reduce NO_x emissions), as a by-product of NH_3 oxidation, or as a result of the thermal breakdown of NH_4NO_3 that creates when NH_3 and NO_2 combine react (eq. (**1**) and (**2**)) (**Preble et al., 2019**).

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad (1)$$

$$2NO_2 + 2NH_3 \rightarrow N_2 + NH_4NO_3 + H_2O \quad (2)$$

N_2O is not only harmful to human health (inactivation of vitamin B_{12}) but impacts climate change as a greenhouse gas and also contributes to the depletion of stratospheric ozone (**Jablonska and Palkovits, 2019**).

Policymakers are considering the reduction of these GHG emissions not only through the use of current CO_2 (such as carbon capture and storage) in different industries but also through the replacement with new types of energy and technologies (**Babacan et al., 2020**).

Table 1 Chemical and physical properties of diesel and gasoline fuels (**Shrivastav et al., 2017**; **Eagan et al., 2019**; **Khorramshokouh et al., 2016**).

Fuel	Density (g.m/L)	Net heating value (MJ/L)	Freezing point (°C)	Latent Energy (KJ/Kg)	Max Aromatic Content (%)	Flash Point (°C)	Boiling point (°C)
Gasoline	0.735	31.8	−73.33	350–400	30	−40	40–250
Diesel	0.837	36.2	0	250	35	45	130–160

Table 2 The influence of different technology for CO_2 mitigation

Reference Fuel	Engine Type	Operating Condition	Emission Control Technology	The influence of technology on the CO2 emission	Ref
Diesel	single-cylinder, four-stroke, water-cooled, CRDi	Different brake power	Using different plant oils (camphor, cedarwood, wintergreen oil, and lemon peel oil	All of the additives could reduce CO_2 by up to 25%. Cedarwood and wintergreen oils had a bigger influence on this reduction than other additives	EdwinGeo et al. (2021)
Diesel	single cylinder, 4S VCR DI test engine	Various engine load	Nerium-based catalytic converter and avocado oil as an additive	Higher avocado oil content caused a reduction of up to 15% in CO_2 emissions. Higher content (higher than 10%could have a negative influence. Higher engine load resulted in higher CO_2	Hemanandh et al. (2021)
Diesel	single cylinder, four-stroke, diesel engine	Different brake mean effective pressures and additive contents	Thermol-D as a multi-functional fuel additive	1.5% Thermol-D could reduce CO_2 up to 10%. Biodiesel had around 10% more CO_2 emissions compared to pure diesel	Ashok et al. (2020a)
Diesel	1-liter single-cylinder engine system modified from modified from 6-liter, 6-cylinder heavy-duty diesel engine	Different operating load conditions as well as different substitution ratios	Different combustion modes (homogeneous charge compression ignition, dual-fuel premixed charge compression ignition, and premixed charge compression ignition	DF-PCCI combustion caused more than a 14% reduction in CO_2. When the Substitution ratio increased, CO_2 emissions reduced. So, an increase in operating load conditions triggered higher CO_2. HCCI and PCCI caused higher CO_2 due to low combustion quality	Shim et al. (2020)
Gasoline	Three types of engines	Different speeds	Different vehicles: EV, Plug-in Hybrid Electric Vehicle	in the lower speed, EV showed the lowest CO_2 emission, while in the high speed, it recorded the highest amount. From the middle to high speed, Plug-in Hybrid Electric caused the lowest CO_2 emission that could meet EPA standards	Rahman et al. (2021)
Gasoline	Electric DC-type dynamometer, a two-stroke uniflow gasoline engine	0–40% of ethanol	Ethanol	Although it was expected to increase CO_2 emission, ethanol could reduce this emission due to the lower carbon content of gasoline + ethanol than pure gasoline	Kaya (2022)
Gasoline	Four-stroke SI engine	Different lambda and engine load	Methanol + Hydrogen	Blending 20% of methanol didn't affect the emissions of CO_2, while hydrogen caused a reduction of up to 5%. Higher engine load and lambda triggered increased CO_2 emissions.	Sarıkoç (2021)

CO_2 emissions are expected to reduce slightly in the following decades. Researchers on carbon monitoring anticipate this reduction to meet the 1.5 and 2 °C targets (**Liu et al., 2022a**); however, the emissions of another GHG, N_2O, are expected to increase slightly from 2030 to 2050 (**Fig. 3**). Regarding the 1.5 °C limits, there are multiple views; one is reflected in research on carbon monitoring, which suggests that the opportunity to meet that target is missed, while IPCC AR6 still has comparatively optimistic scenarios. This difference could be due to data collection time. Carbon monitoring used NRT CO_2 data, while IPCC AR6 used data from 2018 to 2019 (**Liu et al., 2022a**; **IPCC, 2021**).

The emission of CO_2 from fossil fuel combustion is to reduce the emissions of GHGs, including regulations from EPA and the Paris and Glasgow agreements; however, a steeper reduction is required to mitigate climate change (**Brown and Caldeira, 2017**). One such agreement was the Paris agreement of the UNFCC or COP21, with an outcome to limit the maximum allowed global temperature rise to 2 °C (preferable to 1.5 ° C). After five years, in November 2021, the COP26 meeting in Glasgow reduced the target to 1.5 °C above pre-industrial levels by 2050 (Cop26 explained, 2021); however, research indicates more considerable reductions are needed to address climate change (**Masood and Tollefson, 2021**).

The other regulation to be mentioned is the IMO guidelines, which issue regulations to control the emissions, especially CO_2 emissions (that announced to make 50% reduction in CO_2 emissions by 2050 (**Wang et al., 2022a**)), security, and safety of global maritime shipping. These policy guidelines are important nowadays due to the latest forecast that expected higher CO_2 emissions in the future from this shipping system. In this case, technologies should be used to meet these regulations (**Hoang et al., 2022**; **Nguyen et al., 2021b**). For this, several methods, such as recovering waste heat from marine engines (**Ampah et al., 2021**), can influence the fuel economy in this system.

3.2. Carbon monoxides

CO is a poisonous, odorless, and colorless gas that is generated when carbon-containing fuels are burned incompletely. CO is approximately 250 times more likely than oxygen to bind to the hemoglobin's heme group and remove oxygen from hemoglobin, limiting blood's ability to transport oxygen (**Zazzeron et al., 2019**). CO from internal combustion engines indicates whether the combustion is complete. High CO emission (that can cause bladder cancer) from the exhaust signifies incomplete combustion and waste of chemical energy provided to the combustion chamber (**Atarod et al., 2021**).

Table 3 The influence of engine and fuel technologies on the different emissions regulations.

Engine Type	Techniques for emission reduction	Studied Regulations	Ref
A 4-stroke marine diesel engine (WD10C190–15) with HSDF (3.09% m/m S) was used	EGR and scrubber system	NO_x emissions under IMO Tier III, PM emissions increased. The results could pass the emission requirements of the different countries	Wang et al. (2022b)
4-cylinder compression ignition types	heavy EGR, high boosting, and advanced injection timing	with advanced injection timing EURO-VI emission regulation was met after more than 80% reduction in NO_x. By heavy EGR and high boosting, EURO-VI emission regulation was met after around an 80% reduction in NO_x	Ju et al. (2021)
4 Stroke & In-line 4 Cylinder, water-cooled, non-road used	DOC and DPF	China's national emission regulation was met with around 24% conversion in NO_x after using DPF, which was reduced by five orders.	Hu et al. (2021a)
YN4PL mode, 4-cylinder, water-cooled, turbocharged	CDPF and DOC	Regarding NO_x, China-IV emission regulations were met with after-treatment. For PM, China-III emission regulation was met without after treatment, but a combination of DOC and CDPF could meet China-IV emission regulations	Zhang et al. (2023)
12.6 L heavy-duty diesel engine from FAWDE	SCR after-treatment	NOx and PM emissions were met by the CARB	Shiyu et al. (2022)
CRDi, A single-cylinder version of the 6-cylinder diesel engine	SCR and DOC (biodiesel 50% soybean methyl ester)	By SCR, NO_x emissions met the Euro VI emission standards. With DOC, the amount of CO and UHC emitted was in the range of Euro VI standards	Kim et al. (2016)

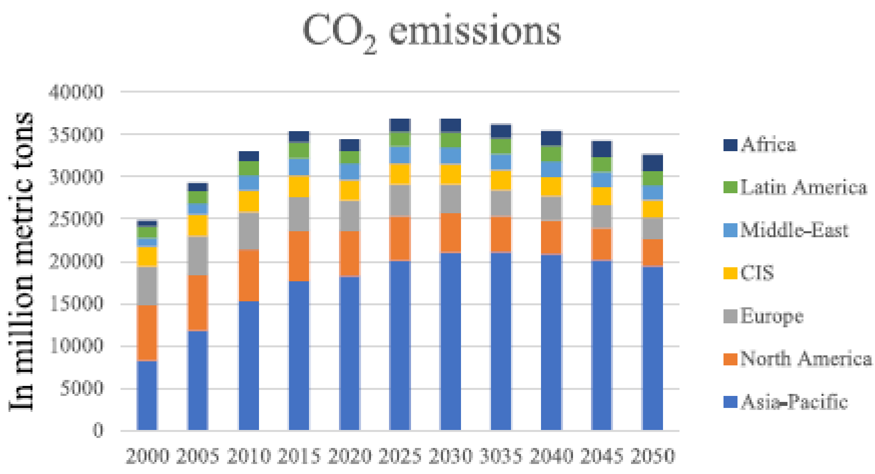

Fig. 3. The amount of CO_2 emission from 2000 to 2020 and forecast to 2050 (**Regional carbon dioxide, 2021**).

3.3. Nitrogen oxides

The oxidation of N_2 to NO_2 and NO is known as NO_x (**Chen et al., 2018b**). NO_x in gasoline and diesel engines is produced by the interaction of N_2 and O_2 at temperatures exceeding 1500 °C during fuel combustion (**Farrauto et al., 2019**). Anthropogenic NO_x are important pollutants responsible for substantial environmental issues and millions of premature deaths due to ozone as an oxidizing agent hurting the human respiratory system (**Farrauto et al., 2019**).

NO_x contributes to photochemical smog production, acid rain, acceleration of climate change, and stratospheric ozone depletion (**Li et al., 2019**). Although NO_x emissions were reduced widely, the rate of roadside NO_2 emission was not reduced as much as expected (**Grange et al., 2017**). Long-term NO_2 exposure can lead to various severe health concerns, including heart and cardiovascular disease, diabetes, and hypertension (**Ogen, 2020**). Moreover, several studies have shown that the cities with higher concentrations of NO_2 have higher rates of COVID-19 fatalities (**Ogen, 2020**; **Yao et al., 2021**), although some studies raised limitations in that work. Some suggested that several atmospheric parameters contribute to the COVID-19 pandemic (**Contini and Costabile, 2020**), while others concluded that atmospheric aerosols in cities with higher air pollution are the main contributors (**Prather et al., 2020**).

Regulations have been made to limit NOx emissions and become more stringent over time. For gasoline-powered engines, euro 4, euro 5, and euro 6 standards limited NO_x release at 0.08, 0.06, and 0.06 g/km, respectively. For diesel-powered engines, euro 4, euro 5, and euro 6 limited this emission to 0.25, 0.18, and 0.08 g/km, respectively. According to Europe and USA regulations, NO_x controllers should be used in heavy-duty diesel and gasoline engines to meet the standards (**Yang et al., 2021b**).

3.4. Unburned hydrocarbons

UHC are one of the primary pollutants that result from incomplete combustion and are released into the atmosphere along with another combustion byproduct. As complete combustion is facilitated by high temperature, high oxygen levels, and enough reaction time, UHC emission is reduced. Diesel engine efficiency is also decreased as UHC levels rise. The primary sources of UHC emission are evaporation, crankcase ventilation, and exhaust. Wall quenching and crack effect are the key determinants of gasoline engine production. When the engine is cold-starting or warming up, the primary cause of UHC emission is likewise large-volume quenching (**Zhao et al., 2022a**).

The most dangerous types of UHC are PAHs, which can be present in particles as well as gases, are common air pollutants produced by incomplete combustion of biomass and fossil fuels, and have negative (carcinogenic, mutagenic, and immunosuppressive) impacts on human health (**Fayyazbakhsh and Pirouzfar, 2016**).

3.5. Particulate matters

PM emissions are a combination of liquid and solid particles in the air, some of which are visible, while the smallest and most harmful are not visible. Annually millions of deaths around the world are linked to PM emissions. Mass concentration, particle size, and particle composition are three factors that characterize the PM and its harmful impacts (**Daellenbach et al., 2020**). BC, OC, UHC, and some physicochemical substances are the main components of PM emissions, although particles are made of hundreds of chemical components.

Another critical component of PM is also known as soot. Soot has a variety of climate effects: by absorbing SW radiation, soot particles warm the Earth-atmosphere system, lowering relative humidity, modifying atmospheric stability, and changing the process of cloud formation processes (**Lohmann et al., 2020**).

BC absorbs light from all wavelengths of the sun and heats the air, while OC or brown carbon can absorb only UV and blue wavelengths. OC has a short lifetime (around hours) due to further photochemical reactions, whereas BC has a longer lifetime (around weeks) compared to other pollutants (**Yu et al., 2019**). Gasoline and diesel combustion can emit BC, OC, and other aerosols that can act as nuclei of condensation cloud, changing the characteristics of clouds.

PM_{10}, which includes particles with diameters no larger than 10 μm, about 1/7 the diameter of a human hair, can trigger lung problems, among many other health concerns. **Fig. 4** represents the concentration of PM_{10} in the USA from 1990 to 2020, which shows a sensible reduction, especially in the last two years.

$PM_{2.5}$ or fine particles contain particles with diameters no larger than 2.5 μm and are generated mainly through wood-burning or gasoline and diesel exhaust emission that increases the risk for a wide range of health impacts and growing evidence for impacts on dementia (**Livingston et al., 2020**). Premature deaths caused by $PM_{2.5}$ are shown in **Fig. 5** by WHO regions and sectors (**Romanello et al., 2021**). It can be seen that there are slight reductions in most regions; however, more endeavor is required to reduce this factor even more.

In the Americas, premature mortality is lower than in other regions. This is due to reduced fine particles by 70% (because of USA regulation for limited pollution from vehicles) since 1981, which led to lower infant mortality, higher income, and improved life expectancy and productivity (**Colmer et al., 2020**). Recent research shows that even with improvement in air pollution quality and clean-air policies, human health remains adversely affected and premature deaths may increase in the future (**Liu et al., 2022b**).

3.6. Interaction of pollutants

The pollutants emitted from the exhaust could interact and influence each other. Although CO is not a GHG, it influences tropospheric chemistry. The OH radicals will oxidize CO to make HO_2, which then combines with nitrogen oxides-rich surroundings to form O_3. HO_2 destroys O_3 in the absence of NO_x (**Jain et al., 2021**). The final product of CO in the atmosphere is CO_2, the exact final product of the techniques used to reduce emissions (such as using catalysts and blending alcohols as an oxygenated additive with diesel or gasoline) (**Datye and Votsmeier, 2021**; **Chen et al., 2021**).

When NO_x, UHC, and VOCs combine with sunlight, a combination of pollutants called photochemical smog creates a brown cloud over cities. It contains anthropogenic air pollutants, organic compounds, ozone, and nitric acid, which are stuck near the earth due to temperature inversion. The main problems related to photochemical smog are foul odor owing to gaseous compounds, health problems, and plant damage. Internal combustion that generates NO_x primarily influences the creation of photochemical smog. In this regard, NO emitted as an exhaust emission reacts with oxygen in the presence of ultraviolet, creating ozone. Moreover, the emission of hydrocarbons (hydrocarbons with more than two carbons) in the presence of sunlight and other organic compounds causes several chemical reactions, leading to photochemical smog creation (**Brusseau et al., 2019**).

4. Techniques for emission control

Three techniques are used to meet the ever-stricter pollution regulations: in-cylinder purification, exhaust gas after-treatment, and fuel technologies (**Mohd Noor et al., 2018**; **Ni et al., 2020**). To choose one of those techniques, several factors such as how old the diesel engine is, the level of pollution, and cost should be considered. One of those techniques is using biodiesel to address environmental issues and meet the abovementioned regulations. It is beneficial due to its lower pollution, renewability, and compatibility with existing engines. Reduction of emissions can be divided into three categories (fuel modification, engine, and after-treatment technologies) as well as techniques used for CO_2 reduction.

4.1. Techniques for CO_2 control

Several techniques have been used to reduce CO_2, such as CO_2 conversion and CO_2 capture, additives, catalyst, etc. One of the most important catalysts or adsorption materials is MOFs (**Jiang et al., 2020**; **Trickett et al., 2017**; **Li et al., 2021a**). MOF is a tool for creating porous materials and precisely engineering their interiors to address the world's environmental and energy issues (**Furukawa et al., 2013**). Different metals can be used in this technique, such as titanium (**Padial et al., 2020**), aluminum (**Kurisingal et al., 2020**), and copper (**Jablonka et al., 2021**). Although MOF is not used to reduce the rate of CO_2 emissions of diesel and gasoline, it is a promising material to reduce this gas broadly. Researchers have investigated different methods such as the conversion of CO_2 to alcohols (although cost still limits the use of this technique because it requires a catalyst) (**Zhuang et al., 2018**; **Li and Yu, 2021**; **Gao et al., 2017**), DAC, and CCS to reduce CO_2 emission (**Madhu et al., 2021**). However, fossil fuel combustion is an effective dependent solution. With COVID-19 restrictions, the reduction in the use of fuels caused lower CO_2 emissions than before (**Weir et al., 2021**; **Tollefson, 2021**). This reduction happened suddenly and was the biggest reduction since the global financial crisis in 2009 (**Forster et al., 2020**; **Davis et al. Ciais**).

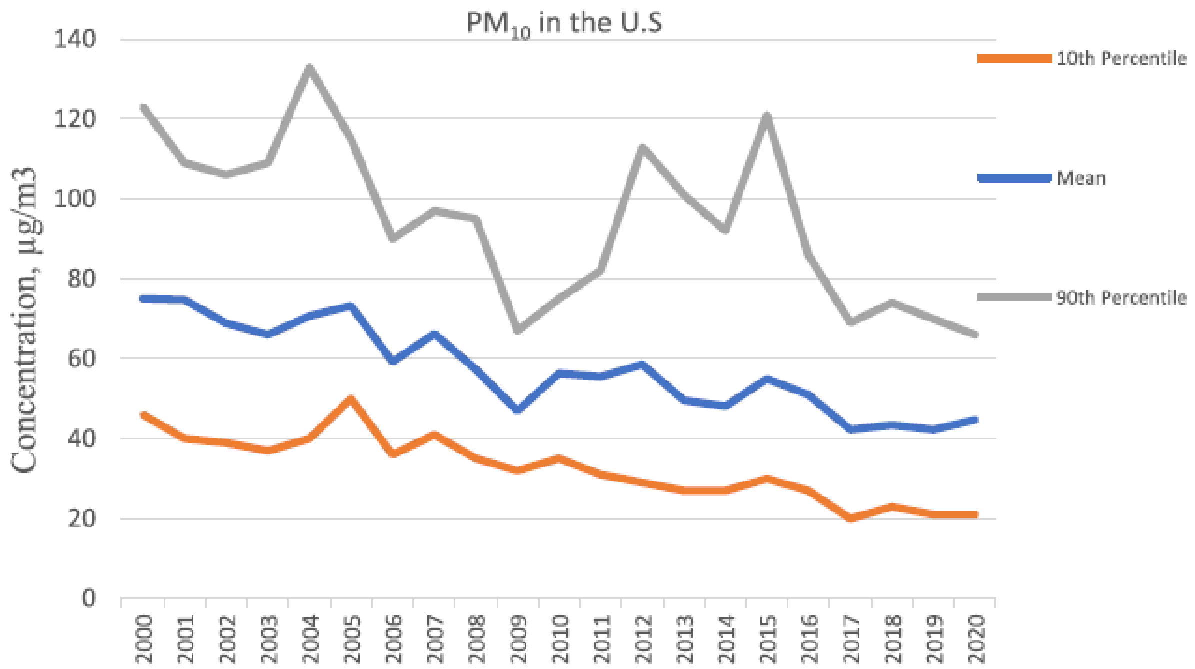

Fig. 4. The trend of PM_{10} in the USA atmosphere (**United States environmental protection agency (EPA), 2021**). The study reported a 26% reduction in the levels of PM_{10} from 1990 to 2020.

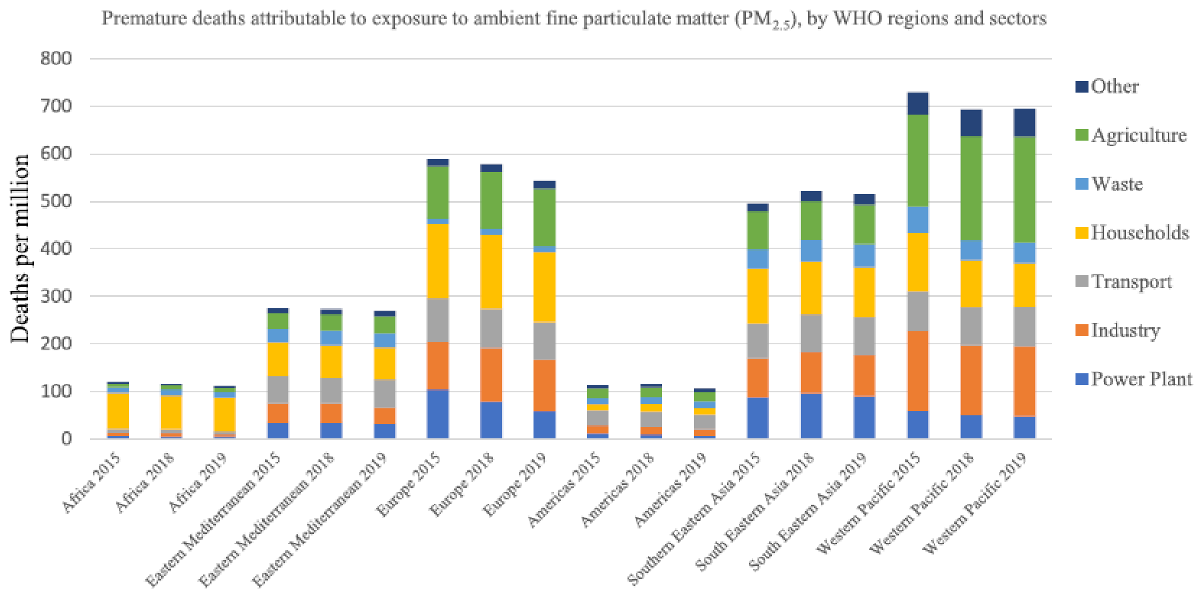

Fig. 5. Premature deaths caused by PM_{25} worldwide, by WHO sectors and regions (**Romanello et al., 2021**).

4.2. Engine technology for emission control

According to enhanced fuel efficiency, the GDI engine has become a favored technology as it injects the fuel directly into the combustion chamber with high pressure (even over 300 bar (**Lee and Park, 2020**; **Jiang et al., 2017**; **Jiang et al., 2019**)). Although GDI has several advantages, such as lower CO_2, higher output power, and greater economic performance than PFI, it has some drawbacks, such as higher particle concentration emission (about twice more than PFI engines (**Chan et al., 2020**)) (**Kalwar et al., 2020**). Accordingly, due to the stringent emission standards (especially regarding the emissions of CO_2 as it generated less CO_2 than PFI and diesel engines), PFI is not as efficient as GDI nowadays.

Regarding innovative technologies, like GDI for gasoline engines, $CRDi$ technology for diesel is used to reduce emissions, which is an injection system found in the state-of-the-art diesel engines (**Mariappan et al., 2021**). This system can provide a flexibility level to control emissions, fuel consumption, and engine power (**Jayabal et al., 2022**). $HCCI$, $PCCI$, and LTC are examples of $CRDi$ engines' benefits that use high injection pressure. On the other hand, higher injection pressure causes higher combustion temperature, leading to NO_x creation.

NO_x reduction was first handled by EGR. This method enhances engine heat capacity and reduces the maximum temperature achieved, triggering a condition with the lower formation of NO through the reaction between N_2 and O_2. Moreover, EGR temperatures also influence the emissions of CO, UHC, and NO_x; higher EGR temperature causes higher NO_x emissions but lower CO and UHC emissions.

4.3. Fuel modification for emission control

One of the earliest control methods is blending oxygenated additives with fuel, such as ethanol and butanol. Blending alcohols with gasoline started as a technique to improve the octane number of gasoline and reduce the pollutants (**Ruddy et al., 2019**). For example, a blend of 10% ethanol and 90% gasoline ($E10$), which is approved by EPA (because of its possibility to reduce even the emissions of CO_2 as the carbon content of ethanol + gasoline is lower than that of pure gasoline), is commonly used as gasoline due to its higher octane number and lower exhaust emissions than pure gasoline; however, these additives negatively influence the cetane number of diesel. Consequently, using such additives requires a secondary additive to eliminate the problem related to the cetane number of diesel. In this case, the cetane number improver can solve this problem, and its market is expected to grow with a $CAGR$ of 5.2% from 2018 to 2023 due to several strict regulations implemented to reduce air pollution (**Cetane Number Improver, 2021**). Blending alcohols leads to the completed oxidation of CO to CO_2.

As listed in **Table 6**, alcohols can reduce the emissions of CO due to their higher oxygen contents than pure diesel and gasoline. In this regard, methanol can reduce the CO more than any other alcohols. However, it is not a suitable additive due to its poisonous characteristics and higher potential for engine corrosion problems than other alcohols. On the other hand, due to the higher oxygen content of the fuel, the oxidization of CO to CO_2 will be enhanced and could make the fuel, especially diesel, non-standard in case of GHG emissions.

Blending oxygenated additives (almost alcohols) with diesel and gasoline fuel is also one of the earliest methods for PM reduction, which leads to fuel combustion to completion due to oxygen content improvement. This can enhance the octane number of gasoline, causing high-quality combustion and lower CO_2 emission. However, in ethanol use, compatibility problems in traditional engines and lower energy density are reported as the main drawbacks (**Deneyer et al., 2018**).

Moreover, blending alcohols, of which the most practical is ethanol, causes further problems, such as enhancing local ozone and NO_x pollution (compared with gasoline) and physical condition for diesel fuel (problems related to volatility and miscibility) (**Eagan et al., 2019**; **Salvo and Geiger, 2014**). Moreover, CO_2 and NO_x emissions are enhanced by blending alcohols with diesel fuel. It can be concluded that the primary key issues of biodiesel are the problems mentioned above of alcohol as well as the problems related to the blending of vegetable and plant oils (due to the competition of using these oils in food and food technology) (**Zhou et al., 2018**). Regarding the use of ethanol as gasoline engine fuel (in the USA and Brazil), the main problem is corrosion of engines and pipes because ethanol absorbs water from the air. Moreover, it has only about 70% of gasoline's energy content (**Peralta-Yahya et al., 2012**).

Another drawback is reducing heat value and enhancing the latent heat of vaporization of the fuel by alcohols, especially ethanol. These factors can lead to higher UHC emissions in both gasoline- and diesel-powered engines. It is axiomatic that more ethanol or methanol leads to lower UHC emissions. However, increasing alcohol contents can lead to higher heat of vaporization, lower volatility, and causing partial combustion during the cold transient time (make lots of misfires), causing higher UHC emissions.

4.4. Aftertreatment for emission control

The engine technologies that can fuel medication cannot entirely remove the emission of pollutants. For gasoline engines, TWC is still the dominant controller for gaseous pollutants (NOx, CO, and UHC), while for non-gaseous pollutants, GPF (for solid and liquid particles) and TWC for liquid phase particles have been proven as efficient techniques. For diesel engines, DOC has been shown to be a practical system for reducing gaseous pollutants. Moreover, two after-treatment systems for diesel engines, Selective SCR and LNT, can reduce the NO_x in the fuel-lean exhaust. For PM reduction, DPF has proven to be an effective system; however, it causes to enhance the CO_2 emissions owing to its high required fuel consumption (**Leach et al., 2020**).

For the stoichiometric exhaust emitted from gasoline engines, TWC is the prevailing technique (often combined with EGR) to simultaneously lower NO_x, CO, and UHC emissions using a single catalyst (**Getsoian et al., 2019**). In the technique, each pollutant requires a specific catalyst component. For instance, Pt and/or Pd are promising and efficient for the oxidation reaction of CO and UHC (**Xie et al., 2021**; **Kothari et al., 2021**), while Rh is more suitable for the reduction of NO_x (**Nagao et al., 2015**; **Heo et al., 2020**). However, TWC cannot control the NO_x emission from lean burn engines like diesel engines due to high air/fuel ratios of exhausts. SCR and NSR have been specially developed to control NO_x emissions with high air/fuel ratios (**Beale et al., 2015**).

In the SCR system, the emitted NO_x was selectively reduced into N_2 by feeding NH_3 or urea. Small-pore Cu-exchanged zeolites are effective SCR catalysts that can enrich the exhaust gas stream with NH_3 to minimize NO emissions (**Becher et al., 2021**). These de-NO_x reactions on Cu catalysts are sensitive structurally, by which NH_3 reacts with NO to form N2 on atomically dispersed Cu species (**Liu and Corma, 2021**). However, the overoxidation of NH_3 or the incomplete reduction of NO_x could create a GHG, N_2O (**Livingston et al., 2020**). In the SCR system, the slipped NH_3 is also an air pollutant. An ASC can be added as a short zone directly after the SCR to convert the ammonia exiting the SCR zone to nitrogen. The ASC increases the conversion of NH_3 in its NH_3 oxidation layer (AOC), which uses a Pt catalyst on a supported oxide (**Bendrich et al., 2022**).

The SCR with a warmed-up engine shows a promising performance (even more than 90% reduction); however, during cold-start, the emissions of NO_x would be beyond the emission regulations such as EURO 6 (**Praveena and Martin, 2018**; **Mera et al., 2021**). Researchers have developed several methods to overcome this problem, such as dual layers SCR and $ACCT$ (**Gao et al., 2021a**). Dual layers SCR can be beneficial due to its structure containing two active phases in two separate layers. $ACCT$ is another technique that showed promising performance in reducing NO_x emissions during cold-start; however, its high price limits its use (**Gao et al., 2021b**).

One of those technologies is to store emitted NO_x until a high operating temperature is reached using PNA (with $PGMs$). Dual layer monolith catalysts are one of those types that showed high performance for absorbing NO_x at low temperatures and desorbing them at high temperatures (**Azzoni et al., 2022**; **Selleri et al., 2018**). The stored NO_x can be released at high temperatures and is further reduced in the downstream SCR (**Ji et al., 2017**). Furthermore, the stored NO_x can also be reduced in rich-burn conditions in the LNT system. LNT, also known as NSR (not for gasoline-powered engines), primarily uses a cutting-edge catalytic system pioneered by Toyota (Pt/BaO/Al_2O_3) (**Takahashia et al., 1996**). NO is initially oxidized to NO_2 on the Pt sites through the lean-burn period in this system. In the following step, Pt/BaO/Al_2O_3 catalysts or other NSR catalysts have a storage component such as K, Ba, and Sr that stores NO_x by producing nitrates and/or nitrites. When the engine exhaust changes to a short fuel-rich cycle, the stored NO_x is released and reduced to N_2 on the neighboring Pt sites by reductants (CO, H_2, or hydrocarbons) (**Jablonska and Palkovits, 2019**). However, the NSR technology requires an optimized lean/rich switching strategy, increasing the system's complexity.

For the current catalytic de-NO_x systems, the NO_2/NO_x ratio is a crucial factor. In the SCR system, the ratio of NO_2 to NO_x in the exhaust gas affects the selectivity of the main reactions, which are Standard SCR (Eq. (**3**)), Fast SCR (Eq. (**4**)), and NO_2 SCR (Eq. (**5**)) (**Bendrich et al., 2018**)

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (3)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (4)$$

$$4NH_3 + 3NO_2 \rightarrow 3.5\ N_2 + 6H_2O \quad (5)$$

Maximum NO_x conversion of SCR usually occurs when NO_2/NO_x ratio is 0.5. It should be noted that a higher NO_2 value causes further reactions, which results in higher N_2O (Eq. (**6**)).

$$2NH_3 + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O \quad (6)$$

The NO_2/NO_x ratio for the SCR system can be controlled by the upstream DOC, which can convert a part of NO to NO_2 by the oxidation catalysts therein (**Chatterjee et al., 2009**). Moreover, designing the SCR catalyst formulations to improve the oxidation activity of NO to NO_2 could enhance the fast-SCR reaction at low-temperatures, for example, by loading manganese oxides (**Li et al., 2021b**), cobalt oxides (**Irfan et al., 2008**) or iron oxides (**Zhang et al., 2021**).

The NO_2/NO_x ratio is also a determinative factor for NO storage in PNA and LNT because NO_2 is more easily adsorbed on catalysts rather than NO. The catalyst loading noble metals, such as Pt (**Theis and Lambert, 2015**), Pd (**Onrubia-Calvo et al., 2020**), or Rh (**Castoldi et al., 2019**), are able to convert NO to NO_2, increasing the capacity for NO_x storage at low temperatures. Furthermore, some noble metal-free catalysts, for instance, Co-SSZ-13, Ce/BEA (**Wu et al., 2022**) and mesoporous $LaCoO_3$ perovskite (**Xie et al., 2022**), were developed to enhance NO_x storage in a similar way (see **Table 4**).

It is worth mentioning that hydrogen-fueled engines, the most promising clean internal combustion engines without CO_2 emission, emit more NO_x compared to the general fossil-fueled engines (**Dhyani and Subramanian, 2019**). In this case, several researchers have tried reducing this emission by reducing the excess air ratio and delaying injection timing during the cold start, which usually omits the highest amount of NO_x (**Xu et al., 2018, 2019**). Different techniques that have been developed to control NO_x emissions from hydrogen-fueled engines are summarized in **Table 5**, and most of them belong to engine technology. One of these techniques is using EGR, which is beneficial in NO_x reduction and cost optimization due to the reduction of throttling losses in SI engines. However, to improve efficiency, it is better to limit the EGR amount. In this case, after-treatment systems such as TWC would be required to reduce NO_x to the standard level (**Fischer et al., 2017**). X is another factor that can be controlled for NO_x reduction. Excess air ratio is a crucial element influencing engine combustion and emission characteristics, especially NO_x emissions as the air-fuel ratio is the most important factor influencing the NO_x formation (**Mingrui et al., 2017**). The formation of NO_x is a function of the λ/φ. The best condition for a high amount of NO_x is when the λ/φ is at a stoichiometric air-fuel ratio (**Xu et al., 2018**). Combining these techniques with a relative after-treatment system like SCR, the NO_x emissions can be reduced to near zero (**Stepien, 2021**).

A method for eliminating CO is DOC, catalytic converters for diesel-powered engines to reduce HC, CO, and part of PM. CO oxidation by the catalyst is a necessary process, such as the Haber Bosch process that was used firstly by Pt (**Beniya and Higashi, 2019**). DOC converts HC and CO to water and CO_2 and is also used to oxidize NO to NO_2. Later, NO_2 oxidizes soot in DPF (**Kothari et al., 2021**; **Agote-Aran et al., 2021**). DOC can absorb oxygen to their catalytic site, and CO can be absorbed on the surface, favoring CO. Lastly, they can react and make CO_2 (**Fig. 6**A (**Deutschmann and Grunwaldt, 2013**)). SACs are also promising catalysts for reducing CO. These catalysts show significant potential for increased noble metal utilization, remarkable selectivity, and excellent catalytic efficiency; and are effective at low temperatures; and can reduce the demand for PGMs (**Qiao et al., 2011**). The usage of SACs' metals is almost 100%, as they are comparatively environmentally friendly and cost-effective, favored by industry in some cases (**Li et al., 2020**). Another factor that makes this catalyst particularly interesting is that it can be used in advanced engines with lower exhaust temperatures (<150 °C) (**Nie et al., 2017**). However, DOC fails to control the emission of NOx and soot.

A summary of different techniques that have been used to control CO and UHC emissions are listed in **Tables 6** and **7**.

Regarding PM, the most straightforward method is physically trapping PM using particulate filters, including DPF for diesel-powered engines and GPF for gasoline-powered engines. DPF and GPF can serve as support SCR and TWC catalysts by coating, respectively, to simultaneously remove other pollutants.

Typical DPF is constructed from cordierite, SiC, or Al_2TiO_5 (**Buschow, 2001**). It is a honeycomb structured device consisting of ordered square channels through which the diesel exhaust gas permeates into the walls, trapping the soot particles within the porous wall as well as over the inlet channel surface, as shown in **Fig. 7**. The soot particles deposited on the monolith channels are oxidized into CO_2 at temperatures of exhaust gases.

The regeneration of DPF is inevitable following the problem that the accumulated soot particles need to be combusted periodically to decrease the back pressure of systems, prevent plugging and maintain economic efficiency (**Yang et al., 2022**). There are two kinds of regeneration processes: active one and passive one. For active regeneration, the temperature of the exhaust gases is increased through injecting more fuel or electrically heating. To trigger passive regeneration, the activation energy of the soot combustion is reduced by chemical methods. For instance, combining a DPF with catalysts is an efficient passive regeneration technique, and highly active oxidation catalysts play a crucial role. The catalysts coated on DPF or upstream DOC can promote NO oxidation to NO_2 with strong oxidizing properties.

Table 4 The influence of different emission control technologies on the emissions and other factors of diesel- and gasoline-powered engines.

Fuel	Engine Type	Operating Condition	Emission Control Technology	Influence on emissions and other properties	Ref
Diesel	A 4-stroke marine diesel engine (WD10C190–15) with HSDF (3.09% m/m S) was used	Load from 25% to 100%	EGR and scrubber system	EGR scrubber causes 98% PM reduction. The problem (PM emissions) regarding using the EGR technology in the marine engine has been solved with this new technique	Wang et al. (2022b)
Diesel	4-stroke, 2-cylinder, constant-speed, CRDI turbocharged CI engine	1500 rpm engine speed, 1.5 ± 0.3 bar turbocharged pressure	New CRDI/HSD, Delphi, Dual fuel filter injection system as well as Methanol as an additive	The new injection system lowered the smoke opacity while it caused an enhancement in NO_x emissions. EGR was the solution to overcome this problem. The reduction in soot and NOx was made by bypassing turbocharged air and port injection of 30–50% of methanol	Agarwal et al. (2022)
Diesel	4-cylinder, turbocharged, and intercooler CRDI engine	Different boost pressure as well as various AB content in the fuel	Multicylinder CRDI engine and AB as an additive	In the CRDI engine, increasing boost pressure caused a reduction in UHC, NO_x, CO_2, smoke, and CO emissions. Increasing AB% enhanced the brake power, then reduced it (the oppositive behavior for BSFC has occurred)	Singh and Sandhu (2021)
Biodiesel	Four cylinders, direct injection, four-stroke, water-cooled	Using ANCF catalysts in various power as well as studying the influence of biodiesel on emissions	Fe_2O_3-based DOC and SCR catalyst	Smoke remained stable at low power but increased at high power when they used ANCF. UHC emissions were reduced by ANCF. Biodiesel reduced CO emissions. Using ANCF caused a reduction in excessive air factors, but it could increase the BSFC	Zhang et al. (2021)
Diesel	4-cylinder, water-cooled, turbocharged, electronic, agricultural diesel engine	Different catalyst loadings	DOC coupled with a CDPF	DOC and CDPF could reduce CO and UHC, especially with a higher engine load. DOC reduced PM by 34%, while CDPF could reduce it by 98%. Both of them enhanced NOx emission. The fuel consumption enhancement was negligible with the after-treatment system, while the engine power enhanced significantly, especially at higher speed and lower engine load	Zhang et al. (2022)
Diesel	4 stroke & in-line 6 cylinders	Different speed and load	After treatment: DOC + DPF/ POC + SCR + ASC	UHC, PM, and NO_x emissions could be reduced by DPF more than POC (without more CO_2 generation).NOx emission was reduced effectively by SCR. DOC oxidized NO into NO2 but didn't influence NOx emission and just changed the composition	Feng et al. (2022)
Gasoline	2.4 L naturally aspirated GDI	Different operating temperatures	Using the TWC catalyst system to reduce the emissions of NO_x	NO_x reached the lowest amount when the mixture of 5% alumina and 75% Pd/Ba/CeO_2 was used as NO_x storge material. PGM ration had limited influence on emission, but higher PGM contents resulted in more NOx storage	K and LEE (2012)
Gasoline	Air-cooled, 4-stroke, V-2 cylinder, horizontal PTO shaft, OHV	Different air/fuel of HE and different water content of HE	Hydrous ethanol	Raising water content up to 30% cause a reduction of up to 50% of NO_x conversion. More water content didn't reduce NO_x more. Higher air/fuel of HE causes the high lean condition, triggering lower NO_x emissions. The lower content of HE (HE 5%) showed higher brake thermal efficiency. But higher content reduced the efficiency and enhanced NOx removal efficiency	Al-Harbi et al. (2022)
Gasoline	Combined injection 4-cylinder SI engine.	Different ethanol volume fractions, different EGR ratios as well as different excess air ratios	EGR, direct EDI plus GPI	A Higher EGR ratio dropped NO_x emission significantly while a higher excess air ratio resulted in higher NO_x emission. A higher excess air ratio triggered lower CO emissions. Accumulation mode particle number and nucleation mode particle number were reduced and then raised with increasing EGR and EDI	Zhao et al. (2022b)
Gasoline	In-line, 4-cylinder, water cooling, combined port- plus direct-injection system SI, GDI	Different excess air ratios, EGR, and CO_2 dilution rates	EGR dilution at half-load, stoichiometric and lean-burn	An increase in EGR and CO_2 dilution rate reduced the emissions of soot and NO_x but enhanced UHC and CO emissions. Higher excess air rates reduced NO_x, CO, and soot emissions but enhanced UHC emissions. Slightly reduction in maximum heat release rate by increasing EGR and CO2 dilution rates	Gong et al. (2022)

Table 5 Different methods used in hydrogen-fueled engines to control NO_x emissions.

Engine Type	Operating Condition	Emission Control Technology	The influence of technology on the NOx emission	Ref
A single-cylinder engine based on a 4-stroke diesel engine	Different EGR% and engine speeds	EGR	High levels of EGR cause reduced NO_x emissions and also enhance engine torque.	Tsujimura and Suzuki (2019)
Hydrogen/diesel dual-fuel in an inline 4-cylinder water-cooled diesel direct injection engine	Different EGR% and H_2 energy share	EGR	Higher levels of EGR resulted in lower NO_x emissions. The model is also useable for gasoline/hydrogen engines.	Kumar et al. (2018)
A multi-cylinder SI engine fueled with hydrogen	Different EGR rates and WHR	EGR and water injection	An increase in WHR and EGR causes a reduction in the emissions of NO_x. The influence of WHR is more than EGR	Dhyani and Subramanian (2019)
A 1.6L commercial gasoline engine with four cylinders	The different times during cold-start and different excess air ratios	Controlling excess air coefficient	Adopting H_2-rich combustion in cold-start is an excellent method of lowering NO_x. Moreover, a decrease in excess air can sharply reduce NOx emissions.	Xu et al. (2018)
A 2.3 L, 4 St, PFI hydrogen engine with a turbocharger	Different engine speeds and equivalence ratios	TWC and control the equivalence ratio	From an equivalence ratio of 0 to around 0.6 and higher than 0.9, the emissions of NO_x are at the standard level. A high equivalence ratio in H_2 combustion in the presence of TWC can reduce NO_x emissions.	he Luo et al. (2019)
A single-cylinder hydrogen research engine	Different equivalence ratios,	Boosting lean-burn technology and intake valve timing retardation	Zero ppm NO_x emission was achieved by using boosting lean burn technology. Intake valve timing can control the backfire, which influences the emissions of NO_x.	Lee et al. (2014)
A single-cylinder DOHC sparkignition engine	Different intakevalve opening timing and boosting pressures	Using supercharger, lean-burn, and late intake valve opening	In ultra-lean burn, high boosting pressure and low equivalence cause to reduce the NO_x emissions to the standard level	Lee et al. (2010)

Table 6 The influence of different techniques on UHC emissions.

Reference Fuel	Engine Type	Additive or Used Technology	Operating Condition	Influence on UHC emission	Ref
Gasoline + Diesel	single-cylinder engine based on a 1.7 L four-cylinder direct-injection	Blending gasoline and diesel in various contents as well as EGR	Different EGR rates, ignition delays, and gasoline contents	Higher ignition delay, intake pressure, and EGR, resulted in higher UHC. Higher gasoline content causes lower UHC.	Han et al. (2012)
Gasoline	SI, 4-stroke, 998	Ethanol as well as TWC as an aftertreatment system	Different ethanol percentage	Higher ethanol causes lower UHC, but to a point. By increasing ethanol more than 20%, UHC can be reduced	Iodice et al. (2016)
Gasoline	Maruti Suzuki make four stroke three-cylinder MPFI engine	Ethanol-H_2O_2	Different ethanol and H_2O_2 contents	10% of Ethanol reduced the UHC. Higher H_2O_2 resulted in lower HC	V Barboza et al. (2022)
Gasoline	V6HCCI/SI model, GDI engine	A prototype three zones monolith catalyst	SI mood (before using catalyst) and HCCI (after using catalyst)	UHC and CO reduction by conversion was around 90%	Hasan et al. (2016)
Diesel	A single cylinder, four stroke, water cooled, direct injection Kirloskar TV1 diesel engine	Fe_2O_3 based DOC and SCR	Different engine torque. ATCF and ANCF	At low torque, just ATCF caused reduction in UHC, while in high torque all both catalytic systems trigger lower UHC	Resitoglu et al. (2020)
Diesel	Kirloskar, cylinder (One), CRDI vertical water-cooled Diesel engine	Hexanol/hydrogen additives	Different engine loads and EGR%	Higher hexanol and EGR% causes higher UHC, higher load% triggers lower UHC.	Seelam et al. (2022)
Diesel	A single cylinder, four stroke, air cooled, direct injection diesel engine	WCO biodiesel, gasoline and kerosene	Different engine load	The best additive was kerosene with more than 70% reduction (10%), gasoline and biodiesel also caused reduction in UHC	Gad and Ismail (2021)

The presence of NO_2 can transform the reaction mode from solid—solid—gas (cata-lyst-soot-O_2) into solid—gas—solid (catalyst-NO_2-soot). NO_2 can further oxidize soot particles under the temperature of 350 °C of the exhaust gas, achieving the regeneration of DPF (**Li et al., 2021c**), that is, NO_2-assisted regeneration which is extensively used in heavy-duty vehicles (**Jiaqiang et al., 2016**).

The catalysts are generally coated on DPF to catalyze the combustion of soot particles, called $CDPF$. Noble metal catalysts for soot combustion have been extensively developed for their excellent activity and stability, such as Pt/Fe_2O_3 (**Yang et al., 2021c**) and Rh/CeO_2 (**Lee et al., 2021**), although their poor thermal stability represents a problem. Recently, various cost-effective catalysts such as transition metals (**Yang et al., 2021c**; **Cui et al., 2020**), alkali metals (**Liu et al., 2018**; **Wang et al., 2021b, 2021c**), ceria-based oxides (**Wei et al., 2020**; **Grabchenko et al., 2020**), and perovskite-type (**Zeng et al., 2020**) oxides have been investigated for catalytic soot combustions. Besides optimizing the intrinsic catalytic activity, structure improvement is also a feasible solution to provide sufficient contact points through enhancing the soot-catalyst contact efficiency. Two main strategies are present: (1) introducing macropore into the catalyst, such as 3DOM structures (**Mei et al., 2020**; **Zhao et al., 2021**), porous nanotubes (**Fang et al., 2020**), and nanoflower structures (**Wang et al., 2020**); and (2) selecting a suitable substrate to increase the surface area, to provide more O_2 activation sites on the catalyst (**Wu et al., 2019**).

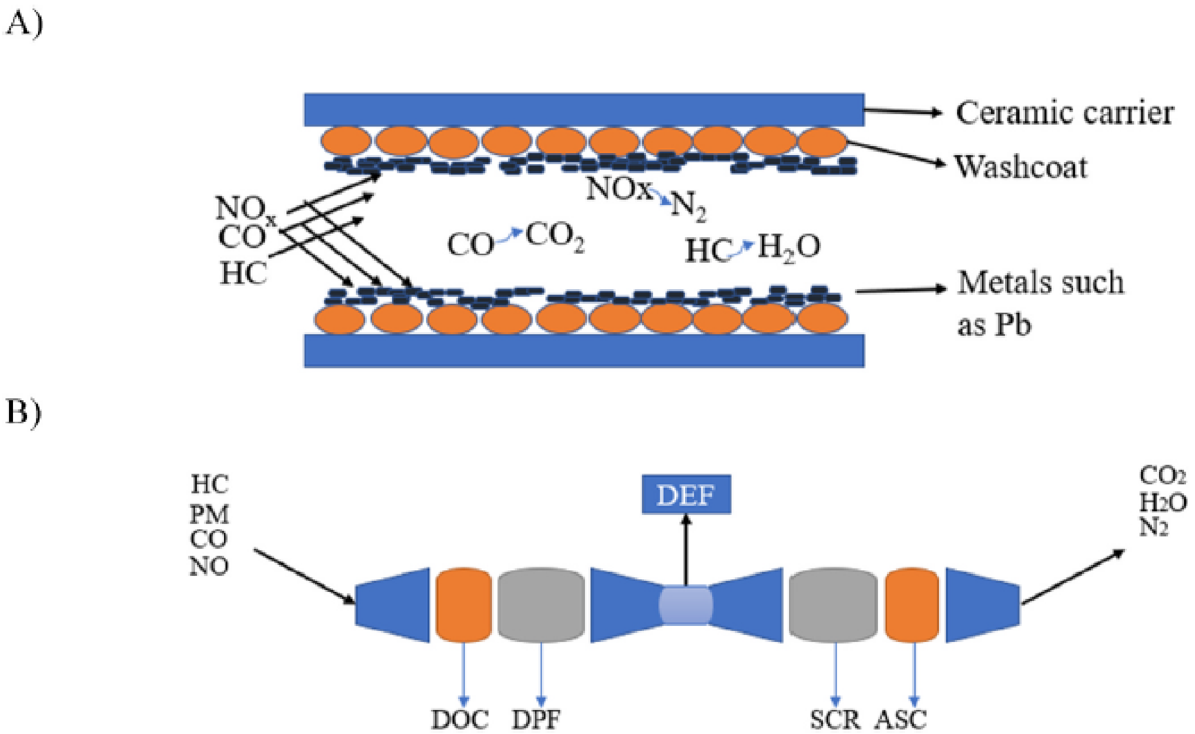

Fig. 6. A)Typical shape of modern catalyst for elimination of gasoline emission, B) Typical configuration of modern catalyst for eliminating diesel emission (**Wang and Olsson, 2019**). DOC is used to eliminate CO and UHC; then particulates are removed by DPF. Later, SCR is used to remove NO_x. The last part is the ASC applied to eliminate excess ammonia.

Table 7 The influence of different factors on the emission of CO in gasoline- and diesel-powered engines.

Fuel	Engine	CO influencer	Additive content (%) or condition	Influence of CO emission (%)	Main outcomes	Ref.
Gasoline	EW 10 J4 (RFR), Max power: 137 hp/6000 rpm Max Torque: 19.8 kg-m/4100 rpm	Bioethanol	3 6	−18.2 −25	Bioethanol raised the ratio of oxygen in fuel that cause to complete combustion and reduce the rate of CO, while it causes its oxidize into CO_2	Jhang et al. (2020)
Gasoline	spark-ignition engine with LRB. Max Power: 1.5 KW	Bioethanol and bio-acetone	3.5–3.5 5–5	−53 −67	The influence of bio-acetone was more than bioethanol in reduction of CO emissions	Elfasakhany (2020)
Gasoline	turbocharge direct injection spark ignition. Four cylinder and Orthostichous	Methanol Ethanol Butanol	10 10 10	≈ −10 @4000 rpm ≈ −8 @4000 rpm ≈ −6 @4000 rpm	Higher oxygen content of the additives means higher reduction in CO emission. In the lower speed (1000r/min or lower), CO emission is almost zero	Tian et al. (2020)
Diesel	A single cylinder, four stroke, water cooled	Diesel oxidation catalyst with Alumina, cerium oxide and barium oxide mixed with phosphoric as a wash coat	At load 5 Nm At load 10 Nm	≈ −42 −25	DOC is able to convert CO to CO_2 The higher load means lower oxygen in combustion chamber that lead to incomplete combustion that causes higher CO emission	Nadanakumar et al. (2020)
Diesel	4.45L turbocharged, in-line 4 cylinder diesel engine	DOC CDPF DOC + CDPF + SCR	At load 10 Nm and 1650 rpm	≈ −82 ≈ −90 ≈ −95	Due to higher selectivity of CO than UHC in DOC, the efficiency of this catalyst for reducing CO emission is almost 100%. Changes in the speed was negligible in the emission of CO	Hu et al. (2021b)
Diesel Biodiesel	Single cylinder, 4 S Diesel, Constant-speed, direct-injection, Compression Ignition engine	D-Thermal	1 ml 2 ml 1 ml 2 ml	≈ −21 ≈ −26 ≈ −30 ≈ −34	Higher transformation of CO to CO_2 gas by adding D-Thermal and also reduction in ignition delay (higher cetane number)	Ashok et al. (2020b)
Diesel	1.9 MultiJet Diesel Engine, Transverse (4 in line)	neem seed Camelina	5 10 5 10	≈ −7 ≈ −10 ≈ −13 ≈ −15	the reduction in CO by plant oils might be due to too big droplets in a diesel engine or inadequate turbulence or swirl formed in the combustion chamber. Moreover, higher amount of plant oils means higher amount of oxygen in combustion chamber that cause to burn more carbon molecules	Oni and Oluwatosin (2020)
Gasoline	single cylinder, four strokes, water cooled, variable compression ratio and PFI equipped spark ignition engine	Lemon peel oil	20	≈ −11	The temperature after combustion is higher when the load in higher and it means lower CO emission.	Biswal et al. (2020)

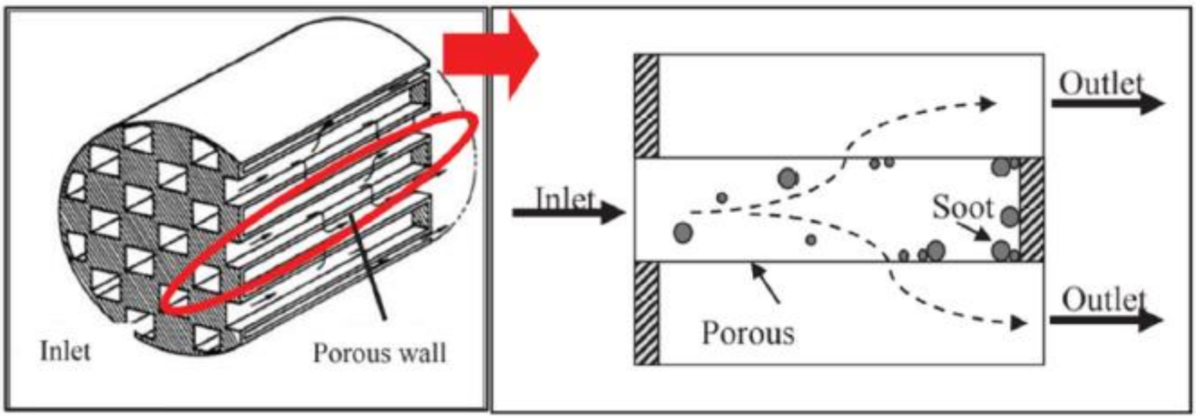

Fig. 7. Functioning of typical DPF (**Mokhri et al., 2012**).

Conventionally thermal catalysis can reduce the combustion temperatures of diesel soot to within the exhaust temperatures (300-500 °C), and thereby the emitted soot can be continuously removed. However, the exhaust temperatures are often within 100-200 °C due to the frequency of idling of the urban diesel vehicles in traffic jams, while the ignition temperatures for most catalytic soot combustion are >200 °C, and the higher temperatures are required to maintain the combustion. Recently, some technologies have been developed to promote the combustion of soot. One is that NTPtechnology can simultaneously remove PM and NO_x from DPF (**Ji et al., 2020**). NTP technology can achieve oxidative PM decomposition at a relatively low temperature (>180 °C) due to the extremely high active groups such as O and O_3 (**Liu et al., 2021**). Recently, an electrification strategy was developed for catalytic soot combustion based on the principle of electro-thermal heating on the contact interface of conductive catalysts and soot. Voltages are applied to the catalyst-soot mixture, forming passing electric currents, and Joule heating is generated on the interfaces, triggering soot combustion. The catalysis strategy breaks through the reaction temperature limits, decreasing the ignition temperature for 50% of soot conversion to <75 °C (**Fig. 8**) (**Mei et al., 2021**).

5. Conclusion and future prospect

Although there are movements toward renewable energies, the use of gasoline and diesel fuels remains high such that eliminating the use of fossil fuels is challenging. In this case, modifying the engines, fuels, and exhausts can improve the environmental impact of the above-mentioned technologies and meet emission regulations for pollutants control, while green energies are simultaneously developed. Although using alternative fuels such as ethanol in some countries (such as Brazil) has received significant attention, the benefits of using such fuels are still hindered by challenges. Applying alcohol (as an additive) to reduce the most dangerous pollutants has been shown to be more practical.

This technology still needs progress in the case of energy for diesel engines. Moreover, these types of additives cause to increase in the oxygen content of fuel that is leading to higher NO_x and CO_2 emissions. As combustion and the environmental performance of alcohols are still high (regarding CO and soot), it is also worth making new studies to reduce NO_x and CO_2 emissions. In the case of NO_x emissions, different technologies such as EGR have been used to overcome this problem, but there should be a focus on the emissions of CO_2 to meet the new stringent regulations.

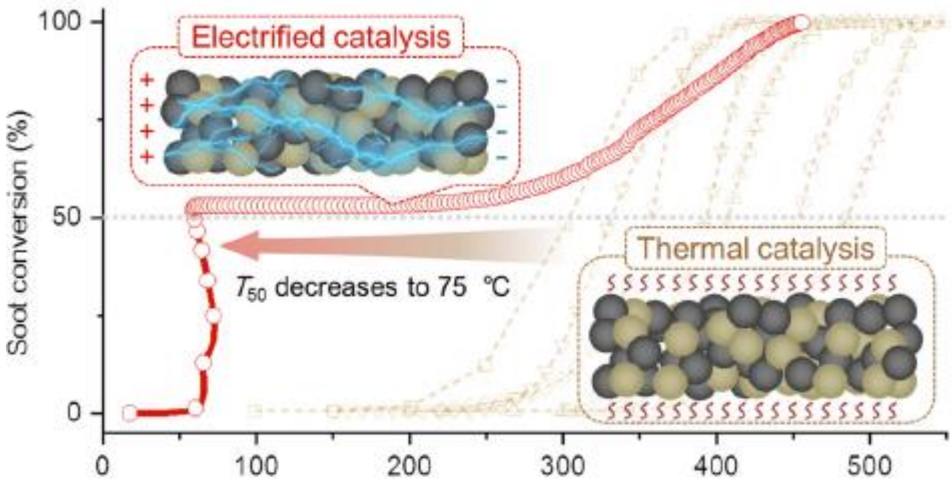

Fig. 8. Comparison of soot ignition temperature of electro-thermal heating catalysis and conventional heating catalysis (**Mei et al., 2021**).

Using catalysts to filter and oxidize dangerous pollutants is an advanced technique to address them. DOC, DPF, SCR, ASC, SAC, GPF, and TWC are different catalysts used for gasoline and diesel engines thus far. For example, TWC, as a gasoline after-treatment step operated with stoichiometric air-fuel ratio, CO, NO_x, and UHC are converted to N_2, CO_2, and H_2O.

Understanding the potential of reducing air pollutants and greenhouse gases by additive, engine modification, or catalysts is critical to minimizing the harm from energy production to human health and the environment. Moreover, each technique could be supplemented with techno-economic analyses to understand its impacts best. In addition, working on new types of metal alloys, such as blending different metals, is important to prevent engine corrosion. Moreover, the new research should consider not only studying the optimization of the new fuel types, such as hydrogen/biofuel blends but also their influence on engine corrosion and overcoming this problem. In addition, studying new combinations of after-treatment technologies would be beneficial not only for emission (PM, NO_x, CO, and UCH) reduction simultaneously but also for overcoming problems caused by metal alloys and even thinking about the engine performance and fuel properties as the following priorities. It is worth mentioning that nowadays, electric and hybrid propulsion systems are of actual value due to energy problems the world is struggling with. In this case, new studies are required to study the performance improvement of these types of systems regarding energy usage and air pollution reduction.

Moreover, it is axiomatic that human health and saving our planet are two factors that deserve attention in shifts to clean energy and improvements in the use of traditional fuels, such as through technological development or penalties (e.g., economic penalties).

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