



**University of  
Nottingham**

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# **Internal Combustion Engines MMME4066**

## **Pollutant and Emissions control**

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- Introduction to exhaust emissions from engines
- Emission–control legislations
- Routes to engine fuel economy and CO2 reductions
- Driving cycles
- Emission control legislations: current and future
- Main pollutants from SI engines and control strategies
- Main pollutants from CI engines and control strategies
- Emissions from shipping

Advanced Powertrain Engineering (MMME4066),  
Can you take a few moments to complete the SEM Survey for our module.  
You can access the survey using the following link:

Students can access the survey at <https://bluecastle-uk-surveys.nottingham.ac.uk>



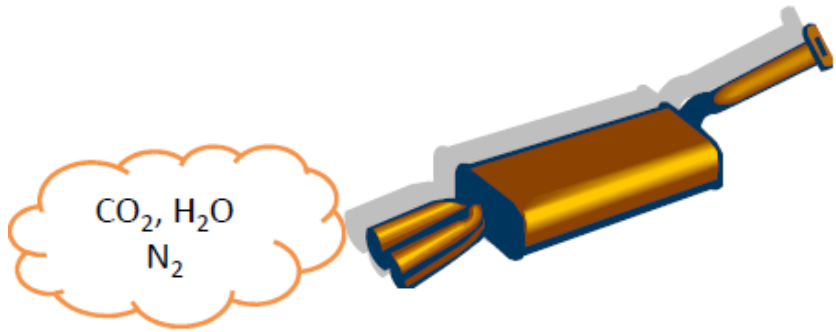
Survey Starts	01/12/2025 07:00
Survey Ends	12/12/2025 23:00

Your feedback is incredibly important to me, and I'd love to see a good number of responses. Last week, I was pleased to receive some great feedback regarding the course, particularly about uploading lecture materials in advance and making lecture recordings available promptly afterward. I'm happy to confirm that this will now be implemented moving forward!

I truly hope you've found the module interesting and enjoyable this year.



Major components of wet exhaust gasses:



H<sub>2</sub>O : Condenses out when cooled; source of visible exhaust plume on cold days; 12% by volume

CO<sub>2</sub> – Major greenhouse gas; constitutes 10% of exhaust gas; can only be reduced by reducing fuel consumption

N<sub>2</sub> – Constitutes 75% of exhaust gas; not directly involved in combustion

Then few percent of:

CO : Incomplete, rich burning

O<sub>2</sub> : Lean mixtures

HC : Unburned hydrocarbons

NO<sub>x</sub> : Oxides of nitrogen

PM : Particulate Matter, mainly for diesel and GDI engines



Industrialized countries have introduced:

- emission-control laws
- test procedures employed to confirm compliance

Transport emissions are divided in

- Passenger cars
- Light commercial vehicles
- Heavy commercial vehicles
- Off-road (agricultural/construction)
- Marine/ Shipping sector





Emissions of CO, HC, NO<sub>x</sub> and PM into the atmosphere are restricted by EU regulations

Stage	Date	CO	HC	HC+NO <sub>x</sub>	NO <sub>x</sub>	PM	PN
		g/km					#/km
<b>Compression Ignition (Diesel)</b>							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)	-
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08	-
Euro 2, DI	1996.01 <sup>a</sup>	1.0	-	0.9	-	0.10	-
Euro 3	2000.01	0.64	-	0.56	0.50	0.05	-
Euro 4	2005.01	0.50	-	0.30	0.25	0.025	-
Euro 5a	2009.09 <sup>b</sup>	0.50	-	0.23	0.18	0.005 <sup>f</sup>	-
Euro 5b	2011.09 <sup>c</sup>	0.50	-	0.23	0.18	0.005 <sup>f</sup>	6.0×10 <sup>11</sup>
Euro 6	2014.09	0.50	-	0.17	0.08	0.005 <sup>f</sup>	6.0×10 <sup>11</sup>
<b>Positive Ignition (Gasoline)</b>							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-	-
Euro 2	1996.01	2.2	-	0.5	-	-	-
Euro 3	2000.01	2.30	0.20	-	0.15	-	-
Euro 4	2005.01	1.0	0.10	-	0.08	-	-
Euro 5	2009.09 <sup>b</sup>	1.0	0.10 <sup>d</sup>	-	0.06	0.005 <sup>e,f</sup>	-
Euro 6	2014.09	1.0	0.10 <sup>d</sup>	-	0.06	0.005 <sup>e,f</sup>	6.0×10 <sup>11</sup> *g
<p>* At the Euro 1..4 stages, passenger vehicles &gt; 2,500 kg were type approved as Category N<sub>1</sub> vehicles  † Values in brackets are conformity of production (COP) limits  a. until 1999.09.30 (after that date DI engines must meet the IDI limits)  b. 2011.01 for all models  c. 2013.01 for all models  d. and NMHC = 0.068 g/km  e. applicable only to vehicles using DI engines  f. 0.0045 g/km using the PMP measurement procedure  g. 6.0×10<sup>12</sup> 1/km within first three years from Euro 6 effective dates</p>							

Specified as upper limits in g/km emitted from tail pipe (after any exhaust gas aftertreatment) during an NEDC test

European Union legislation adopted in mandatory emission reduction targets for CO<sub>2</sub> exhaust emissions due to concerns over climate change.

The fleet average to be achieved by all new cars is 95g/km.

The targets that will apply from 2025 onwards are based on the WLTP (Worldwide harmonized Light vehicles Test Procedure) and were set out in [Commission Implementing Decision \(EU\) 2023/1623](#):

- Cars: 93,6 g CO<sub>2</sub>/km (2025-2029) and 49,5 g CO<sub>2</sub>/km (2030-2034)
- Vans: 153,9 g CO<sub>2</sub>/km (2025-2029) and 90,6 g CO<sub>2</sub>/km (2030-2034)

Pushing OEMs to look for low emission alternatives.

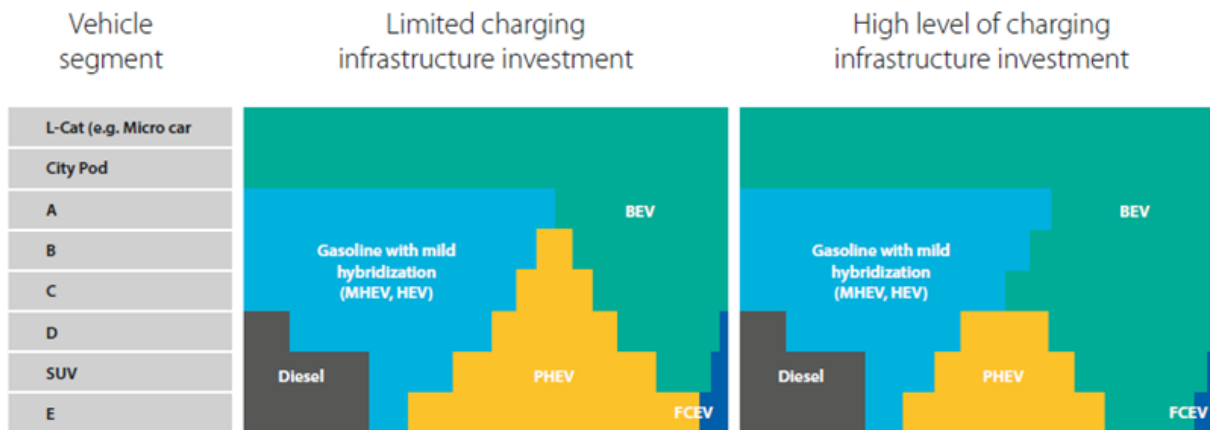
From **2035 onwards**, the EU fleet-wide CO<sub>2</sub> emission target for both cars and vans is 0 g CO<sub>2</sub>/km, corresponding to a 100% reduction.

An interesting report published by Ricardo: Driving automotive electrification white paper

Trend goes towards the increased electrification of passenger car powertrains – (hybridization or battery-electric architectures) driven by need to improve fuel economy and reduce CO<sub>2</sub> emissions.

Ricardo evaluates the current position with regards to passenger car powertrain electrification, and demonstrate how the market is likely to develop throughout the next ten years and beyond. Overall an interesting read.

## Ricardo view of the 2030 passenger car electrified powertrain mix in Europe



Source: Ricardo analysis



Represents a set of vehicle speed points versus time.

Useful to assess fuel consumption and pollutants emissions of a vehicle in a normalized way, so that different vehicles can be compared.

European Driving cycles:

- NEDC
- Artemis driving cycle

American Driving cycles:

- FTP cycle (for Federal Test Procedure) has been created by US EPA (Environmental Protection Agency)

Global harmonized standard for determining the levels of pollutants and CO<sub>2</sub> emissions:

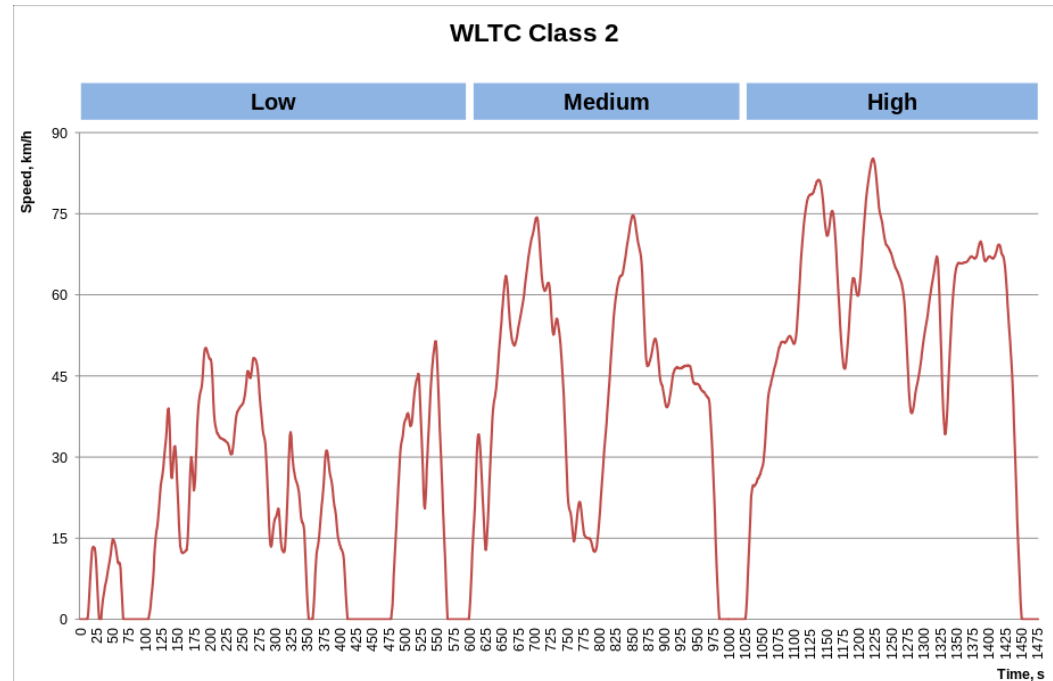
- Worldwide Harmonized Light vehicles Test Procedures (WLTP)

Real Driving emissions of interest

WLTP : much more realistic testing conditions; mimics realistic driving behavior

- A greater range of driving situations (urban, suburban, main road, motorway);
- Longer test distances;
- More realistic ambient temperatures, closer to the European average;
- Higher average and maximum speeds & higher average and maximum drive power;
- More dynamic and representative accelerations and decelerations;
- Shorter stops;
- Optional equipment: CO2 values and fuel consumption are provided for individual vehicles as built;

Enables best and worst-case values on consumer information, reflecting the options available for similar car models.





## Key points likely to be covered:

Particulate matter and NO<sub>x</sub> still high in cities – focus on further reduction

Real Driving Emissions – has led to robust calibration and very low level of emissions but emissions unacceptably high outside the RDE area

Lower emission limits – lower targets for currently regulated pollutant

Limits on new pollutants (e.g. sub23nm particles, NH<sub>3</sub>, N<sub>2</sub>O) likely to be included

Non-exhaust particles (brakes and wear) likely to be also regulated

All driving conditions to be included .



# Euro 7 – Ricardo UK estimates

Euro 7 – Why and how?

Post Euro 6, a final set of regulations is expected, this will include new pollutants and further reductions in those currently regulated, however, further Euro 6 extensions may introduce some of these first

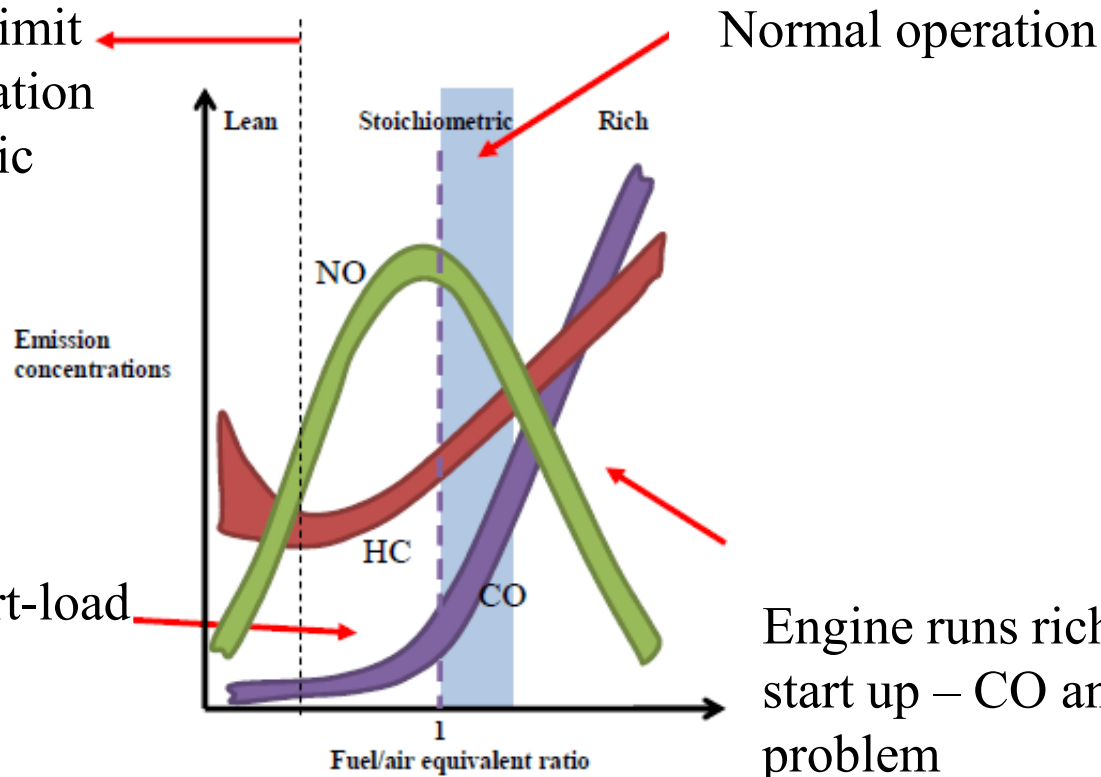


Pollutant (New)	Passenger Car				Commercial Vehicle		
	Euro 6e WLTC (PI) [mg/km]	RDE CF	Euro 7 WLTC (All) [mg/km]	RDE CF	Euro VII WHSC [mg/kWh]	Euro VII WHTC [mg/kWh]	PEMS CF
PN (#/km)	6x10 <sup>11</sup> → 6x10 <sup>11</sup> (incl. 10>23nm)	≤1.5		≤1.2	8x10 <sup>11</sup> → 8x10 <sup>11</sup> (incl. 10>23nm)	6x10 <sup>11</sup> → 6x10 <sup>11</sup> (incl. 10>23nm)	x1.63
NO <sub>2</sub> (Nitrogen Dioxide)	20	≤1.43		≤1.2	120	120	
NH <sub>3</sub> (Ammonia)	M&R		10	≤1.2	10ppm → 10	10ppm → 10	
NO <sub>x</sub>	60	≤1.2	60 → 30-40	≤1.2	400 → 200	460 → 230	x1.5
CO	1000	M&R	1000 → 250-500	≤1.2	1500 → 750	4000 → 2000	x1.5
THC	100	≤1.43	100 → 50	≤1.2	130	160	x1.5
NMHC	68	≤1.43	68 → 35	≤1.2	65	160 → 80	x1.5
PM	4.5		4.5 → 2.5		10 → 10	10 → 10	
THC + NO <sub>x</sub>			90	≤1.2			
CH <sub>4</sub> (Methane)			15 (or CO <sub>2</sub> e)		300 (or CO <sub>2</sub> e)	300 (or CO <sub>2</sub> e)	x1.5
N <sub>2</sub> O (Nitrous Oxide)			10 (or CO <sub>2</sub> e)		10 (or CO <sub>2</sub> e)	10 (or CO <sub>2</sub> e)	
CH <sub>2</sub> O (Formaldehyde)			2.5		5	5	
Total Alds (Aldehydes)			5		10	10	

# SI engine pollutants control

Variation of HC, CO and NO concentrations in the exhaust of a conventional SI engine as a function of fuel/air equivalence ratio.

Lean misfire limit  
– engine operation becomes erratic



Lean operation at part-load to lower HC and CO

Engine runs rich during cold start up – CO and HC problem

For NO<sub>x</sub> control, engine must be run rich but cool.

For CO & HC control, engine must be run lean (but still near  $\phi = 1$ ) to provide good oxidising environment (lean and hot)

Soot formation is not an issue for SI engines (since lean or stoichiometric premixed burn)

Strategies to reduce raw emissions over the period before catalytic converters:

- Improved injection and ignition timing

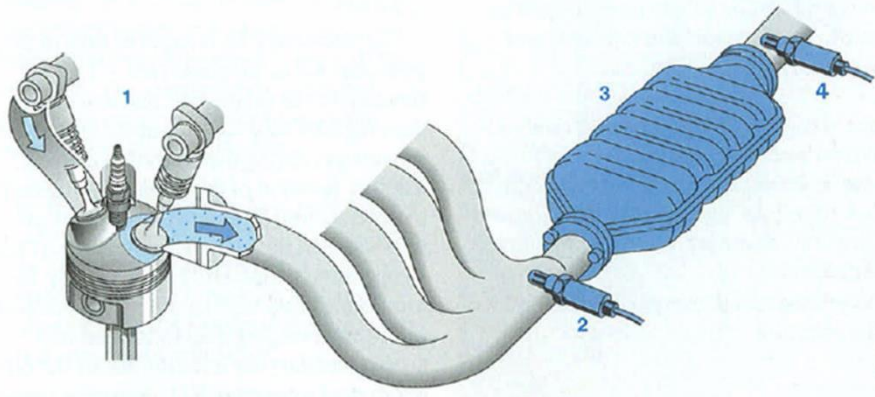
- Lean mixtures during warm-up and continuous operations

Design/Operation features to support rapid catalytic-converter response:

- Late ignition timing and high mass gas flow to induce high exhaust temperature

- Catalytic converter mounted close to the engine 2-phase fuel delivery with direct gasoline injection

## Three-way catalytic converter



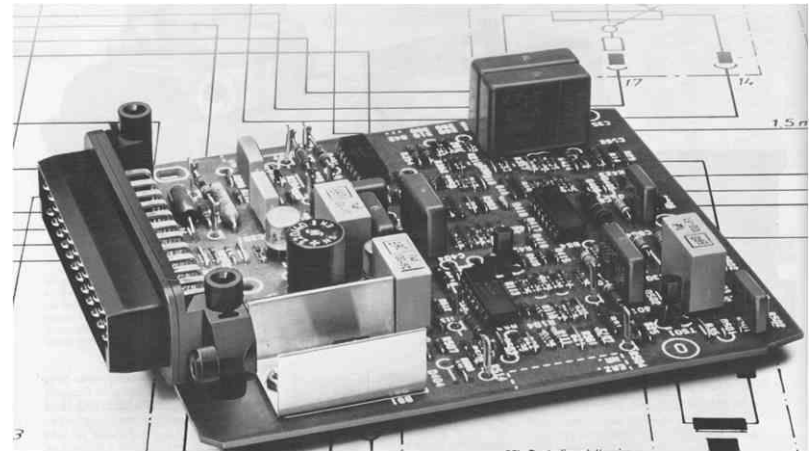
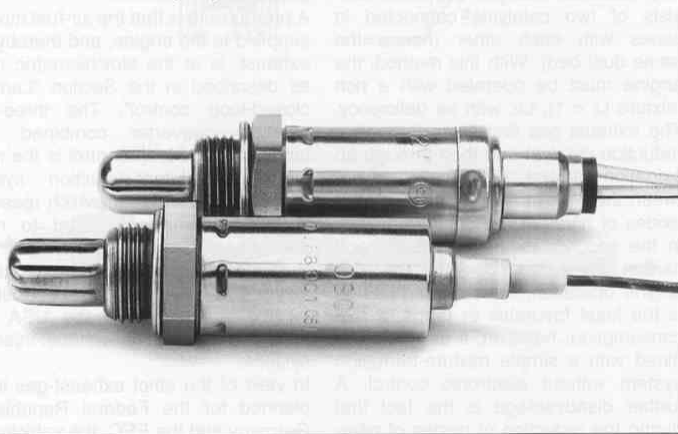
98% efficiency in the conversion of HC, CO and NO<sub>x</sub> into H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>.

Require operating temperature within 400–800 C and  $\phi = 1$  (need good fuel control system with sensor to monitor O<sub>2</sub> level in exhaust, adjust fuel to maintain  $\phi = 1$ ).

# SI engine pollutants control

The conversion of the three-way catalytic converter is as high as possible for the three pollutants, a stoichiometric mixture composition ( $\lambda=1$ ) is required.

Fig. 6: View of the unheated (front) and heated lambda sensors



Sensor measures the oxygen content in the exhaust gas (provide info on mixture composition)

Injecting fuel directly into the combustion chamber leads to mixture preparation issues and fuel rich areas inside the cylinder and particularly at the time of combustion when temperature is very high.

This leads to fuel pyrolysis and formation of carbon nanoparticles

This has historically been an issue of diesel engines but GDI engines suffer for this too (Gasoline previously port injected i.e. well mixed)

These carbon particles are emitted with the exhaust gasses and are highly carcinogenic.

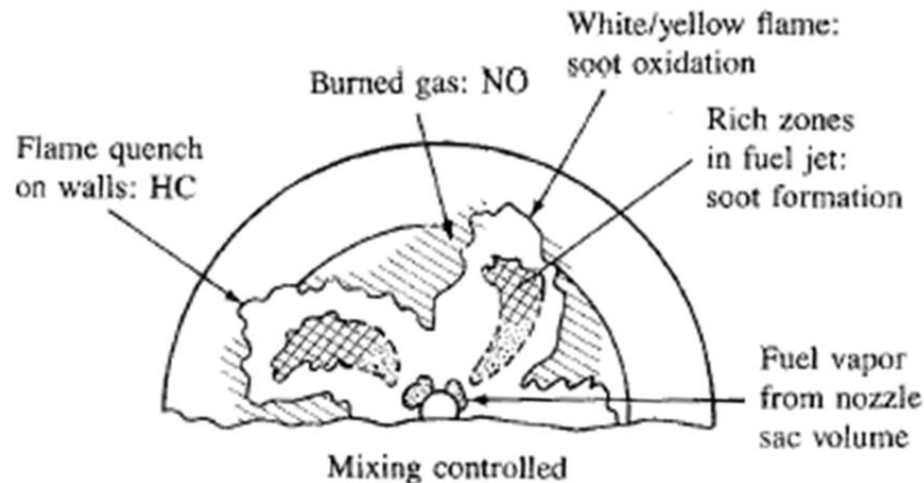
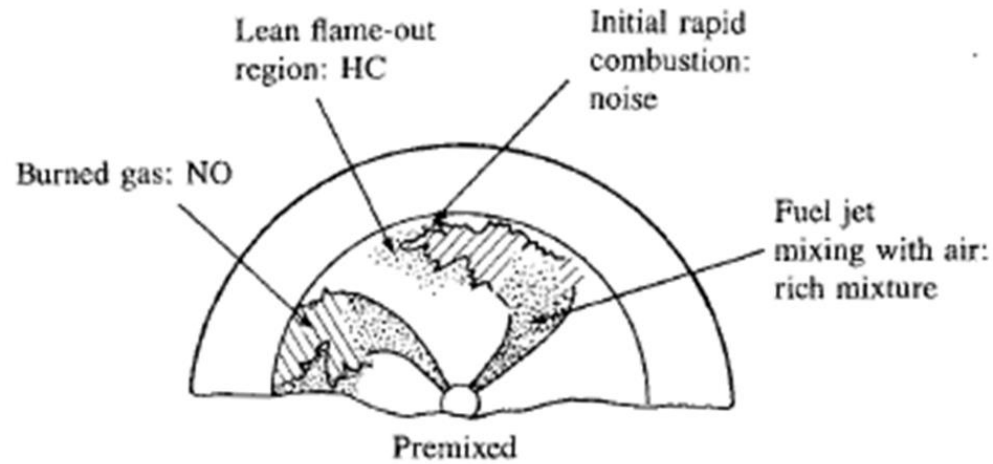
From 2017, new Euro 6 emissions limits were applied to GDI engine cars and particle numbers in exhaust must be less than  $6 \times 10^{11}$  per km.

Particulate filters can be used to trap these particles.

More details will be discussed in the next lecture when we discuss diesel engines

# CI engine pollutants control. In-cylinder

Summary of pollutant formation mechanisms in a direct injection CI engine during premixed and mixing-controlled combustion phases.



Diesels produce less CO and UHC (lean and hot), but more NO<sub>x</sub>.

Use EGR to reduce T adiabatic for NO<sub>x</sub> reduction, but cannot use catalytic converter to reduce NO<sub>x</sub> further since mixtures are always lean.

Soot is the other major problem for diesels – formed at high loads (close to, but still less than stoichiometry).

Particulate traps to capture emitted soot, instead of eliminating soot formation within the engine.

Emissions system must be zero maintenance - (Regulations) - cannot require the driver to remove accumulated soot periodically.

Extra fuel used periodically to burn off soot particles accumulated in traps.

## **Fuel injection:**

Higher injection pressure; pre-injection; injection rate shaping; improved injection timing control.

## **Combustion chamber geometry and air motion optimisation:**

well matched with fuel injection system behaviour.

**Exhaust gas recycle for NO<sub>x</sub>:** cooled for greater impact;

**Exhaust treatment technology:** DOC, NO<sub>x</sub> catalysts; particulate traps.

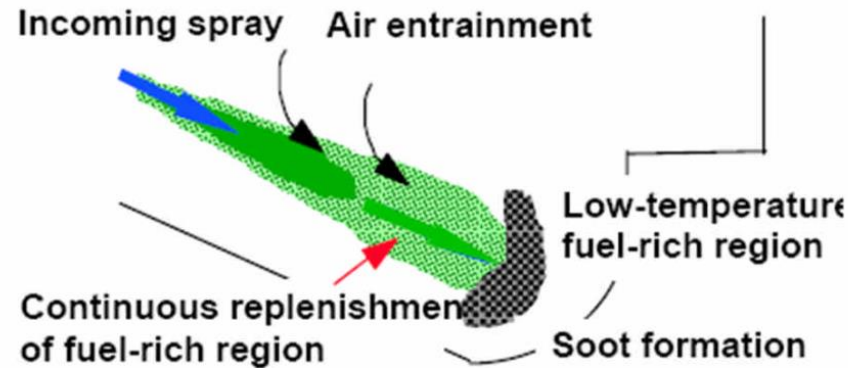
**Cleaner fuels:** sulfur, cetane number, aromatics, oxygenates, volatility.

## Soot reduction mechanism via split main injection strategy

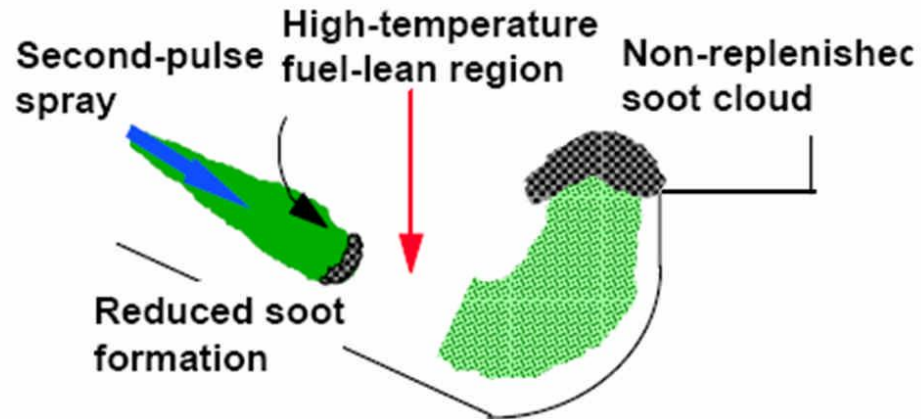
### Mechanism of Soot Reduction

Han et al. SAE 960633

Single injection



Split injection



# Exhaust Gas Recirculation (EGR)

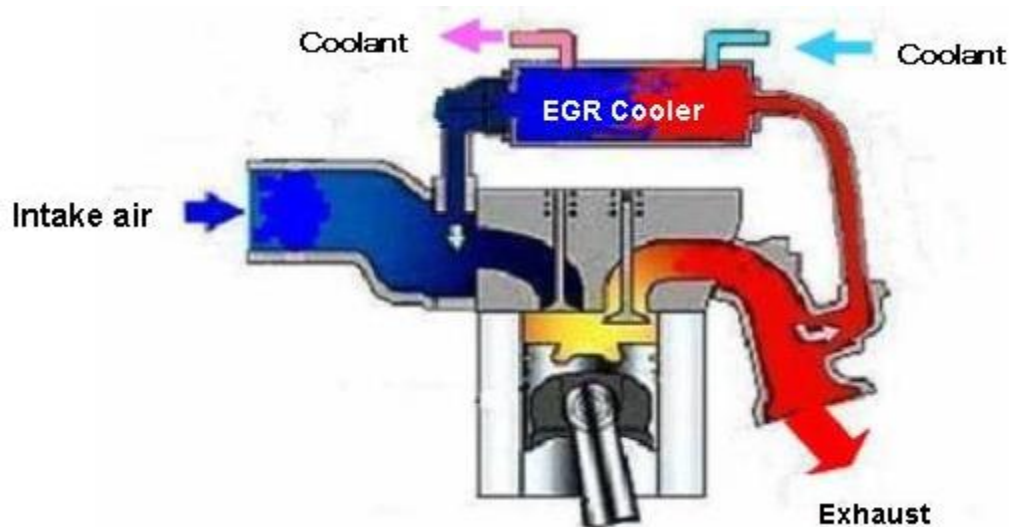
Exhaust stream can be recycled back into the combustion chambers

Dilution of the unburned mixture with EGR leads to lower gas temperature due to the increased heat capacity of the mixture per unit mass of fuel burned

Reduces engine operating temperatures to decrease NO<sub>x</sub> formation



Cons:  
EGR slows combustion and can be detrimental for combustion eff.



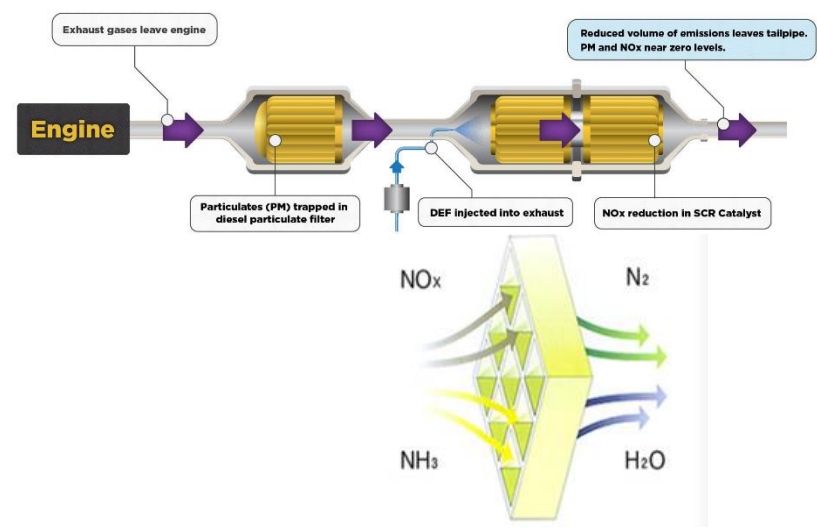
Diesels produce less CO and UHC (lean and hot), but more NO<sub>x</sub>.  
Use EGR to reduce T<sub>adiabatic</sub> for NO<sub>x</sub> reduction, but cannot use catalytic converter to reduce NO<sub>x</sub> further since mixtures are always lean.

## Selective Catalytic Reduction (SCR)

SCR is another technology to reduce NO<sub>x</sub> emissions and especially improved for high-duty vehicles. Because of low exhaust temperature, it has not been used widely for light duty vehicles. But nowadays, it is being developed for light-duty passenger vehicles and a few light-duty vehicle manufacturers like Audi have been using this technology in their automobile

Function is to use NH<sub>3</sub> to reduce NO<sub>x</sub> to diatomic Nitrogen  
Needs base metals but can approach 99% reduction in NO<sub>x</sub> emission

Diesel Emissions Control System



<https://www.dieselforum.org/about-clean-diesel/what-is-scr>

<https://www.audi.co.uk/glossary/a/adblue.html>

Due to the toxic effects of NH<sub>3</sub> and to prevent burning of NH<sub>3</sub> in the warm atmosphere before the reaction, NH<sub>3</sub> is provided from an aqueous solution of urea



## Diesel Oxidation Catalyst (DOC)

The main function of DOCs is to oxidize HC and CO emissions.

Metals catalyze the complete oxidation of unburnt hydrocarbons to CO<sub>2</sub>

Reactions heat exhaust gases up to temperatures in excess of 450°C

Catalyst material coats flow channel matrix

Very efficient catalysis (Upwards of 90% conversion to oxidized products)

## Diesel Particulate Filter (DPFs)

Trapped soot is periodically burnt off through a regeneration event

Active Regeneration: (Fuel is injected into the Aftertreatment system, combusts in the DOC, and this 800° exhaust fully oxidize the soot)

Passive Regeneration:

Catalyzed filter elements allow for exhaust NO<sub>2</sub> to oxidize soot

Requires hot temperatures such as highway driving to function

## Drawbacks of Aftertreatment Systems

Requires more pressure to force exhaust through the filtering mechanisms

Passive regeneration systems require highway driving to clean accumulated soot

Urea injection requires additional tanks, piping, and refueling stations to operate

# Diesel particulate filter (DPF) [similar to GPF]

Ceramic and sintered-metal particulate filters capture soot particulates that pass through with an overall retention efficiency of >95% for particles across the entire spectrum range of 10 nm – 1 μm.

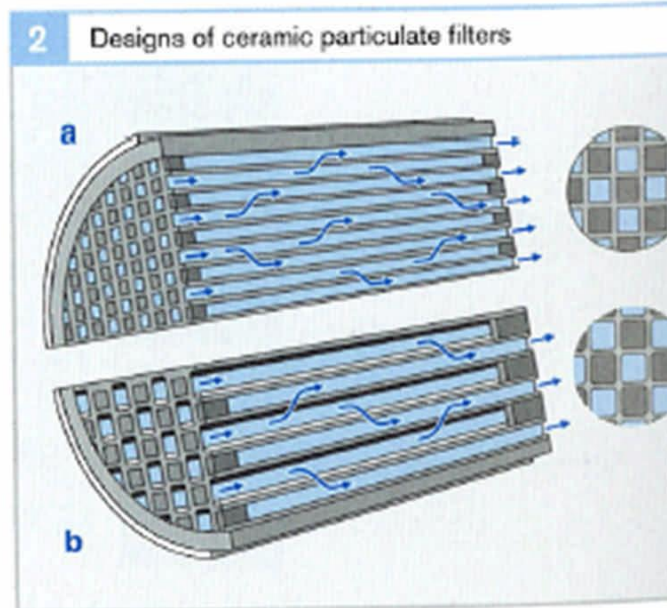
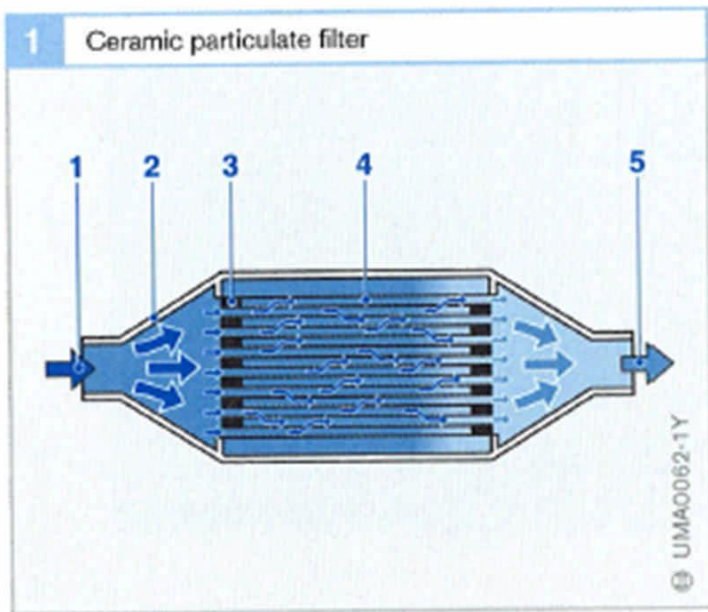


Fig. 1

- 1 Inflowing exhaust gas
- 2 Housing
- 3 Ceramic plug
- 4 Honeycomb ceramic
- 5 Outflowing exhaust gas

Fig. 2

- a Square channel cross-section
- b Octosquare design

Soot deposited in the filter gradually increases exhaust backpressure, impairing engine efficiency and acceleration power.

Filters must be regenerated every 300 – 800 km, by burning off the soot collected using exhaust O<sub>2</sub> at 600°C or NO<sub>2</sub> at 300–450°C.

Smaller hydrocarbon branches form into acetylene and then mainly into Polycyclic Aromatic Hydrocarbons (PAHs).

## **Precursors formation**

Production of polycyclic aromatic species is via:

- Acetylene ( $C_2H_2$ ) molecules react to form polyacetylenes (e.g.  $C_4H_3$ ). These then form benzene ( $C_6H_6$ ) and phenyl radicals ( $C_6H_5$ ). Additional reactions lead to larger PAHs.
- Relatively stable radicals (e.g.  $C_3H_3$ ,  $C_3H_5$  and  $C_5H_5$ ) react to form aromatic species. Subsequent reactions add rings and lead to PAHs.

## **Homogeneous gas-phase inception**

Partial pressure of precursors forces molecules to condense physically and chemically at 300-700 amu. PAH sticks to each other to react and agglomeration seeding the formation of soot.

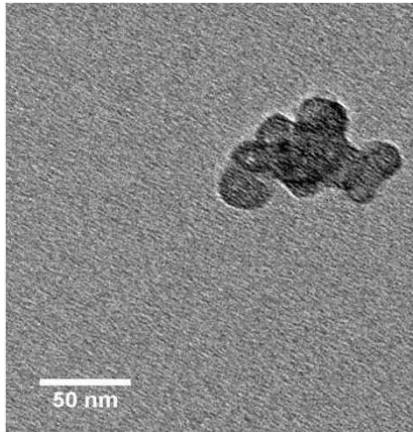
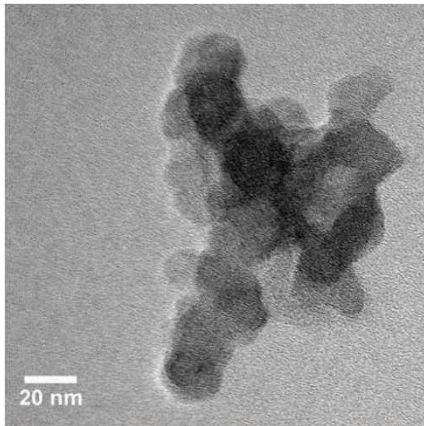
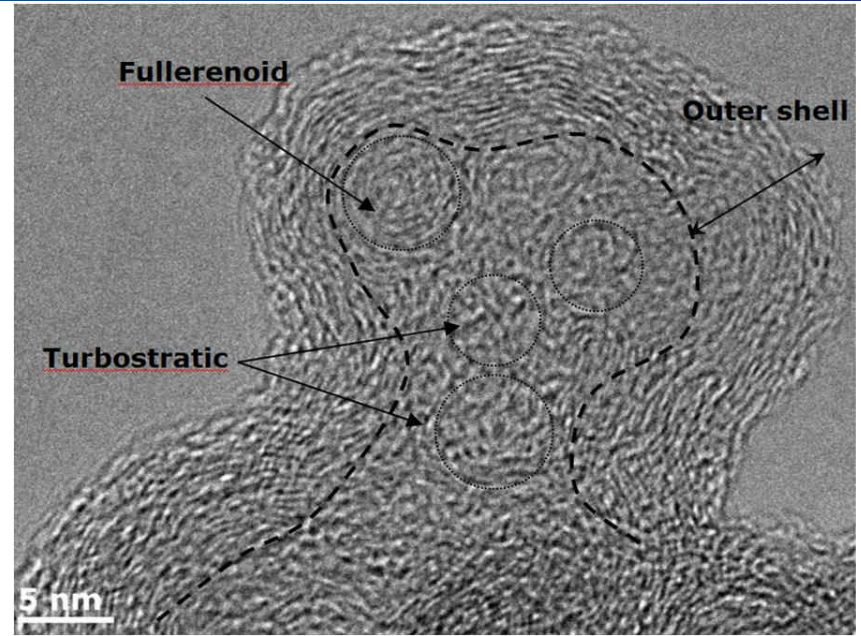
## **Particle coagulation**

Colliding soot particles fuse to form larger particles, but number of particle decreases. This occurs after soot formation. At this point, soot is still young/small where size of soot particle  $\sim$  size of graphite at a density of 1.8 – 2.0 g/cm<sup>3</sup>.

## Surface growth

This is a heterogeneous process where the deposition of gas-phase HC on hot particles surfaces.

Surface reactions add carbon atoms to particles, leading to significant soot loading. This process can occur at low temperature.



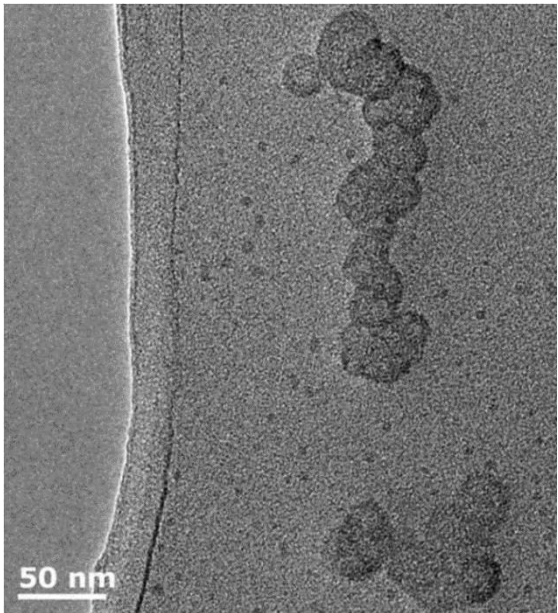
## Particle agglomeration

Mature soot particles reduce in active sites for surface growth. This process leads to not fusion but formation of aggregates (particles sticks to one another).

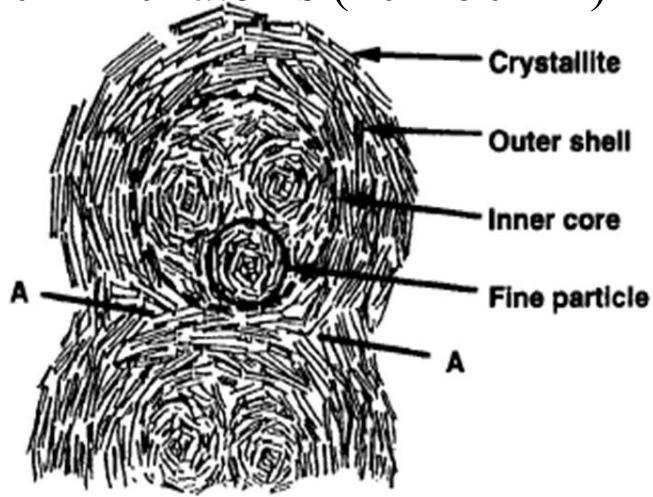
## Adsorption and condensation

Occurs in the dilution tunnel, where hydrocarbons and other organic substances are absorbed into the soot particles, forming particulate matters.

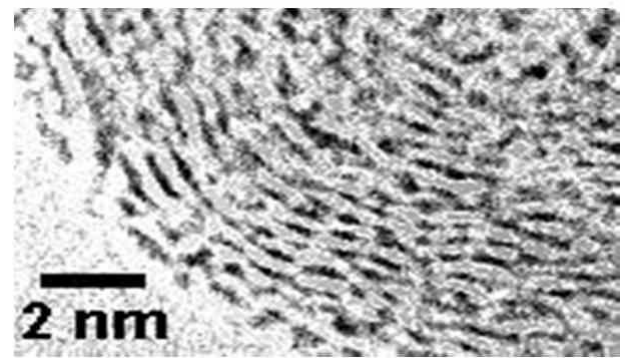
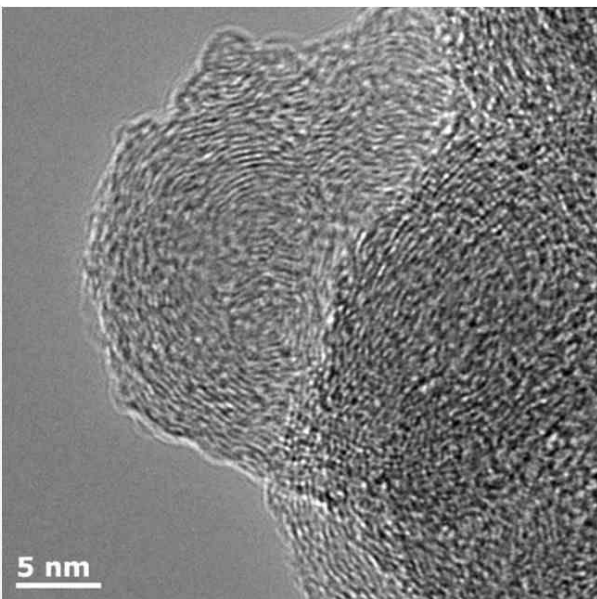
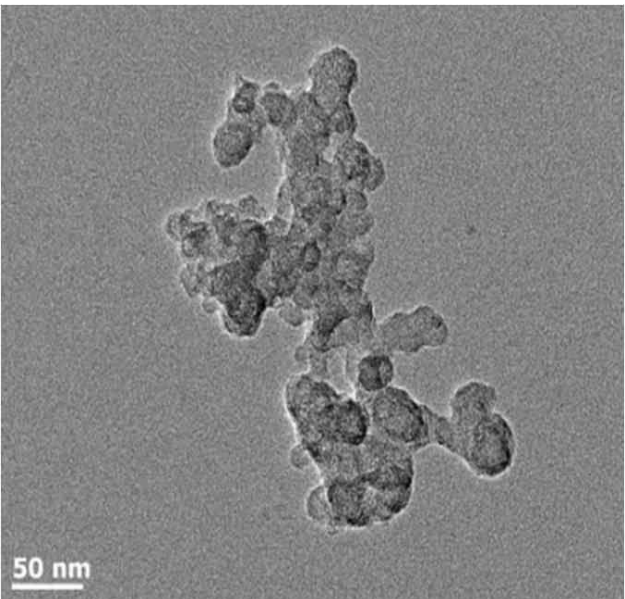
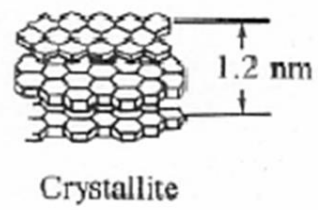
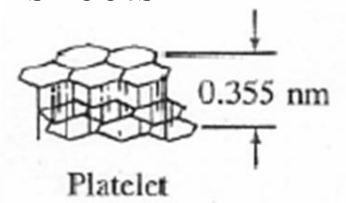
# Particulates formation mechanism



Quasi-spherical particles  
 $10^5 - 10^6$  atoms (10 - 50 nm)



Spherule composed of many  $\sim 10^4$  slabs of graphite carbon sheets

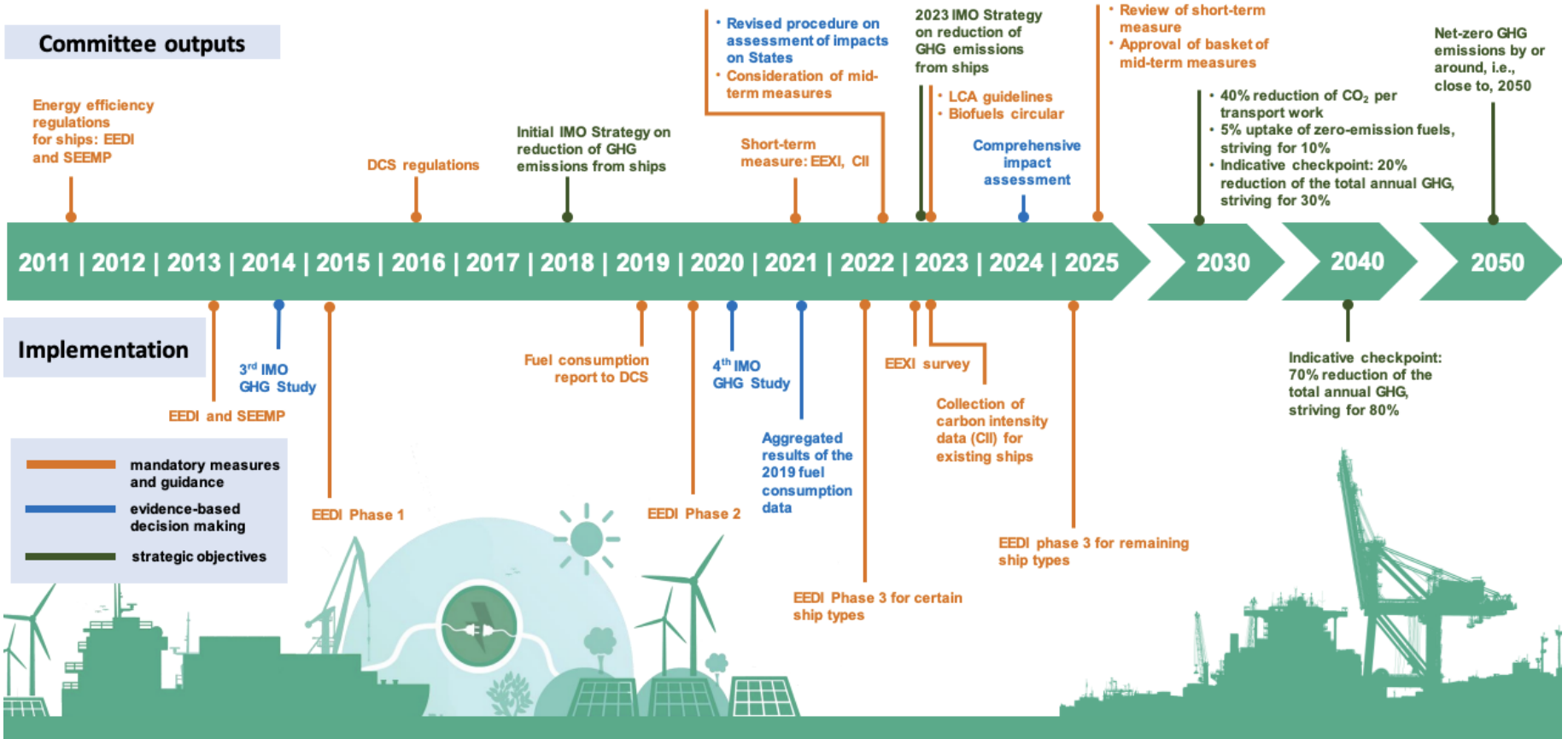


Soot particles from DI diesel engines.

The International Maritime Organization (IMO) implemented guidelines to reduction in carbon intensity of international shipping and other harmful emissions

## Addressing climate change

Over a decade of regulatory action to cut GHG emissions from shipping



Significant developments in maritime fuels are being driven by environmental concerns and the IMO's stringent emission requirements.

The amount of sulphur in marine fossil fuels is being drastically decreased.

To reach aggressive decarbonisation goals, the sector is moving away from conventional heavy fuel oil and towards cleaner substitutes.

Liquefied natural gas, or LNG, is becoming a popular transitional fuel.

Long-term priorities, however, centre on creating and deploying zero-emission fuels such as advanced biofuels, hydrogen, and ammonia.

By 2050, e-ammonia and other such fuels may account for 20% to 60% of all shipping fuels.

Methanol and biofuels are also anticipated to become more popular in the near to medium future.

Rules are becoming more stringent.

Marine engines must have efficient exhaust aftertreatment systems.

Vessels operating in the Emission Control Areas (ECAs) need emission reduction equipment installed in accordance with IMO Tier III requirements.

Typical emissions from shipping: Carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), sulphur oxides (SO<sub>x</sub>), and particulate matter (PM) as the main pollutants produced when fossil fuels are burned in marine compression ignition engines.

Unburned hydrocarbons (UHC) and carbon monoxide (CO) are also produced.

The heavy fuel oil used in international shipping contains on average 2700 times more sulphur than road fuel.

IMO guidelines mandate a global sulphur reduction in fuels with even stricter regulation in specific areas.

The IMO requires the application of low-sulphur fuel (0.1% sulphur content)



**NO<sub>x</sub> emissions:** The **Selective Catalytic Reduction (SCR) systems** are the most recognised aftertreatment method for lowering NO<sub>x</sub> in marine engines. After injecting a reducing agent—usually a urea solution—into the exhaust stream, a catalyst facilitates the chemical reactions that break down the nitrogen oxides into innocuous elements like nitrogen and water.

**SO<sub>x</sub> emissions:** Using low-sulfur fuels is, in fact, the simplest method to guarantee adherence to the MARPOL emission limits

To reduce SO<sub>x</sub> emissions, exhaust gas scrubbers are becoming a crucial part of maritime aftertreatment systems. A wet scrubber system cleans exhaust gases as they approach the funnel by adding water to the gas stream. After being injected, fresh or seawater travels through the scrubber and mixes with the exhaust fumes. The bottom of the scrubber unit collects and releases the dissolved sulphur compounds in the scrubber water.

**Particulate matter:** Sulphates, metallic elements, carbon-based particles, and a variety of organic and inorganic materials make up the complex mixture of PM produced by ships. These particles have a very wide size distribution, with diameters ranging from a few nanometres to several microns.

It is also far more difficult to develop a single, globally applicable aftertreatment solution for maritime applications, and the range of particle sizes necessitates a more advanced approach to emissions management.

Electric precipitators (EP), diesel oxidation catalysts (DOC), diesel particulate filters (DPF), and wet and venturi scrubbers are some of the technologies that have the highest particle removal efficiency, ranging from 85 to 95%.