Early Careers Environmental Brief (ECGECEB No 8)

Diesel particulate matter

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We are becoming increasingly aware of the risks that diesel particulate matter (DPM) poses to humans and the environment. This environmental brief gives an overview of what is already known about DPM and how it can be controlled.

Source and formation

DPM is produced by compression ignition engines and released from diesel exhausts. Diesel engines are popular due to their energy efficiency, durability, reliability, and low-operating costs compared to petrol engines (*1*). They are extensively used for commercial transport (trains, cars, buses, ships, trucks) as well as for industrial activities (mining equipment, agriculture, construction) (*2*). DPM is formed because of incomplete combustion within a diesel engine. Fuel is injected into the combustion chamber at high temperatures and pressures, where it is then atomised. The droplets are not dispersed uniformly, resulting in local oxygen deficient regions around some fuel particles. These conditions lead to incomplete combustion and the formation of DPM through a series of steps (*3*):

1. **Pyrolysis** – The oxygen deficient and high temperature conditions cause the organic compounds within the fuel to undergo a change in molecular structure. This produces acetylene molecules, which then combine to make benzene rings and dehydrogenate to form polycyclic aromatic hydrocarbon (PAH) precursor molecules.

2. **Nucleation** – Hydrocarbons are deposited on the surface of the precursor molecules, which develop to form the nuclei. This process results in the production of numerous small particles less than 3 nm in size (*4*).

3. **Surface growth** occurs within 0.05 ms after the formation of nuclei. Hydrogen molecules are stripped from the nuclei and form spherules, which significantly increase the size of particulate matter (now 20-50 nm), and therefore create soot.

4. **Coalescence** – Inter-particle collisions lead to the formation of agglomerated spherules. The size of these primary spherical particles depends on the engine operating conditions.

5. **Oxidation** – The hydrocarbons are oxidised and then condense on the soot to form DPM.

Structure and composition

DPM is a mix of solid and liquid particles suspended in a gas and formed as agglomerates of primary spherical particles (*1*) (**Figure 1**).

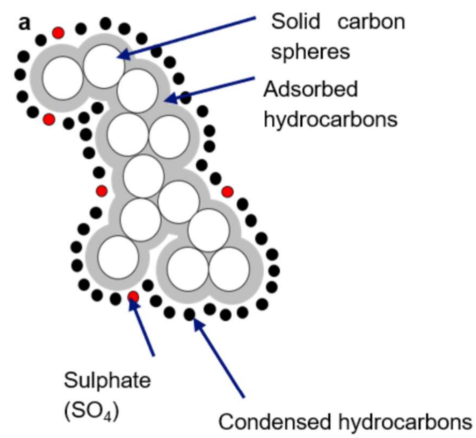

Figure 1. A diagram, redrawn with permission from Mohankumar and Senthilkumar (3), of the structure of DPM.

The exact chemical composition of DPM is difficult to quantify because it is dependent on several factors (fuel structure and/or composition, lubrication oil quality, combustion conditions, and engine type). In general, DPM consists of three main fractions: carbonaceous (soot) fraction, non-volatile insoluble fraction (IF), and volatile soluble organic fraction (SOF). IF is composed of ash content (a mixture of oxides, sulfates, carbonates, metals and non-metals) and other impurities. The SOF consists of organic carbon, sulfate and nitrate compounds which are derived from the lubricating oil, unburned fuel, and compounds formed during combustion (*1*).

Impacts

Most DPM is classed as 'ultrafine' $PM_{0.1}$ as its particles tend to have a diameter of < 100 nm (0.1µm) These can penetrate deep into organs and even enter the bloodstream (2, 5). Humans and animals are primarily exposed to DPM pollution through inhalation, where the particles are deposited within the respiratory system, causing acute inflammation of the lungs. The toxicological effects of DPM depends on the exact size and surface area of the particles as well as the presence of absorbed transition metals or other organic materials. For example, PAHs, which are usually present within DPM, are known human carcinogens, capable of altering the DNA within lung tissue. In addition to respiratory illnesses, DPM may cause adverse health effects in other organs through translocation, whereby DPM particles migrate to a secondary organ post inhalation. Research has shown evidence of this exposure within the brains of monkeys and rats, causing neurological effects (5).

Controls

Diesel Oxidation Catalyst (DOC) – DOCs are catalytic converters with an open monolith honeycomb structure. They decrease the mass of DPM through catalytic oxidation of hydrocarbons that would otherwise be adsorbed onto the solid carbon sphere. Harmful exhaust emissions such as CO, PAH, and the SOF can also be neutralised through oxidation within the DOC through the following reaction:

$$C_nH_{2m} + \left[n + \frac{m}{2}\right] O_2 \rightarrow nCO_2 + mH_2O \qquad \text{(Eq1)}$$

Diesel Particulate Filter (DPF) - DPFs physically trap particulate matter (PM) from the exhaust stream and prevent it being released into the atmosphere. They ensure the entrapment of PM with blocked channels at alternate ends, forcing the PM through the porous substrate (with an efficiency of > 90%). Over time, DPFs accumulate PM and become saturated which can lead to engine failure if left untreated. DPFs must be 'regenerated' to prevent this build up by oxidising the soot at high temperature.

DOCs and DPFs are both well established and popular post combustion DPM control techniques. Since February 2014, MOT tests in the UK have included a check for the presence of a DPF; 'A missing DPF, where one was fitted when the vehicle was built, will result in an MOT failure'. In May 2018, rules were then made much stricter: diesel vehicle exhausts were measured using a diesel smoke meter (6).

Biodiesel – Recently, there has been an increasing number of studies investigating DPM emissions from biodiesel fuels. Overall, findings (7) show the following:

1. PAH emissions and carcinogenic potency is less with biodiesel compared to regular diesel;

2. PM concentration released from biodiesel fuel is less than regular diesel with increasing load (**Figure 2**);

3. Biodiesel PM primary particle size is smaller and has a more amorphous structure; and

4. Using a blend of biodiesel may improve the ease of DPF regeneration.

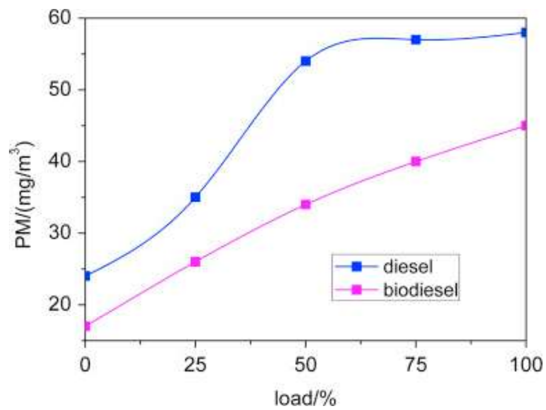

Figure 2. Effect of engine load on PM, reproduced with permission from Wang et al. (7).

Despite these findings, relatively little is known about the toxicology of PM emissions from biodiesel fuel use. Therefore, there is a need for further research to determine whether using biodiesel could be considered an effective DPM control technique in a real world context.

References

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