Carbon Nanotubes, Nanorods, and Nanoparticles from Engines

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Carbon agglomerates comprise most mass from current Diesel engines, different structures evident.

- Metallic ash
- Semi volatile droplets
Dramatic reductions in PM standards have been facilitated by fuel sulfur reductions.

- Future LD standard 5 times more stringent than current HD
- But EU PN standards are much, much more stringent
Diesel engine emission controls

- Diesel engines produce very low CO, HC, and evaporative emissions – NOx and particulate matter (PM) are the main problems
- Engine out controls – managing the mixture composition mixing history
  - Advanced fuel injection systems
  - Air management
  - Cooled EGR
- Aftertreatment
  - For PM control
    - Diesel oxidation catalyst – removes much of organic carbon fraction, also reduces CO and HC (already low)
    - Particle filters
  - For NOx control
    - SCR
    - Lean NOx trap
    - Combined systems
The IARC work based on tests old TDE, very different from modern NTDE used by ACES

Hesterberg, Thomas W.; Long, Christopher M.; Sax, Sonja N.; Lapin, Charles A.; Mcclellan, Roger O.; Bunn, William B.; Valberg, Peter A., 2011. Particulate matter in new technology diesel exhaust (NTDE) is quantitatively and qualitatively very different from that found in traditional diesel exhaust (TDE), Journal of the Air and Waste Management Association, v 61, n 9, p 894-913.
Health concerns about diesel exhaust – who is right? Probably both

Lyon, France, June 12, 2012

After a week long meeting of international experts, the International Agency for Research on Cancer (IA RC), which is part of the World Health Organization (WHO), today classified diesel engine exhaust as carcinogenic to humans (Group1), based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Boston, April 12, 2012

STUDY FINDS FEW HEALTH EFFECTS FROM NEW TECHNOLOGY DIESEL ENGINES: The first results of the most comprehensive study ever undertaken of the health effects of exposure to new technology diesel engines has found no evidence of gene damaging effects in the animals studied, and only a few mild effects on the lungs, according to a report issued today by the Health Effects Institute (HEI) 1. The study – the Advanced Collaborative Engine Study (ACES) – is exposing rats and mice for 16 hours a day to emissions from a heavy duty diesel engine meeting stringent 2007 US EPA standards that reduce emissions of fine particles and other pollutants by over 90% from levels emitted by older engines.
A new worry: Carbon nanotubes (CNTs) and related structures

- Murr and Bang (2003); Murr and Garza (2009) observed nanotube and nanorod like structures
  - In brake shop air
  - Near highways
  - From natural gas stoves and powerplants
  - From propane stoves
- Poland, et al., (2008) raised concerns about hazards associated with growing production and use of nanotube and related materials
- Manoj, et al. (2012) used XRD methods to detect CNTs in DPM and found them rare
- Jung, et al., (2013) identified elongated structures in DPM from 3 different engines but they were rare except when iron added to fuel.
- Many studies of soot morphology, most have not reported nanotubes / rods / or other elongated structures but in low frequency
- Kolosnjaj-Tabi, et al., (2015) report a very high frequency of these structures in air, exhaust, lungs.
Nanotube and nanorod like structures in brake shop air and near interstate highway

Brake repair shop

Roadside near interstate

MWCNTs from natural gas and propane combustion

Natural gas:
(a) stove, (b) powerplant

Propane stove

Nanorods / tubes are rare in normal Diesel exhaust without metal additives

Medium-duty Diesel, LSD fuel, nanorod, 150 nm x 20 nm ~ 2 mn ID, frequency rare

Light-duty Diesel, LSD fuel, + 600 ppm Fe, nanotube, 90 x 8 nm, 0.8 ID, frequency ~1%

Heavy-duty Diesel, LSD fuel, nanorods: 173 x 14 nm, 85 x 20 nm, frequency rare

Typical soot formation models don’t include nanotubes

Important processes in soot growth, adapted from Sander et al. (2011)

Validation of soot formation models

(a) TEM-style projection of a cluster of 50 coronene (Totton et al. (2010)) and (b) experimental HRTEM images of small soot particles sampled from an engine (Mosbach et al. (2009))


Conditions necessary to produce CNTs

- Height, et al., 2004 flame
  - Source of carbon
  - Source of heat
  - Presence of metallic catalyst particles
  - Very sensitive to conditions
- Li, et al., 2004 flow reactor
  - Fe is a very good catalyst
  - S facilitates the reaction of hydrocarbons with Fe
- Engine combustion provides
  - Carbon
  - Heat
  - Fe or other catalyst metals wear, fuel and oil additives
  - S from fuel and oil


Diesel combustion – fuel jet entrains oil that may supply nanotube catalysts

The burning fuel jet also entrains oil atomized and evaporated oil containing metals from additives and engine wear, possible catalysts for nanotube formation.

Temperature composition history for engine combustion

Blue oval shows mixture region where flames form CNTs

Swanson, et al., showed strongly enhanced formation of CNT like structures with high levels of S, Fe.

Diagram: Bar chart showing the number of images out of 100 for different combinations of ppm sulfur (S) and ppm iron (Fe). The chart includes data points for 0/0, 500/0, 4500/0, 0/36, and 4500/36, with 1800 and 2400 ppm concentrations.
Filtration of CNTs

Characteristics of test CNTs

Filter penetration lower for CNTs than spheres.

Summary

- Engines and flames form CNTs, especially in the presence of sulfur and metal catalysts but in **much smaller fractions** than suggested by Kolosnjaj-Tabi, et al.
- Why? Possible explanations
  - Kolosnjaj-Tabi, et al. found dust more enriched in CNTs than engine soot – brake and clutch wear from heavy traffic?
  - Other combustion – domestic, powerplants, incineration
  - Metal fuel additives
    - Ce, Fe, Sr used with some DPFs, but any CNTs should be captured
    - Fe, Mn antiknock agents but not in EU
  - Poor lung clearance of CNTs
  - Sample preparation bias
  - Other??
Outlook

- CNT formation by engines enhanced by sulfur, metals
- Potential for significant CNT formation by engines in developing world
  - High sulfur fuels
  - Metals from engine wear, oil additives
  - Metallic fuel additives, iron, manganese, used as antiknock agents
  - Poorly managed combustion
- In the developed world
  - Exhaust filters very effective
  - Engines without filters could be an issue
- Further study needed
- Archival TEM images
Thank you, questions?
Fig. 1 The experimental system for CNT filtration tests

- Sheath Air
- Acrylic Glass
- Po-210
- H.V.
- DMA
- Kr-85
- Dryer
- Power Supply
- Filter Holder
- CPC
- Make-up
- Po-210
Other CNT synthesis

Evolution of soot size distribution

Figure 6. (a) Time evolution of the size distribution with aggregates present in the trapped residual gases. (b) Size distribution at 10 CAD ATDC for 10 consecutive cycles. The recirculated aggregates can be clearly identified as the ones larger than about 20 nm. (Reproduced from Mosbach et al., 2009. © Elsevier.)
Soot size distribution development

Figure 7. (continued)