Carbon Nanotubes, Nanorods, and Nanoparticles from Engines

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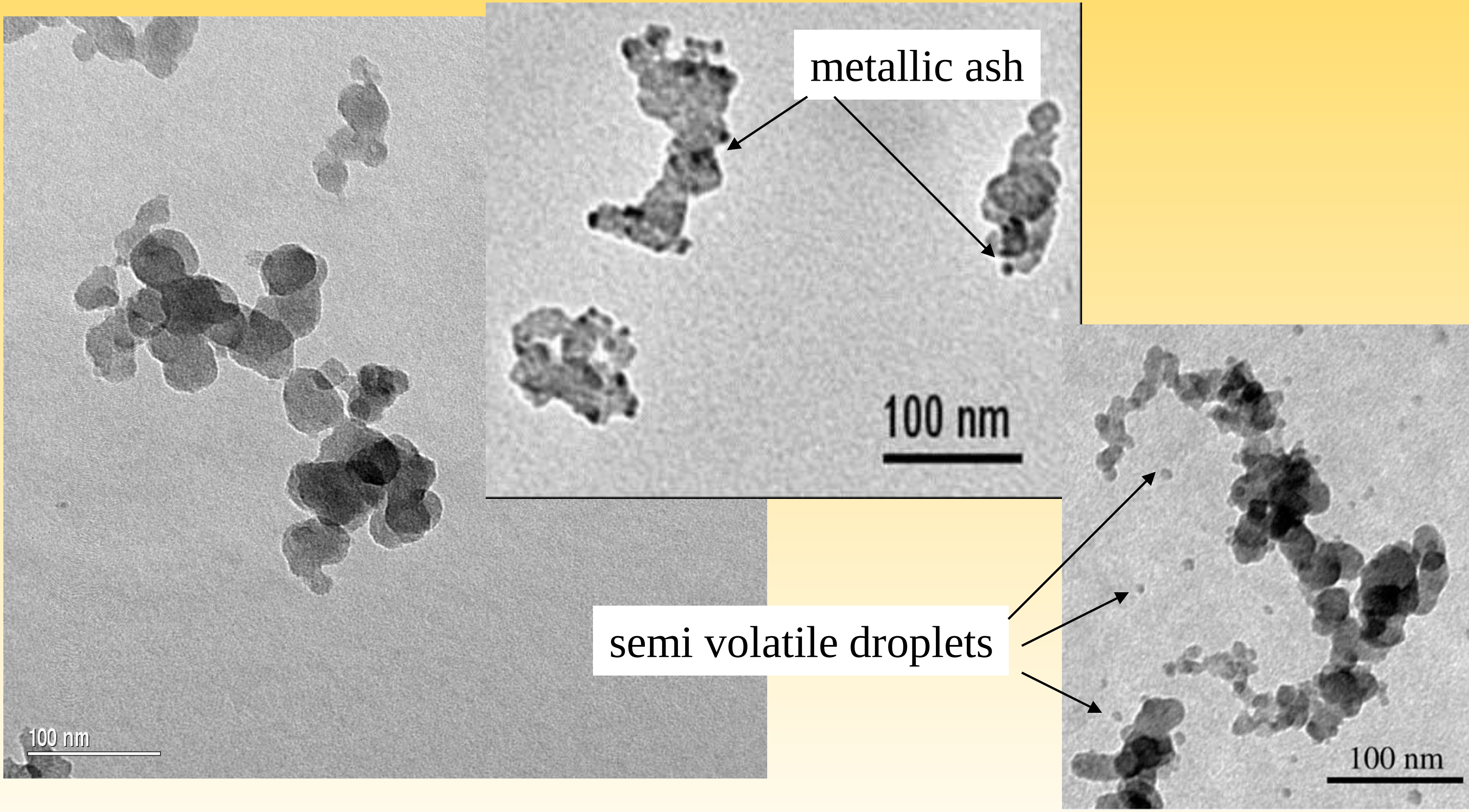
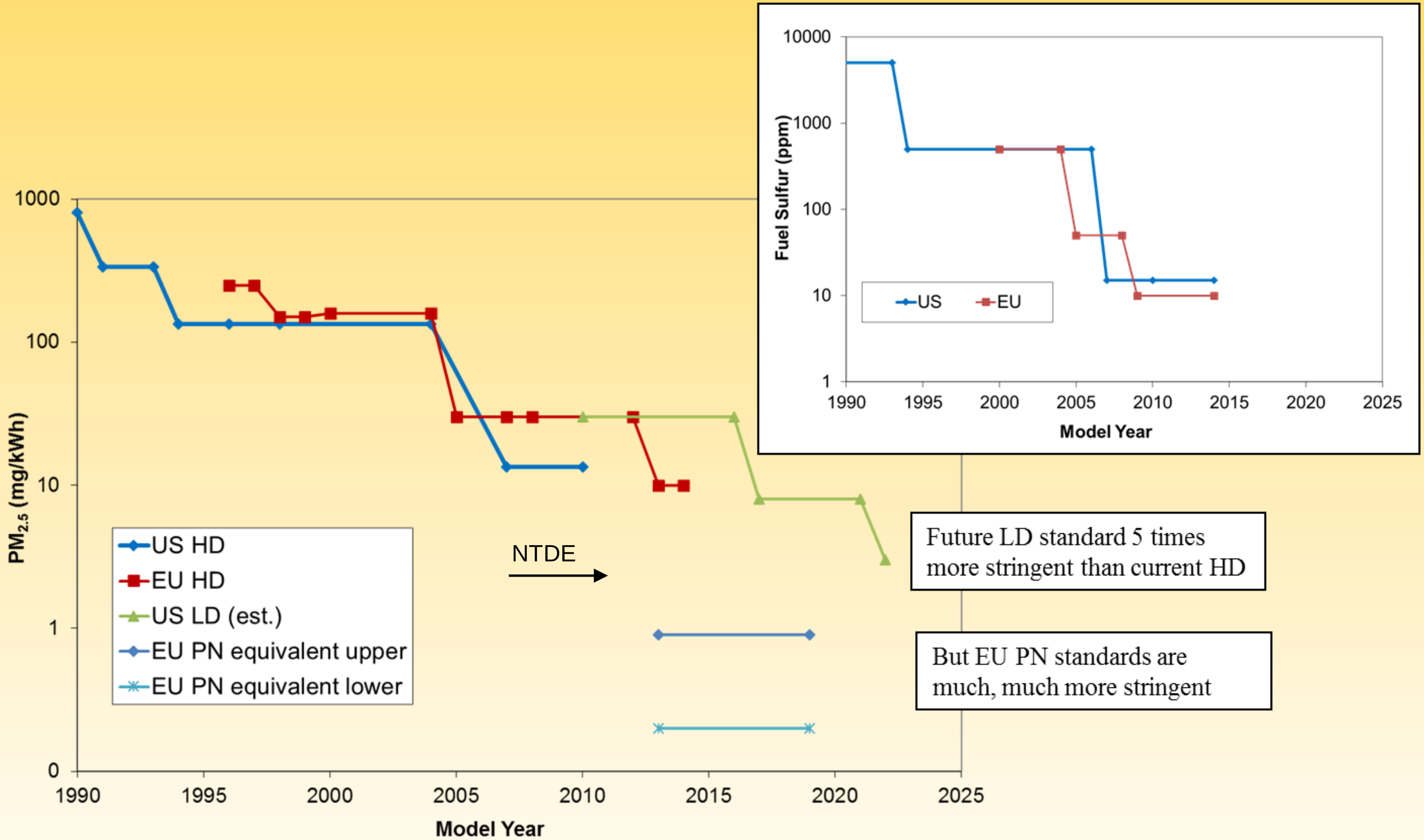
Carbon agglomerates comprise most mass from current Diesel engines, different structures evident

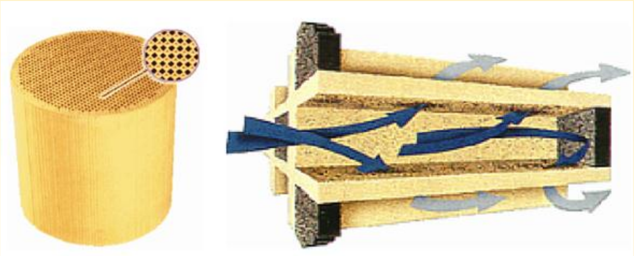


Dramatic reductions in PM standards have been facilitated by fuel sulfur reductions

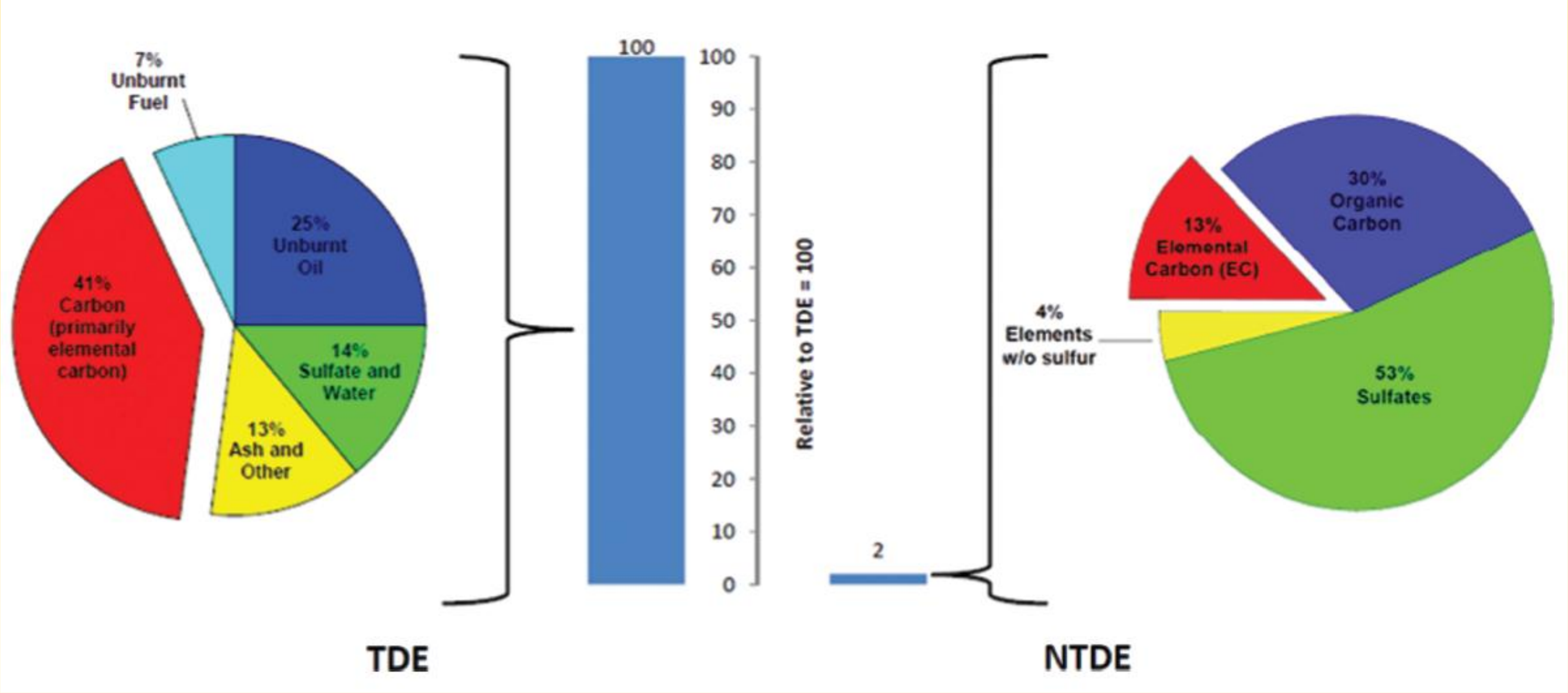


Diesel engine emission controls

- 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



Traditional Diesel Emissions

New Technology Diesel Emissions

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.

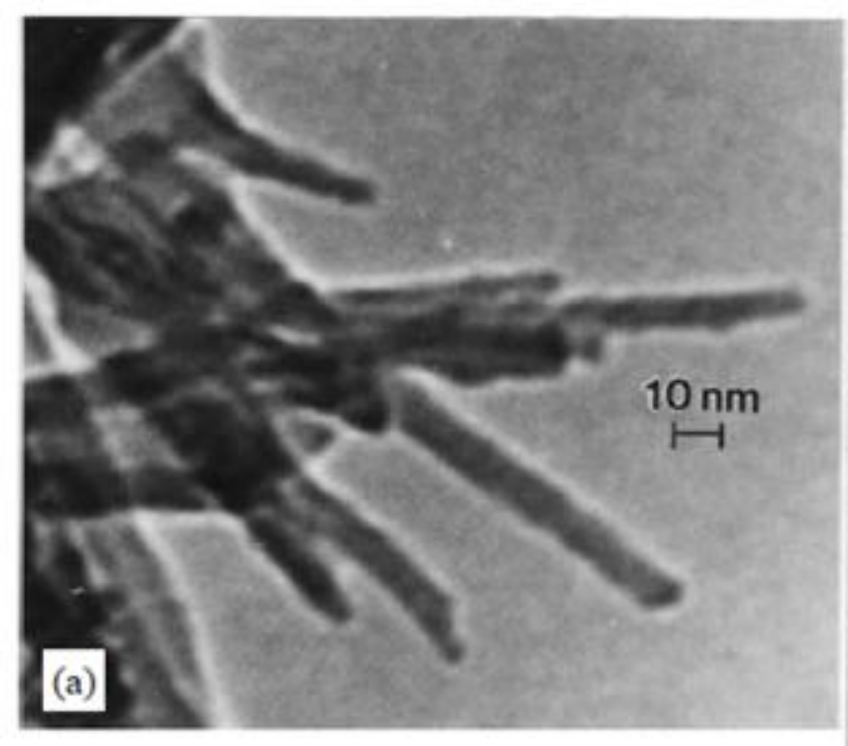
A new worry: Carbon nanotubes (CNTs) and related structures

- 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

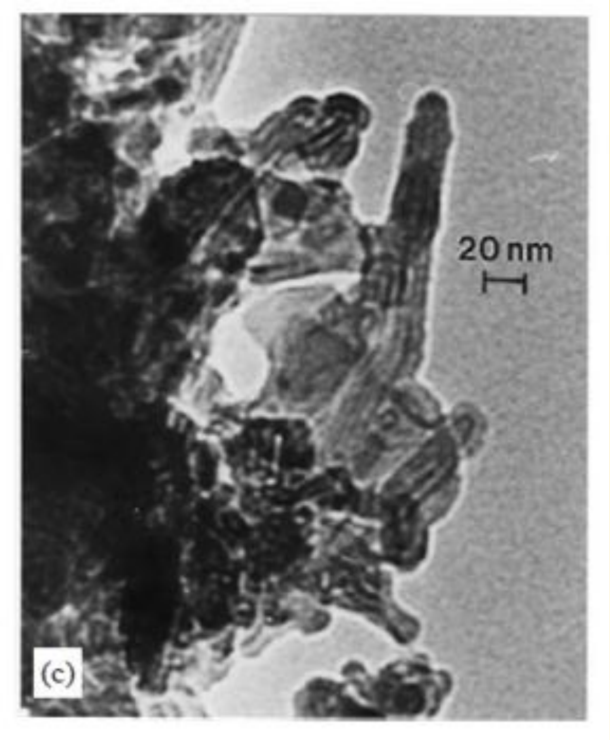
- Kolosnjaj-Tabi, et al., (2015) report a very high frequency of these structures in air, exhaust, lungs.

Nanotube and nanorod like structures in brake shop air and near interstate highway

Brake repair shop



Roadside near interstate

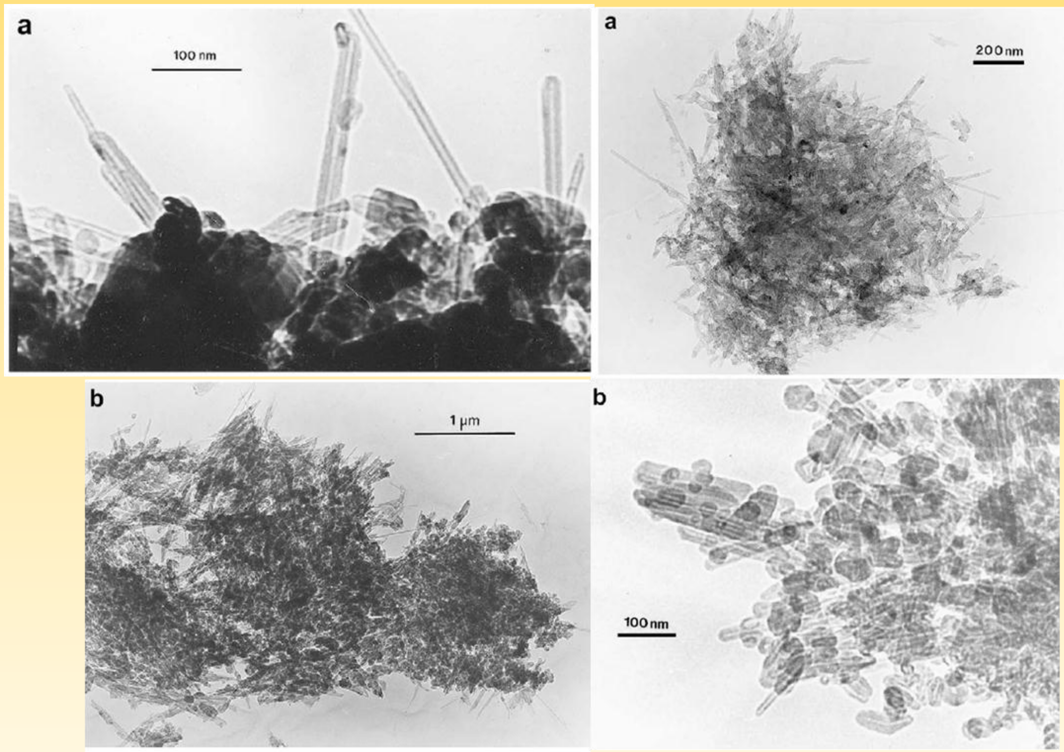


Electron microscope comparisons of fine and ultra-fine carbonaceous and non-carbonaceous, airborne particulates, L.E. Murr and J.J. Bang, Atmospheric Environment 37 (2003) 4795–4806

MWCNTs from natural gas and propane combustion

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

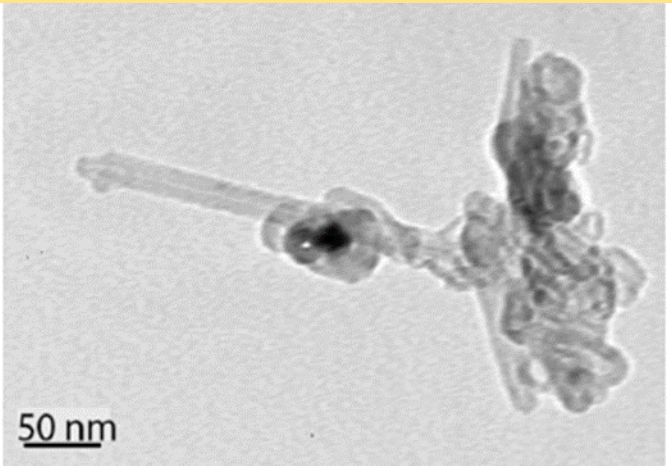
Propane stove



Natural and anthropogenic environmental nanoparticulates: Their microstructural characterization and respiratory health implications, L.E. Murr and K.M. Garza, Atmospheric Environment 43 (2009) 2683–2692

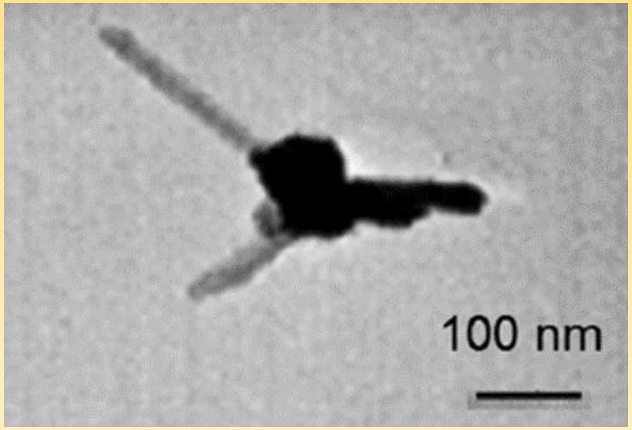
Nanorods / tubes are rare in normal Diesel exhaust without metal additives

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



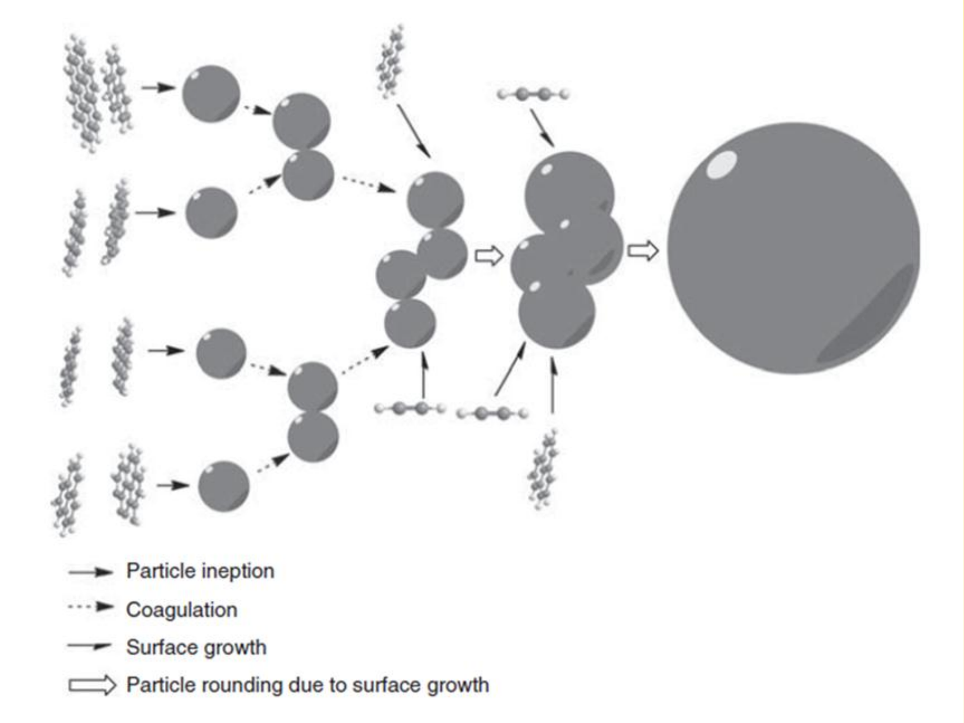
Light-duty Diesel, LSD fuel + ***600 ppm Fe***, nanotube 90 x 8 nm, 0.8 ID, frequency ~1%

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



Jung, Heejung, Art Miller, Kihong Park, and David Kittelson, 2013. Carbon nanotubes among diesel exhaust particles: real samples or contaminants? Journal of the Air & Waste Management Association, Volume: 63, Issue: 10, Pages: 1199-1204.

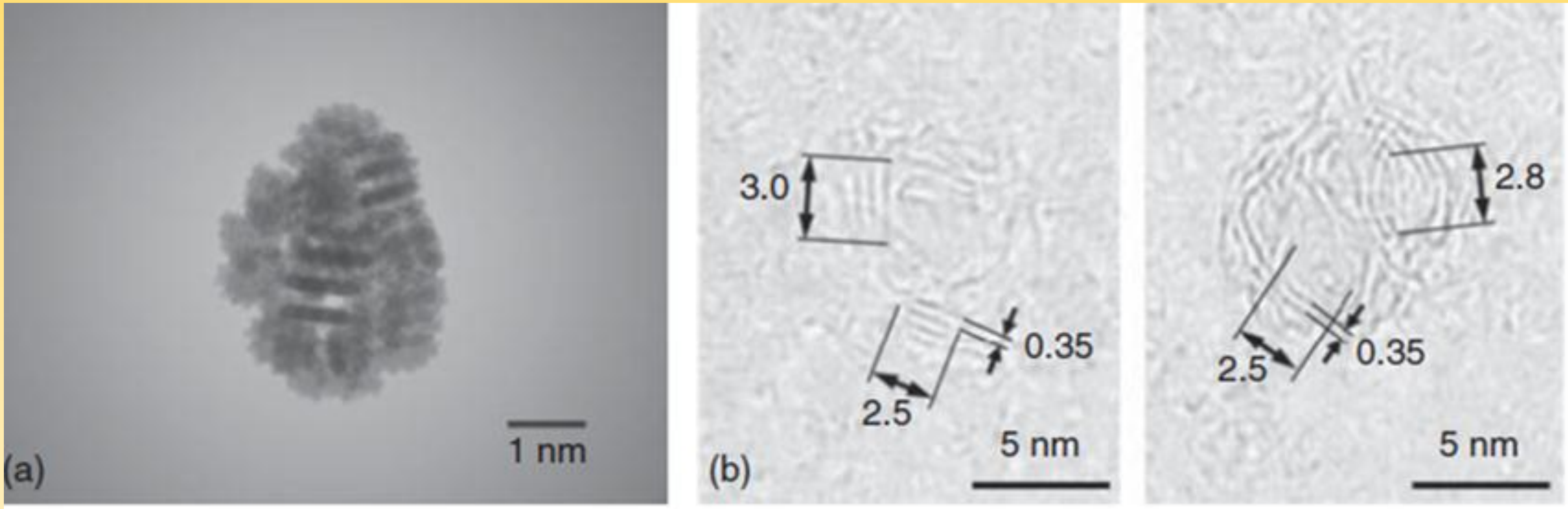
Typical soot formation models don't include nanotubes



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

M. Sander, et al. (2011), Developing the PAH-PP soot particle model using process informatics and uncertainty propagation. Proceedings of the Combustion Institute, 33(1):675–683, 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)

T. S. Totton, et al. Modelling the internal structure of nascent soot particles. Combustion and Flame, 157(5):909–914, 2010

S. Mosbach, et al. (2009), Towards a detailed soot model for internal combustion engines. Combustion and Flame, 156(6):1156–1165, 2009

Conditions necessary to produce CNTs

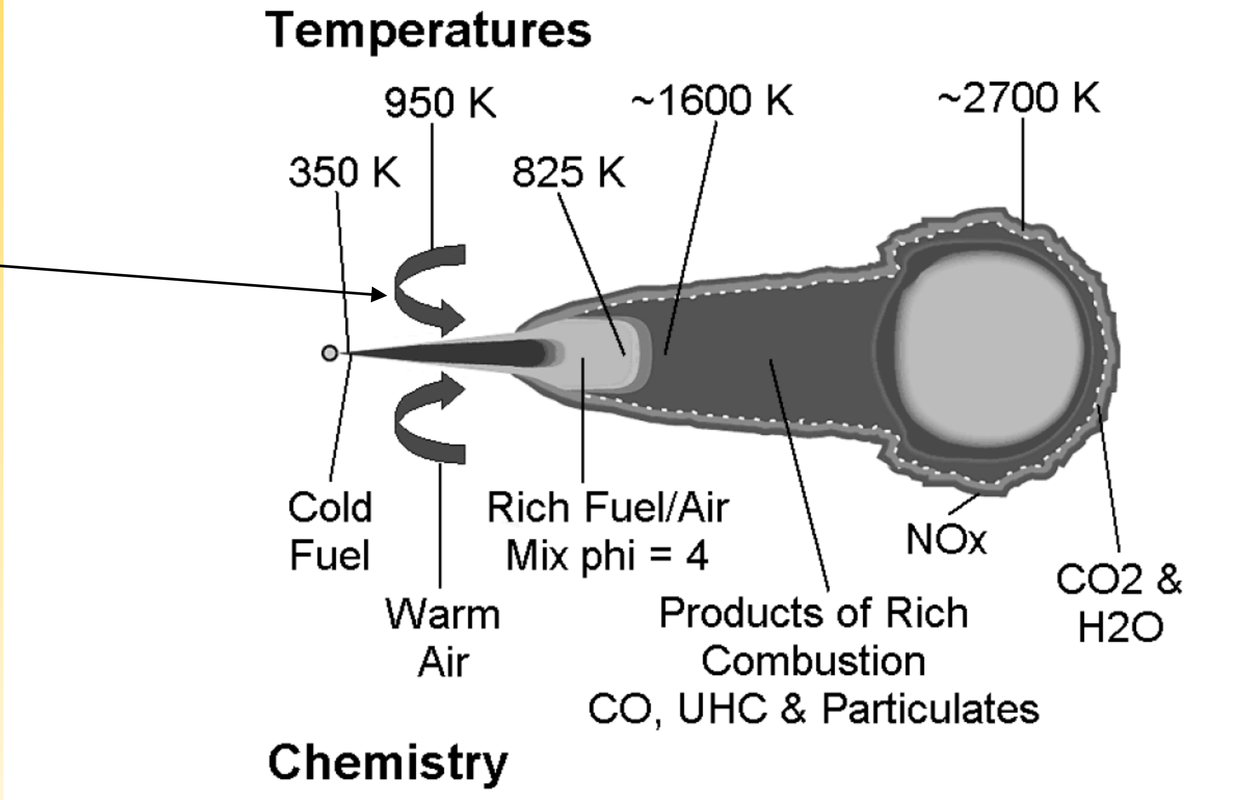
- Height, et al., 2004 flame
  - Source of carbon
  - Source of heat
  - Presence of metallic catalyst particles
  - Very sensitive to conditions
- Li, et al., 2004 flow reactor
  - Fe is a very good catalyst
  - S facilitates the reaction of hydrocarbons with Fe
- Engine combustion provides
  - Carbon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

Li, Y.H., Kinloch, I.A., Windle, A.H. Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis. Science 2004, 304, 276-278.

Height, M.J., J.B. Howard, J.W. Tester, and J.B.V. Sande. 2004. Flame synthesis of single-walled carbon nanotubes. Carbon 42:2295–307.

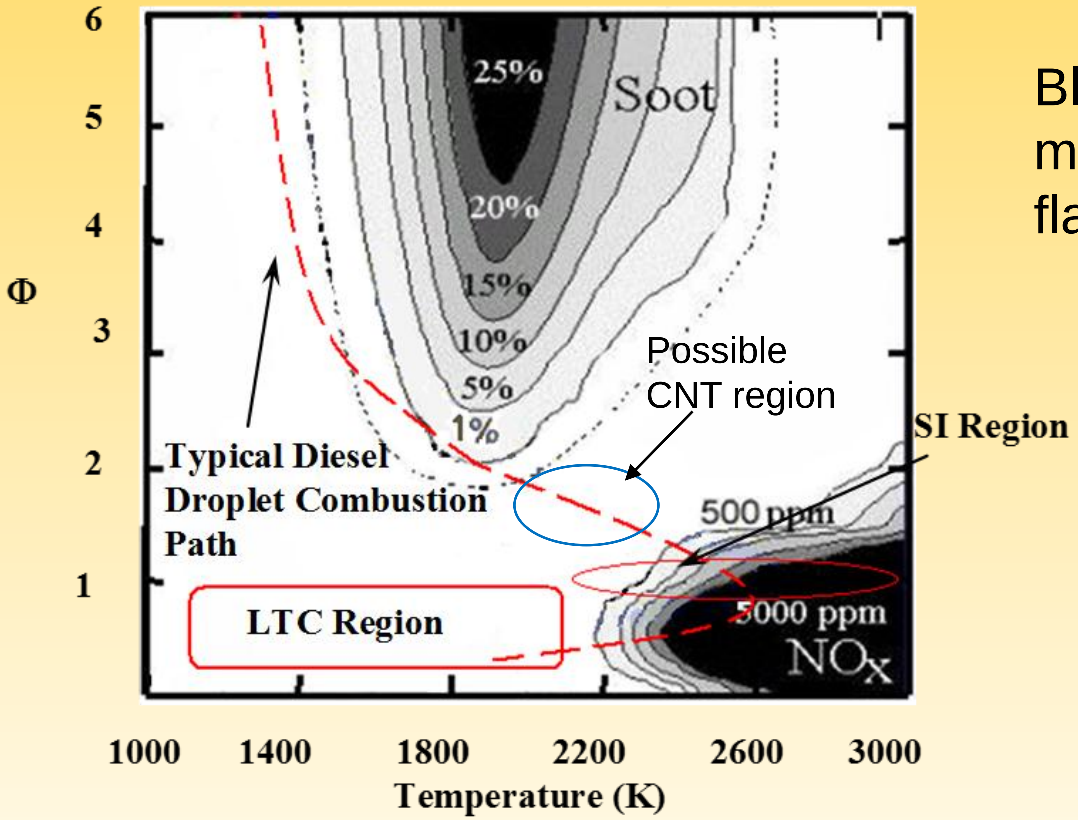
Diesel combustion – fuel jet entrains oil that may supply nanotube catalysts

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



Patrick F. Flynn, et al. (2009) Diesel Combustion: an Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation, SAE paper number 1999-01-0509

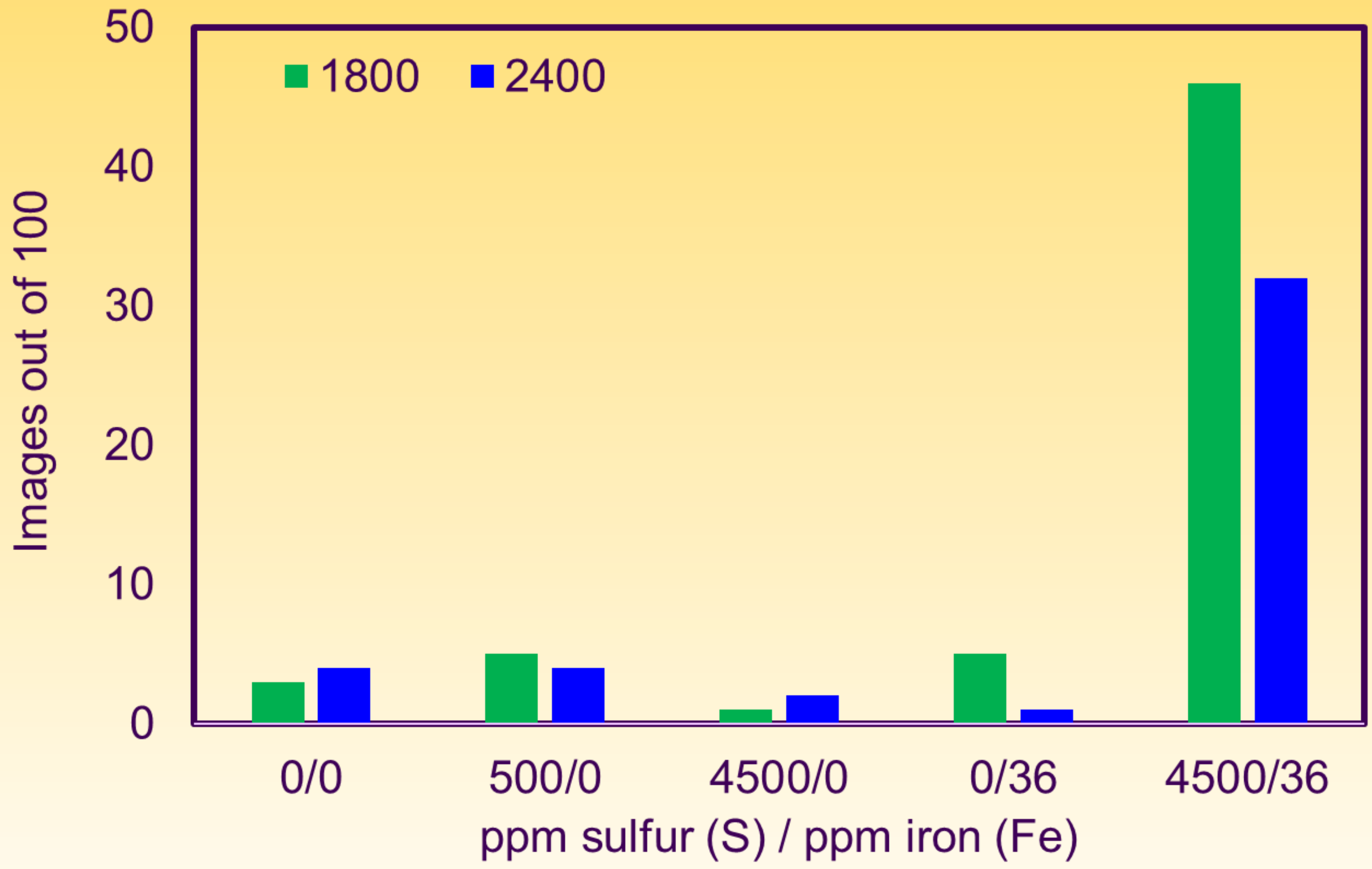
Temperature composition history for engine combustion



Kitamura *et al* (2002)

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



Jacob J. Swanson, et al., Fuel Sulfur Impacts the Formation of Carbon Nanotube-like Particles in Diesel Engines, 20th Conference on Combustion Generated Nanoparticles, 14th June, 2016

Filtration of CNTs

Characteristics of test CNTs

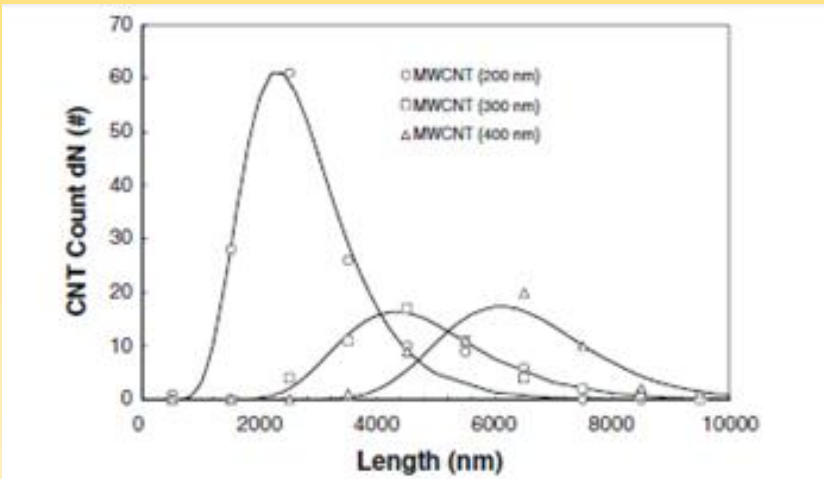


Fig. 3 The CNT number count versus the geometric length measured from SEM images for mobility diameters of 200, 300, and 400 nm. The curves represent lognormal fitting for the data of each mobility size

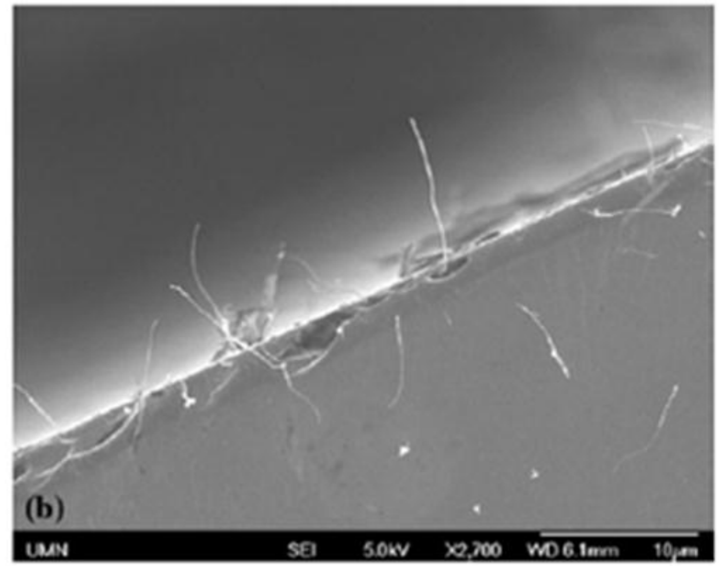
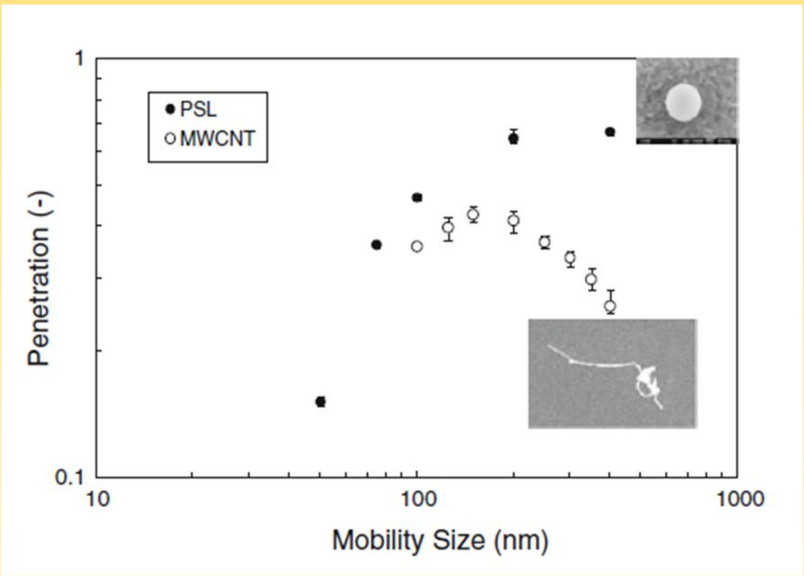
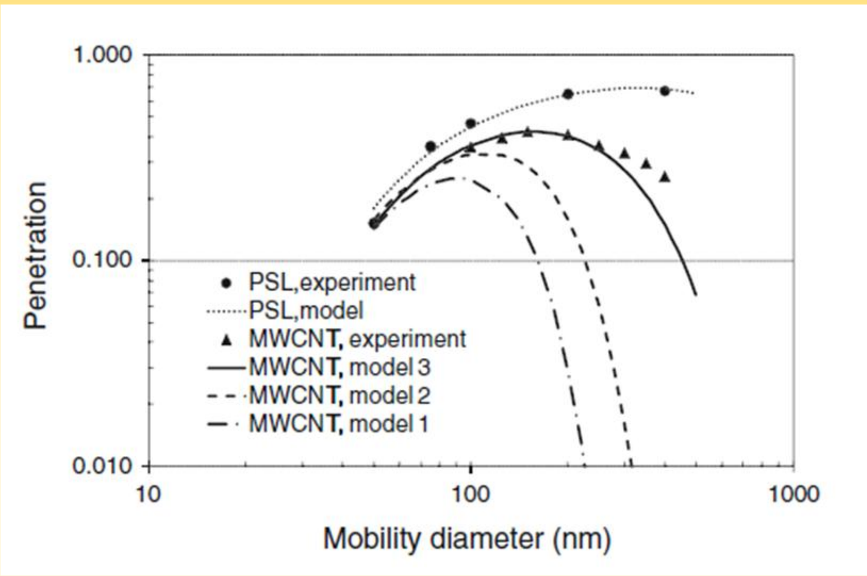


Fig. 2 Examples of the SEM images of the electrosprayed CNTs collected at the edges of the pieces of silicon wafers

Jing Wang, Seong Chan Kim, David Y. H. Pui, Measurement of multi-wall carbon nanotube penetration through a screen filter and single-fiber analysis, J Nanopart Res (2011) 13:4565–4573

Filter penetration lower for CNTs than spheres





Jing Wang, Seong Chan Kim, David Y. H. Pui, Measurement of multi-wall carbon nanotube penetration through a screen filter and single-fiber analysis, J Nanopart Res (2011) 13:4565–4573

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??

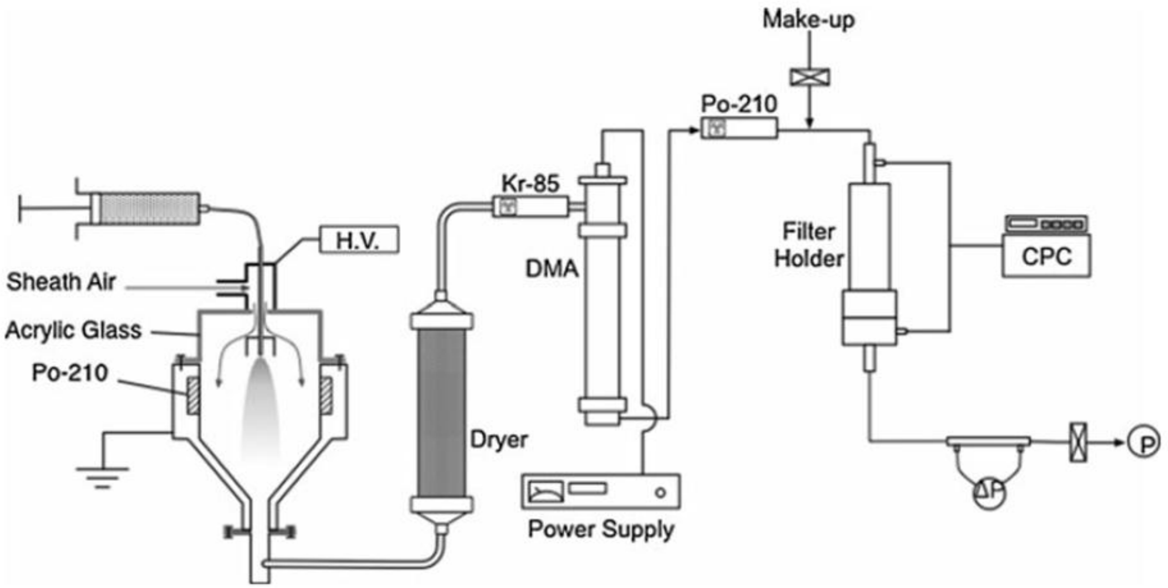
Outlook

- 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?

CNT filtration test setup

Fig. 1 The experimental system for CNT filtration tests



Other CNT synthesis

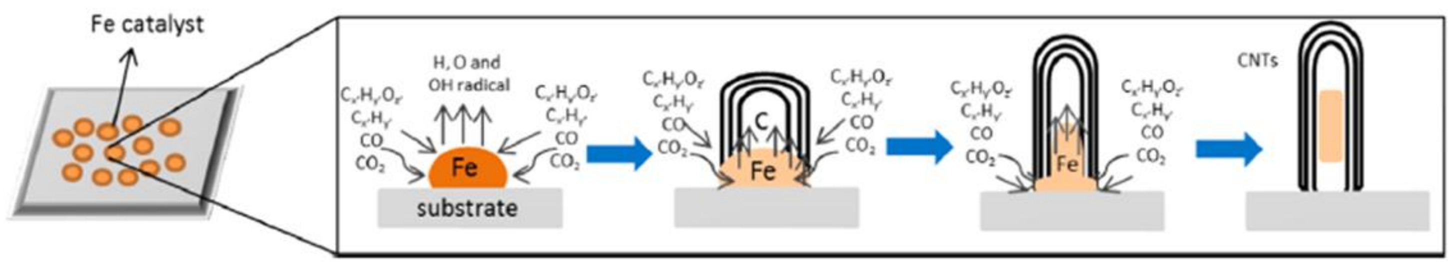


Fig. 3. Growth mechanism of CNTs synthesised from WEO.

Quasi-aligned carbon nanotubes synthesised from waste engine oil, A.B. Suriani et al. / Materials Letters 139 (2015) 220–223

Evolution of soot size distribution

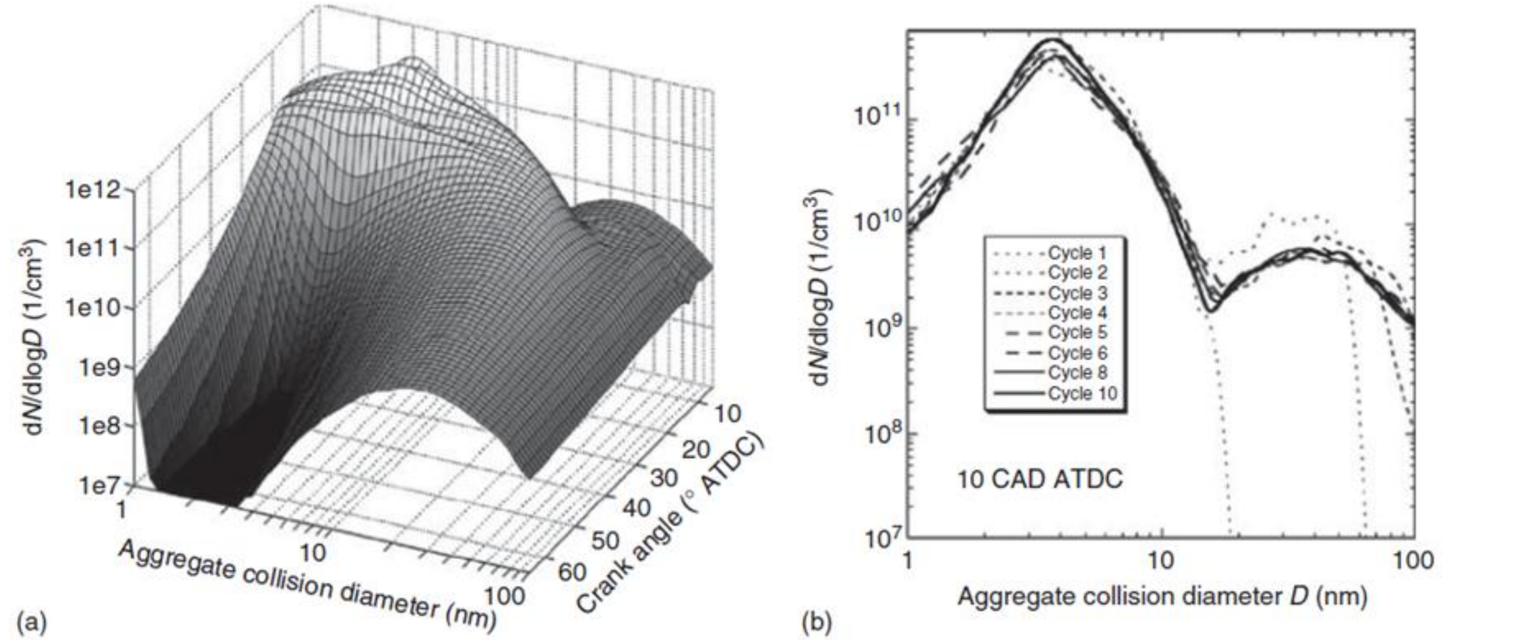


Figure 6. (a) Time evolution of the size distribution with aggregates present in the trapped residual gases. (b) Size distribution at 10 CAD ATDC for 10 consecutive cycles. The recirculated aggregates can be clearly identified as the ones larger than about 20 nm. (Reproduced from Mosbach *et al.*, 2009.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

Soot size distribution development

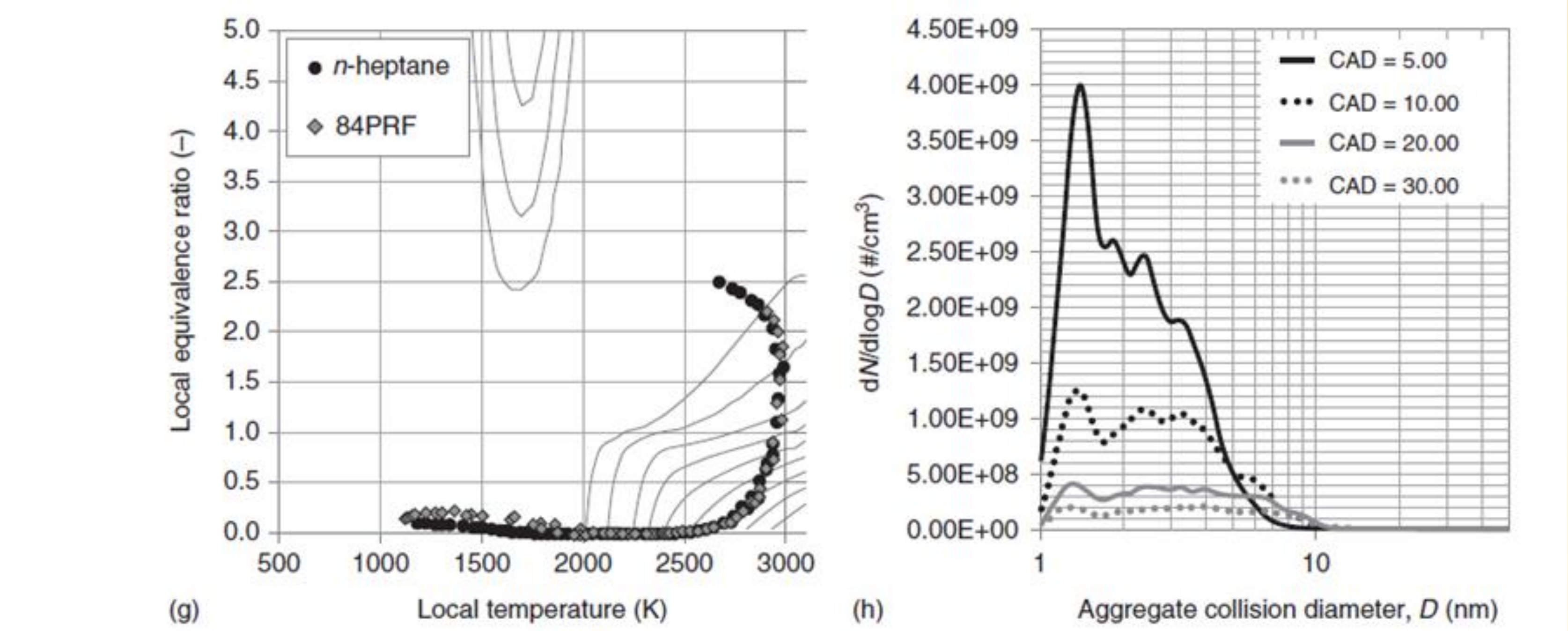


Figure 7. *(continued)*