Fuel Sulfur Impacts the Formation of Carbon Nanotube-like Particles in Diesel Engines

Jacob J. Swanson[1,2], Ryder Febo[1,2], Adam M. Boies[2,3], David B. Kittelson[2]

[1]Minnesota State University, Mankato

[2]University of Minnesota

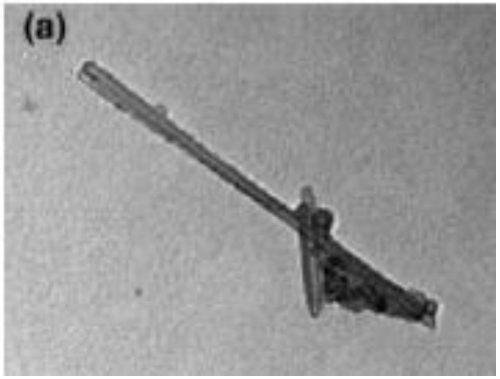
[3]University of Cambridge, Cambridge

20th Conference on Combustion Generated Nanoparticles, 14th June, 2016

Minnesota State University Mankato

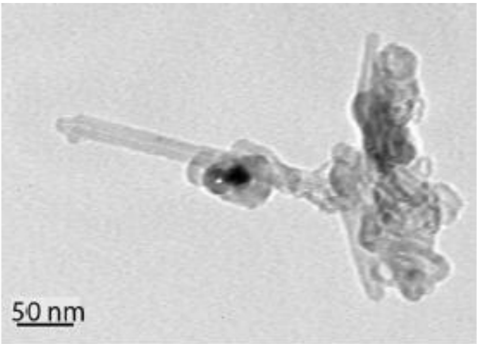
We already know internal combustion processes produces **carbon nanotubes** and other fullerene particles

Gasoline exhaust



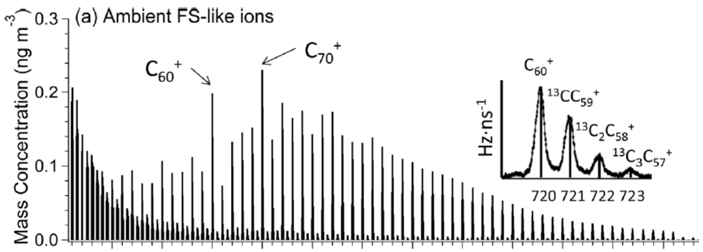
Lagally et al., 2012

Diesel exhaust



Jung et al., 2013

Ambient air



Wang et al., 2016

Given these examples, perhaps its not surprising that recent work indicated the presence of CNTs in the lungs of children exposed to ambient air in Paris

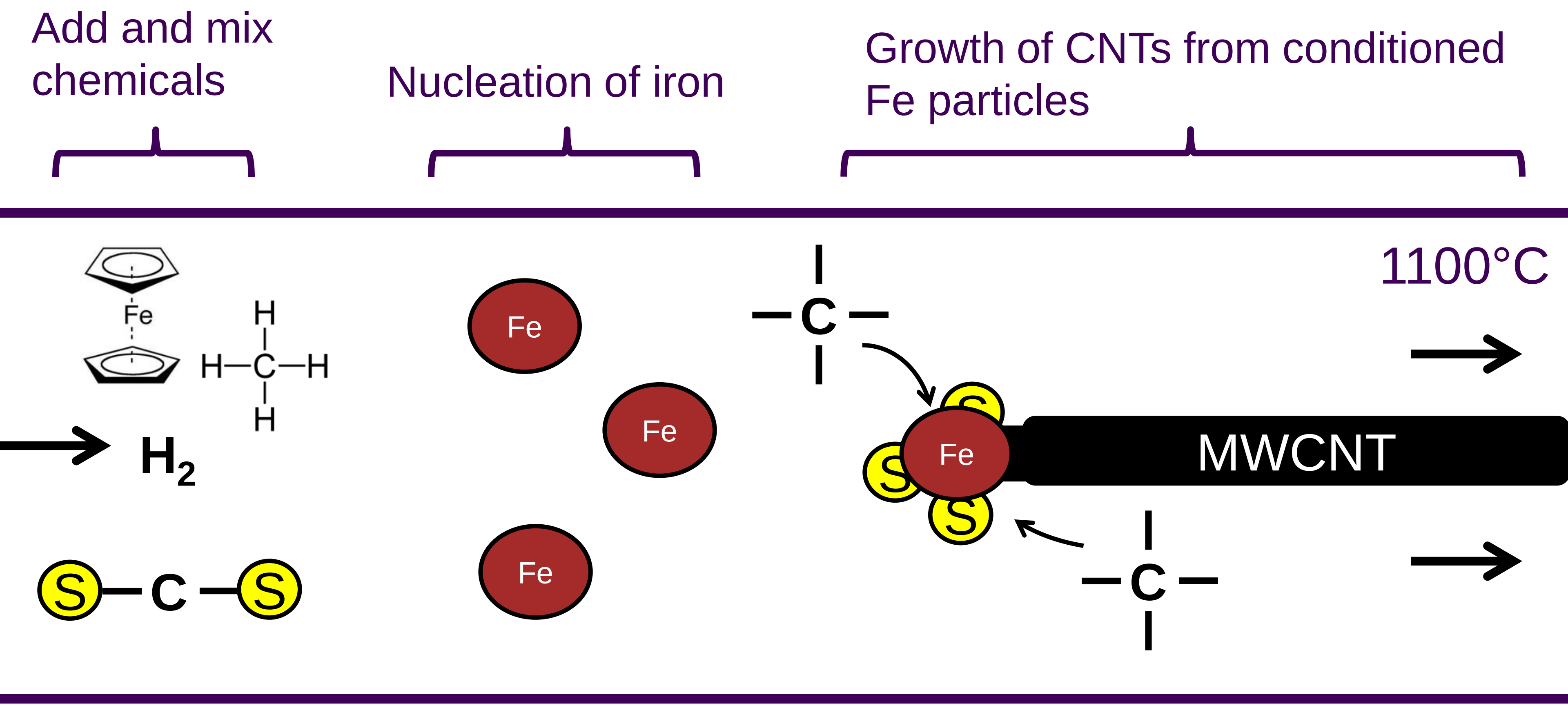
Anthropogenic Carbon Nanotubes Found in the Airways of Parisian Children
Kolosnjaj-Tabi, J. et al. *EBioMedicine* **2015,** 2, 1697–1704

"We show that inhaled PM mostly consist of CNTs."

"These results strongly suggest that humans are routinely exposed to CNTs."

Something here does not fully add up.

A typical floating catalyst process includes a **hydrocarbon source**, an **iron source** (Fe), and a **sulfur** (S) source in a reactor at >1000°C in a reducing atmosphere



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.

Based on the known chemical constituents required for gas-phase synthesis of CNTs, we hypothesized that **fuel S** and **Fe content** and would affect the generation of CNTs in an internal combustion engine

This process is enabled by other favorable conditions:

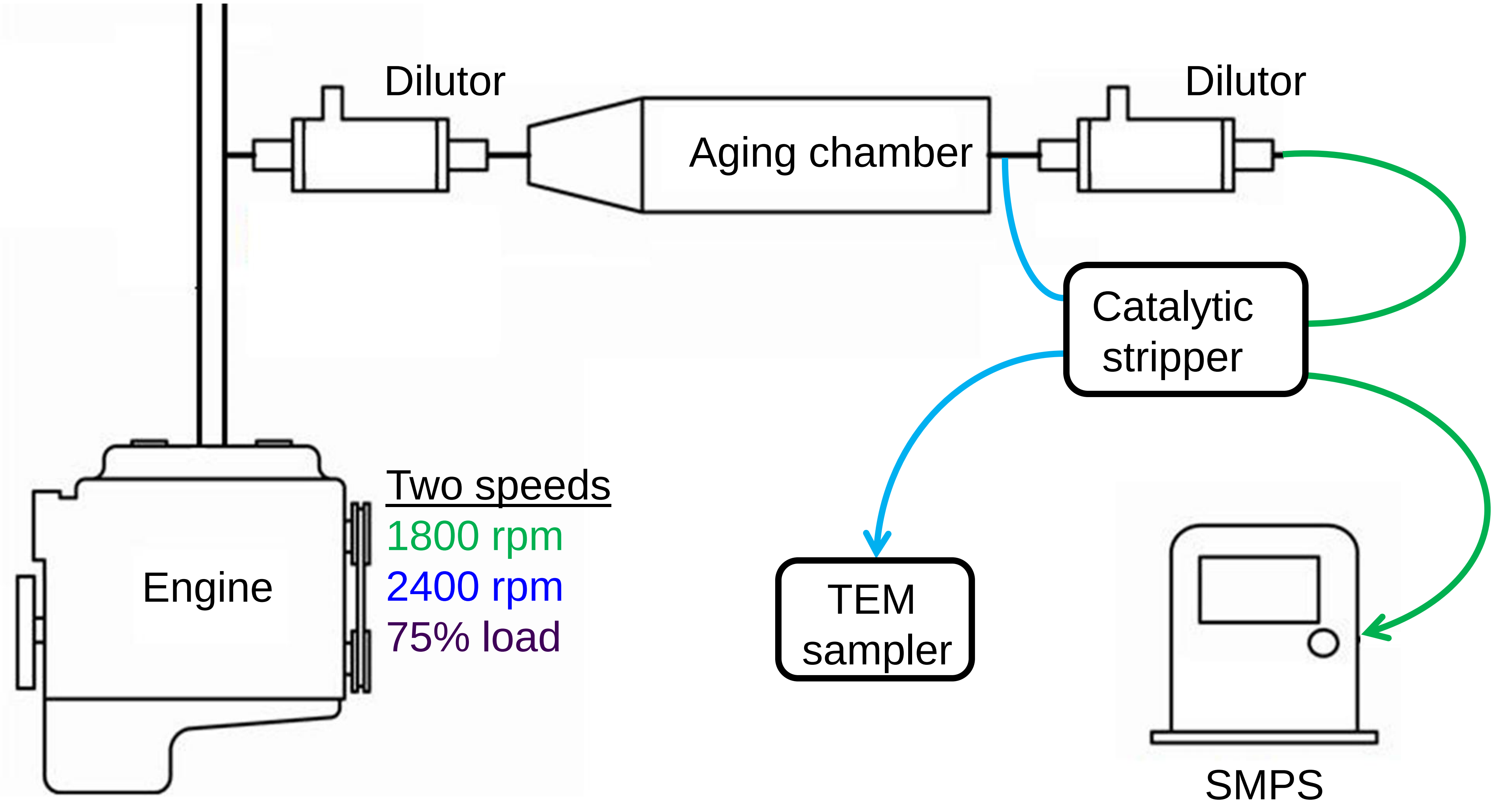
- hydrocarbons
- high temperatures
- locally rich (reducing) fuel zones

Fuel doping and experimental conditions to test CNT hypothesis

<table>
<tr><th>Test point</th><th>Sulfur (ppm)</th><th>Ferrocene (ppm)</th><th>Analyses</th></tr>
<tr><td>1</td><td>0</td><td>0</td><td rowspan="5">• Microscopy (TEM)
• Size distributions
**All particle collection methods with a catalytic stripper</td></tr>
<tr><td>2</td><td>500</td><td>0</td></tr>
<tr><td>3</td><td>4500</td><td>0</td></tr>
<tr><td>4</td><td>0</td><td>36</td></tr>
<tr><td>5</td><td>4500</td><td>36</td></tr>
</table>

Sulfur from benzothiophene (C_8H_6S) and di-benzothiophene ($C_{12}H_8S$)

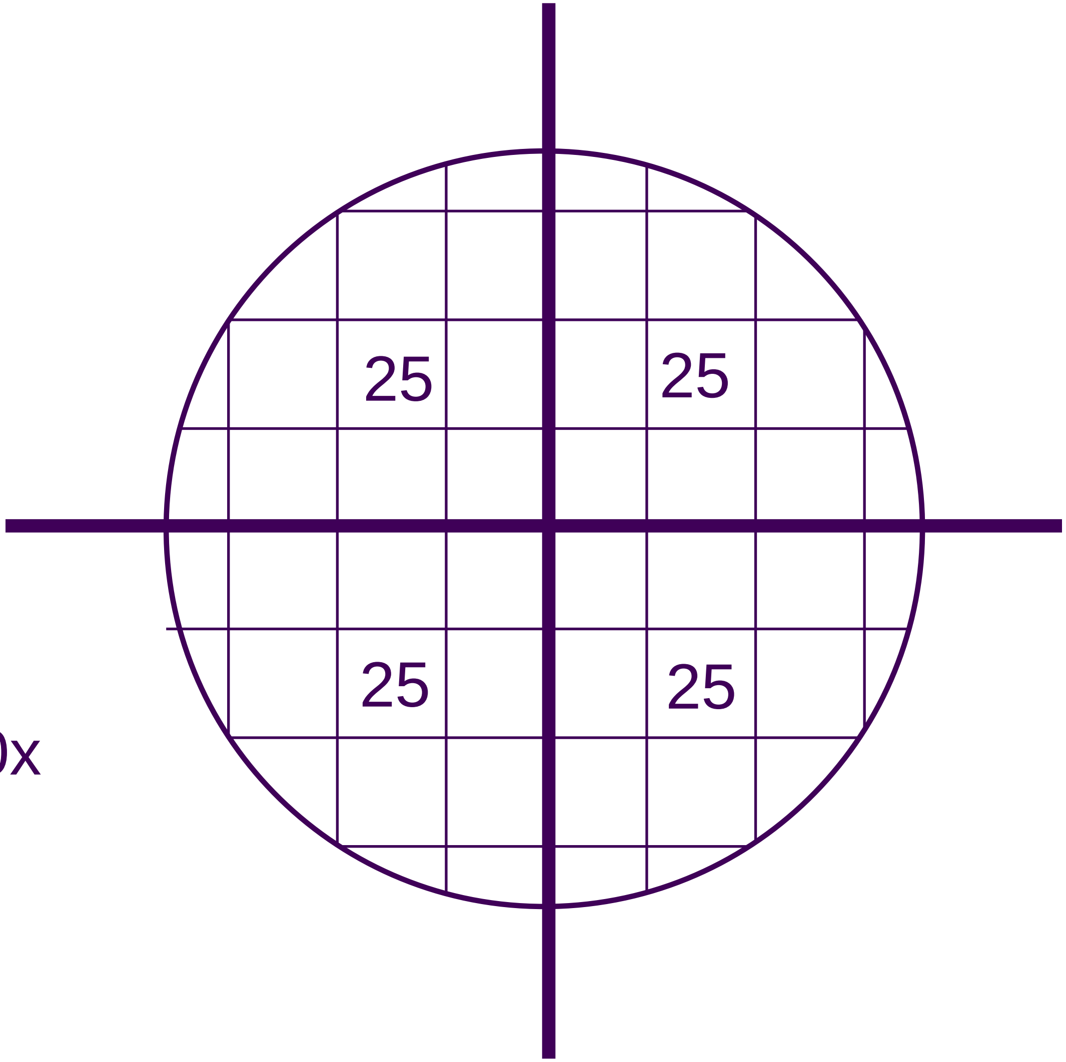
The test diesel engine was a single cylinder, All Power America LLC “Yanmar L100V” clone



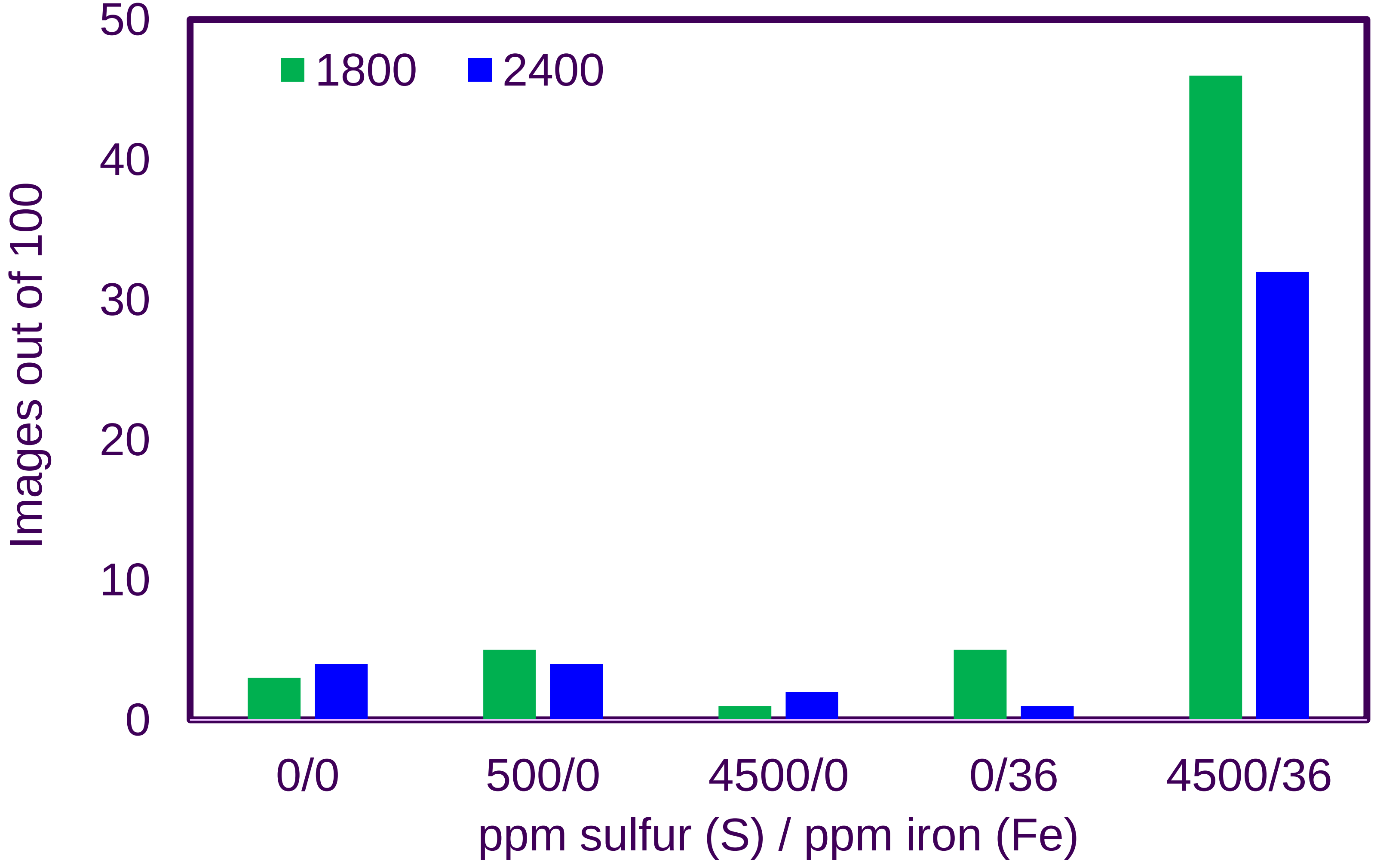
Two speeds
1800 rpm
2400 rpm
75% load

TEM image analysis methods were design to minimize bias

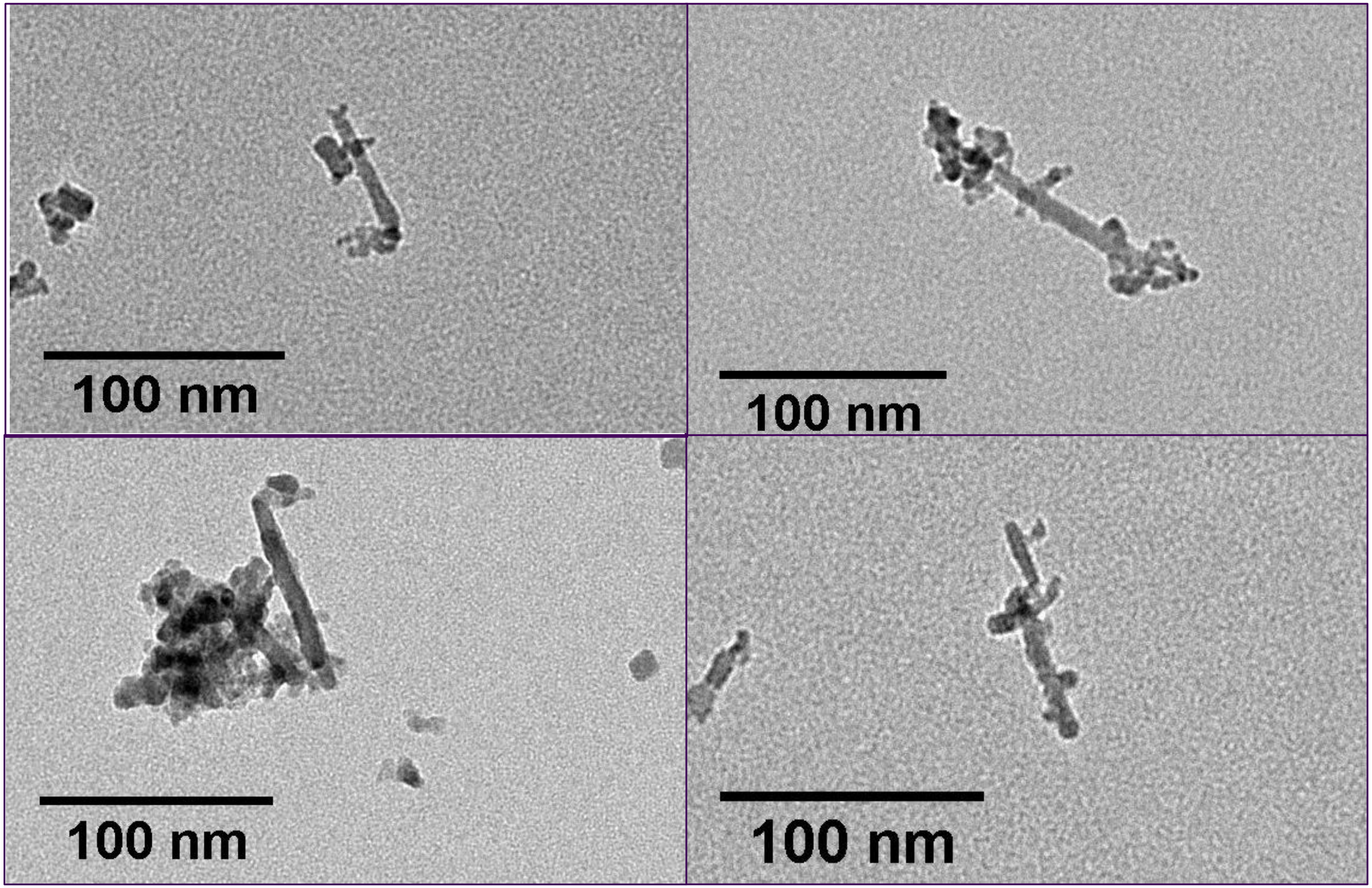
- Images taken from 4 defined regions
- 25 images taken from each regions
- 100 total images taken per grid
- Images taken at 47,000x magnification



Results show number of images out of 100 with CNT-like structures identified

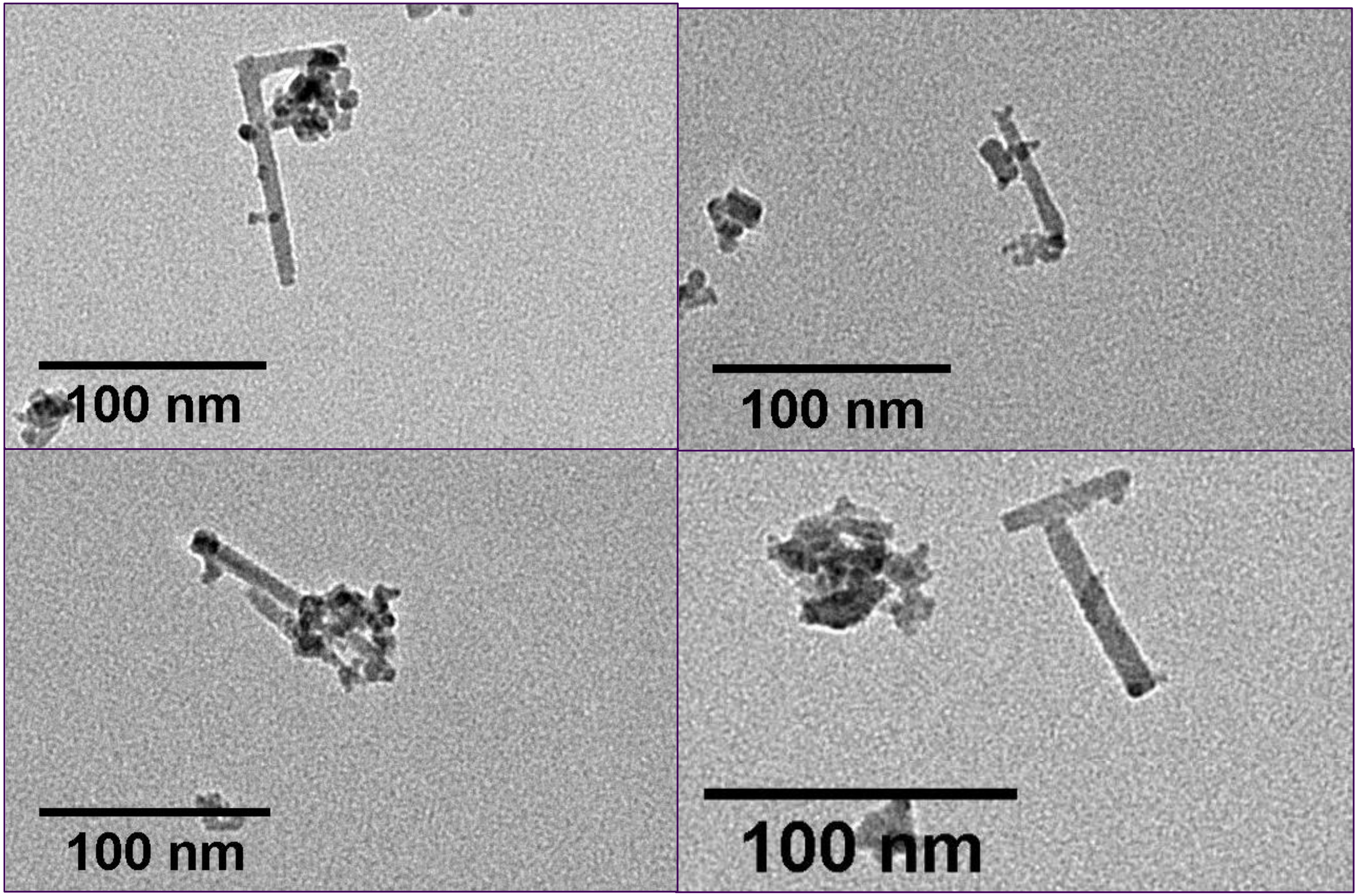


For 4500 ppm S / 36 ppm Fe case, cylindrical structures were distinct, but particles could not be definitively identified as “tubes” or “rods”

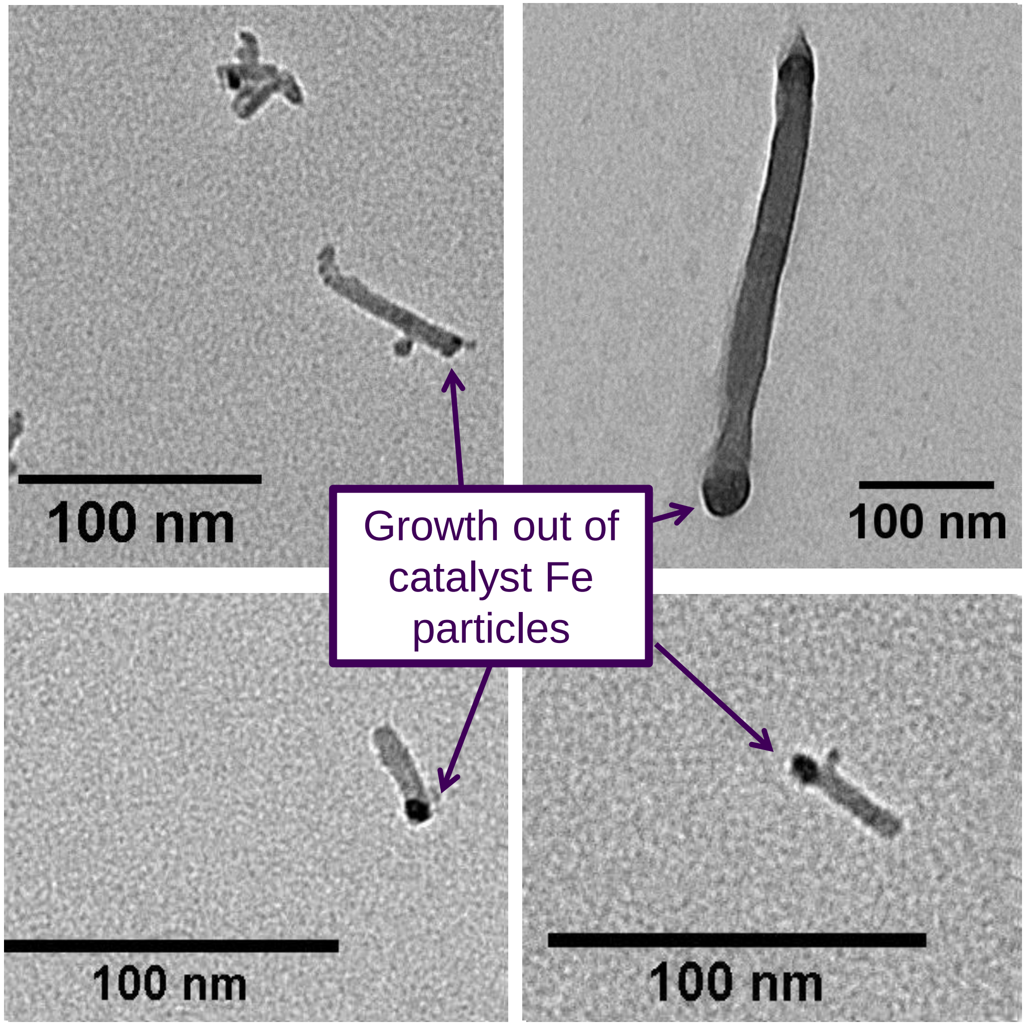


These CNTs from 1800 rpm and 2400 rpm conditions showed no obvious differences

CNT-like structures were approximately 75 nm with a 10:1 aspect ratio

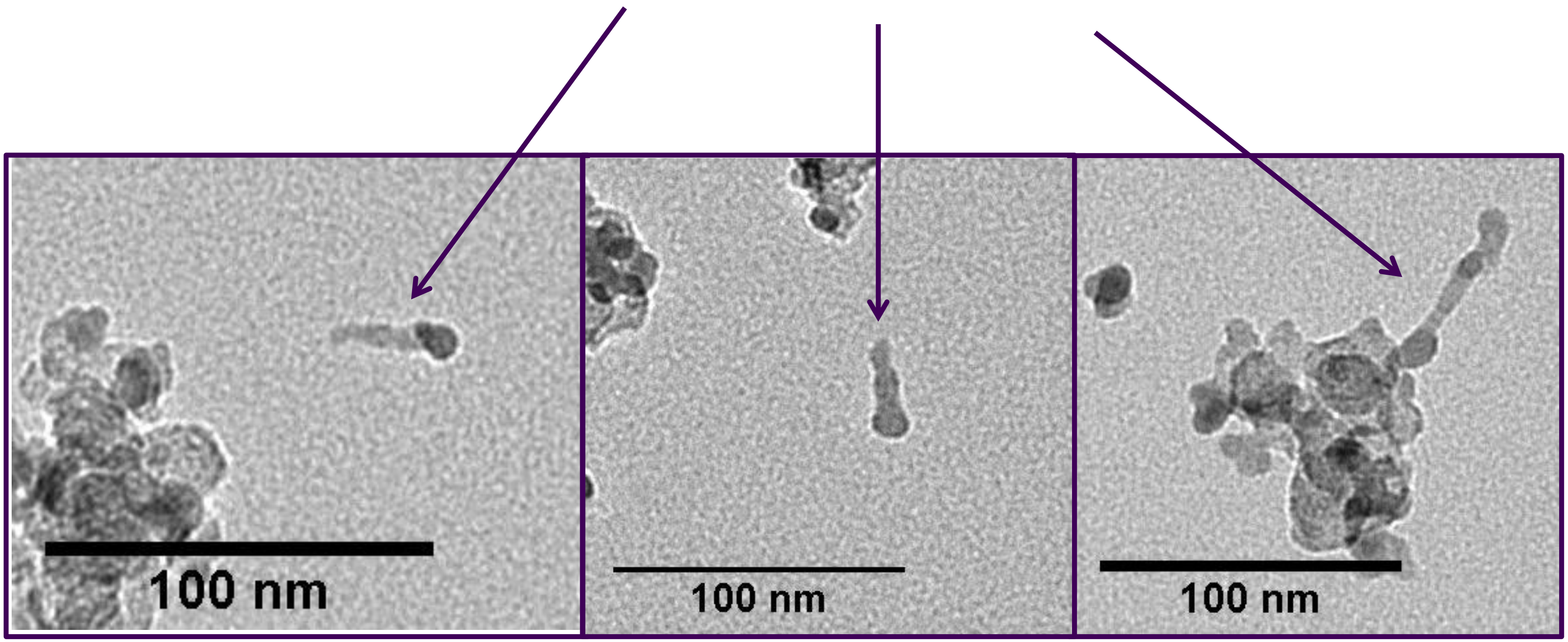


CNT growth out of catalyst Fe particles is typical of a floating catalyst synthesis process



CNT-like structures from all other conditions were small and poorly-defined

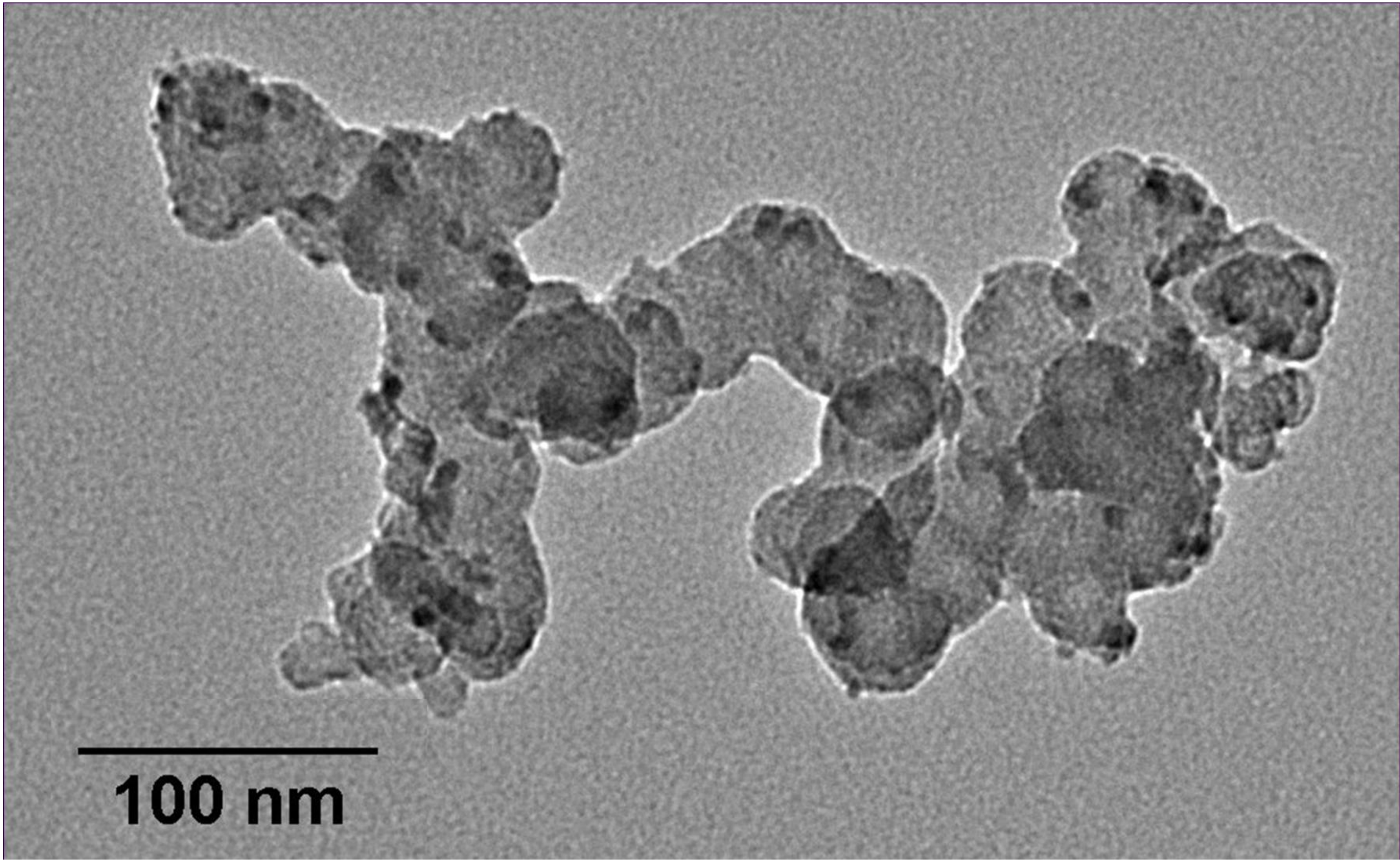
These structures were counted as CNTs



Conclusions

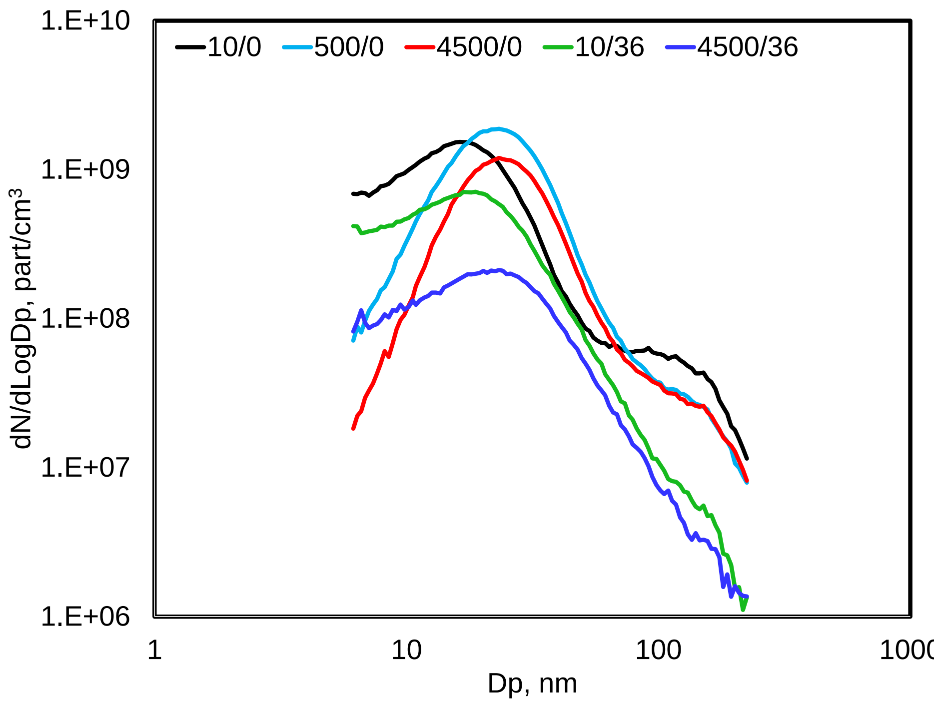
- High levels of fuel S and metallic nanoparticles promotes the formation of CNT-like structures in diesel engine exhaust
- Consumption of lubricating oil produces metallic seed particles, but in this case, the lubricating oil metals were not conducive to CNT formation
- With fuel S and appropriate seed catalysts present, gasoline and diesel combustion in many ways mirrors standard gas-phase CNT production processes.
- S concentrations are relevant for on-road diesel fuel used in other countries, marine fuels, and near levels of aviation fuels. There are many parts of the world, where in addition to high fuel S levels, fuel additives are loosely regulated, and particulate filters are not commonplace.
- More research is needed to understand if other combustion conditions such as lower speeds, temperature/time histories, fuel/oil chemistries, etc, more readily produce CNTs at different Fe and S levels.

Soot aggregates were decorated by metal nanoparticles from lubricating oil



Particle size distributions show both S and Fe reduce solid accumulation mode particles

No catalytic stripper



With catalytic stripper