Fuel composition influences engine emissions of carbon nanotubes

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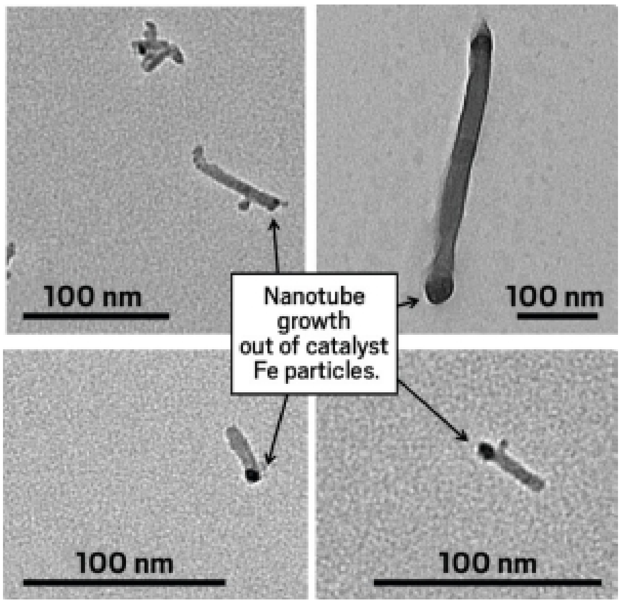
Carbon nanotubes formed when a diesel engine burned fuel with sulfur and ferrocene, a common fuel additive

By Melissae Fellet



In these transmission electron micrographs, carbon nanotube-like structures collected from diesel engine exhaust appear to grow from small catalyst iron particles.

Credit: *Environ. Sci. Technol. Lett.*

Vehicle exhaust includes a variety of emitted particulates including carbon nanotubes, which are worrisome because nanotubes resemble asbestos fibers that can linger in lung tissue. Now a study has shown that sulfur and ferrocene, an iron-containing fuel additive, promote nanotube formation in a diesel engine (*Environ. Sci. Technol. Lett.* 2016, DOI: 10.1021/acs.estlett.6b00313).

Particulate emissions from vehicles are linked to aggravated heart and lung problems, but little is known about whether carbon nanotubes have adverse health effects in humans. In tests on mice and rats, inhaling manufactured carbon nanotubes has been linked to cancer and lung disease.

Carbon nanotubes are a small percentage of particle emissions, and commercially available particulate filters effectively remove them. However, exposure to nanotubes could potentially be greater in countries with high fuel sulfur and additive levels and less stringent emission controls for vehicles, the researchers say.

Jacob J. Swanson, a mechanical engineer at Minnesota State University, Mankato, and his colleagues noticed reports of carbon nanotubes in vehicle exhaust and realized that the conditions inside an engine resemble a common way to manufacture carbon nanotubes: heating a carbon source with sulfur and metallic nanoparticles in a tube furnace.

In an engine, hydrocarbons in the fuel provide a source of carbon, and sulfur is often present. And an iron-containing molecule, ferrocene, is commonly added to fuel to improve engine performance or lower soot emissions.

To test if these components influenced carbon nanotube formation in an engine, the researchers systematically introduced fuel with increasing concentrations of sulfur and ferrocene into a diesel engine running in their laboratory. Then they captured the exhaust and examined the shape of the emitted particles using transmission electron microscopy.

When the fuel had only sulfur or ferrocene, only a few nanotubes appeared. But at the highest concentrations tested of both components, 4500 ppm sulfur and 36 ppm ferrocene, the researchers saw nanotube-like structures in 31% of the images collected. This sulfur concentration is higher than that found in gasoline and diesel in the U.S. and comparable to diesel sulfur levels in some countries in the Middle East, for example.

Swanson hopes this study raises awareness that carbon nanotube emissions observed anecdotally in diesel, natural gas, and gasoline exhaust are real, and leads to additional work to better understand the conditions that affect their formation.

Steven N. Rogak of the University of British Columbia, who has found carbon nanotubes in rickshaw exhaust in India, thinks the particles have always been in engine exhaust but are only starting to be identified now because observing them involves laborious microscopy. He says this work is useful because it shows nanotube formation under controlled laboratory conditions.

In addition, the highest sulfur levels tested here are just one-tenth of what has historically been measured in marine fuels, meaning that combustion engines other than those in cars and trucks could also be producing nanotubes. Therefore it would be interesting to repeat this test with ship engines, Rogak says.

These nanotube emissions could be a potential health problem because they contain iron, and metals are a factor in nanotube toxicity, says James C. Bonner, who studies carbon nanotube toxicology at North Carolina State University. However, the nanotubes imaged in this study were about 100 nm long, which might be short enough for immune cells to remove them from the lungs, he says.

CORRECTION: This story was updated on Oct. 6, 2016, to reflect the correct limits on sulfur in gasoline and diesel fuel in the U.S.

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