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Start Your Engines

Melissae Fellet

As the Volkswagen scandal showed, building fuel-efficient, low-emitting vehicles is no easy task.

In September 2015, the Environmental Protection Agency's revelation that Volkswagen had altered diesel engines to beat emissions tests caused immediate consumer outrage. The agency reported that some diesel-powered vehicles made by Volkswagen and its subsidiaries Audi and Porsche contained software that lowered emissions during tests but not during normal driving. On the road, some vehicles emitted up to 40 times as much NO_x—a combination of nitric oxide and nitrogen dioxide—as allowed.

Short-term exposure to nitrogen dioxide is linked to airway inflammation and increased asthma symptoms. In the atmosphere, nitrogen dioxide contributes to the formation of ground-level ozone and particulate matter, which create further negative health effects. A recent study estimated that excess NO_x released by the altered Volkswagen cars in the U.S. could cause 46 additional expected deaths and $430 million additional damages, compared with if emissions regulations were followed. In Europe, however, excess NO_x from the altered cars may have little impact: High NO_x emissions already plague the region because it has weaker emissions regulations and more diesel passenger cars than in the U.S.

Balancing NO_x emission control with fuel efficiency is a tough nut to crack. Often the most efficient operating conditions for a diesel engine make it difficult to remove NO_x in the exhaust. "I'm certainly not justifying what Volkswagen did, but if the solution was easy, hopefully they wouldn't have done it", says Michael P. Harold, a chemical engineer at the University of Houston. Especially as fuel efficiency standards and NO_x emissions limits tighten, experts say NO_x control systems need big improvements to keep pace. Central to this are improvements to the NO_x-clearing catalysts and systems for diesel vehicles. Meanwhile, new, more efficient gasoline engines skirt the NO_x issue for now—but bring their own emissions challenges. The race is on for a vehicle that saves fuel and releases clean exhaust, too.

Combining fuel economy and low emissions can be a challenge, as the Volkswagen scandal showed. Credit: Shutterstock.

Efficiency vs Emissions

When engines burn fuel, they create a hot mixture of gases that expand and push a piston, converting the fuel's chemical energy to mechanical energy. Diesel engines are 15 to 20% more efficient than conventional gasoline engines in part because they contain excess air during combustion. The oxygen-rich mixture of combustion products in a diesel engine expands more and transfers more energy into pushing the piston than the products of a gasoline engine, generating more mechanical energy for a given amount of fuel. After combustion, the temperature inside both gasoline and diesel engines is high enough to drive the reaction of nitrogen in the air to NO_x. But the excess oxygen present in a diesel engine creates an oxidizing environment that makes it difficult to reduce NO_x back to nitrogen.

That's when emissions control systems need to kick in. If the systems work well, then the engine can run efficiently while the majority of NO_x generated will be removed from the exhaust. But even the best-performing NO_x emissions systems sap fuel efficiency and add to the cost of a vehicle.

The most common NO_x after-treatment system, called selective catalytic reduction (SCR), contains a catalyst that selectively combines NO_x and ammonia to produce nitrogen. Urea, supplied by an onboard tank, decomposes into ammonia, which is injected into the exhaust system. But the biggest problem is that the zeolite catalysts in these systems do not work at temperatures below about 200 °C. Such

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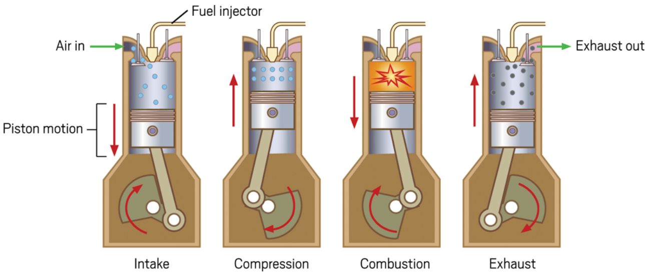
temperatures occur during cold starts or low load conditions, or in the cooler exhaust of more fuel-efficient engines—and they add up. Over a vehicle's lifetime, the majority of its NO_x emissions come during cold-start temperatures.



(1) Air (blue spheres, left) enters the combustion chamber of a diesel engine. (2) The piston rises and compresses the air. Near the top of the piston stroke, fuel is injected (not shown). (3) The fuel-air mixture ignites, generating heat, expanding the gases inside, and driving the piston down, doing work. (4) Carbon dioxide, water, and other combustion products (gray spheres, right) leave the cylinder as exhaust. Credit: Shutterstock.

Cold Conversion

"The challenge to the community is to develop a catalyst that gives 90% NO_x conversion at 150 °C", says Rajamani Gounder, a chemical engineer at Purdue University. He and a team of researchers at Purdue, the University of Notre Dame, and Argonne National Laboratory are studying exactly how one zeolite catalyst at the heart of the emissions control works. The catalyst is based on the aluminosilicate form of chabazite, a naturally occurring, porous mineral that catalyst makers synthesize and then infuse with copper ions. The copper ions provide the active sites for the reduction reaction, and the zeolite's small pores exclude hydrocarbons from the exhaust that could clog the system.

Gounder is focusing on understanding the copper ions. If he and his colleagues can determine the copper ion configurations within the catalyst that are the most reactive at low temperatures, it may be possible to design a material to contain more of those desired active sites, he says.

Meanwhile, a serendipitous discovery by researchers at Pacific Northwest National Laboratory revealed that adding alkali ions to the copper zeolite improved its low-temperature performance. Charles H. F. Peden, a laboratory fellow at PNNL, says his team is working to understand why the alkali ions improve the performance, perhaps to learn how to better improve future catalysts.

NO_x Traps and Tricks

Another type of NO_x after-treatment device avoids the urea tank, which is hard to fit on smaller vehicles. This type, called a lean NO_x trap, takes advantage of the oxidizing conditions that make it hard to chemically reduce NO_x. When the engine is running lean, the trap uses platinum nanoparticles to catalyze the conversion of nitric oxide to nitrogen dioxide, which quickly forms solid nitrates on barium oxide nanoparticles. It then reduces NO_x during quick periods of running rich under lower oxygen conditions. During these periods, the platinum nanoparticles catalyze the reaction of hydrocarbons from the fuel with NO_x released from the trap to produce nitrogen and water.

Lean NO_x traps have been used in some new diesel passenger cars in Europe and the U.S., including at least one of the VW models involved in the scandal, but the burst of fuel needed to regenerate the trap impacts the fuel efficiency of the engine, so they have been less popular than SCR systems. More importantly, they are sensitive to poisoning by sulfur, a common impurity in diesel fuel. Some researchers have tried to make sulfur-resistant catalysts, says William S. Epling, a chemical engineer at the University of Houston. But if a catalyst absorbs nitrogen oxides, he adds, it will likely absorb sulfur oxides too—and sulfates tend to be more stable than nitrates. Increasing the engine temperature and adding a burst of fuel to the trap can remove the sulfates, again at a cost to the vehicle's fuel economy.

Lean NO_x traps could also help solve another cold-start problem with SCR systems: The onboard urea doesn't decompose into ammonia below 200 °C. A lean NO_x trap can be tuned to produce ammonia during the regeneration phase at low temperatures.

One final approach for controlling low-temperature NO_x emissions is to place a NO_x adsorbing material in front of the SCR system. This passive NO_x adsorber, made of a ceria or mixed oxide, collects NO_x during cold starts. As the exhaust warms up and the NO_x reduction catalyst becomes warm enough to work, the NO_x desorbs from the material and flows into the SCR system. This relatively new solution is attracting commercial interest because the system does not require complex controls to operate and allows auto manufacturers to continue using current SCR systems, says Mark Crocker, a chemist at the University of Kentucky.

"Emissions catalysis is by far the most complicated type of catalysis I've ever encountered", Gounder says. "Most industrial processes, like in a refinery, are going to be controlled to operate in a very narrow temperature and pressure window that's been optimized to do the reaction." But the catalysts in emissions systems have to work under a variety of temperatures, weather conditions, engine loads, and engine speeds for the lifetime of the vehicle—10 years or 120,000 miles. "It's an engineering marvel that these things even work", he says.

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Gasoline Engines Catch Up

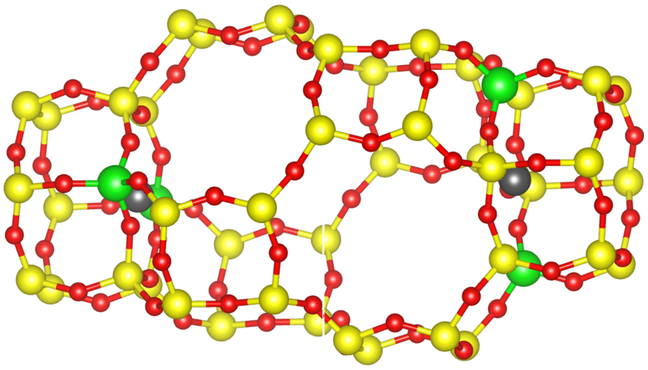
While diesel engines are inherently more fuel efficient than gasoline engines, a new engine technology is allowing gasoline engines to catch up. It's called gasoline direct injection (GDI), and 43% of the passenger vehicles sold in the U.S. in 2014 have the technology—a share that's expected to grow in coming years.

In a traditional gasoline engine, a premixed blend of fuel and air enters the cylinder. But a GDI operates like a diesel engine, in that fuel is injected directly into the combustion chamber. The air in the cylinder cools as the fuel vaporizes, enabling greater compression before ignition and improving efficiency. But unlike the lean conditions of a diesel engine, most GDI engines inject enough fuel that little oxygen is leftover after combustion. Standard catalytic converters effectively reduce NO_x in this low-oxygen environment, so GDI engines do not need the selective reducing power of an SCR emissions system.

But they have other emissions challenges. GDI engines produce more particles than either traditional gasoline engines or diesel engines equipped with filters, especially ultrafine particles less than 0.1 μm in diameter. Particle emissions are associated with health problems like aggravated heart and lung disease.

GDI engines currently meet particle emissions regulations in the U.S., but the cars' ultrafine emissions may not pass tests in Europe: U.S. regulations are based on the mass of particles, while Europe's are based on number—and the permitted number per kilometer driven will drop in September 2017 as part of tightening European regulations. This may mean particle filters will be necessary for GDI engines to meet standards, says Cary Henry, who leads a research consortium of automakers at the Southwest Research Institute.

Diesel cars and trucks are commonly equipped with ceramic or metallic filters, which capture 85 to 95% of particles. But for GDI vehicles, it may not be as simple as putting a diesel filter on a gasoline engine. Subtle differences in particle size and composition between GDI and diesel engines may significantly impact the design of gasoline particulate filters for GDI engines, Henry says. Particulate emissions contain soot—elemental carbon—and volatile organic compounds adsorbed to the soot. Metals like zinc, calcium, and magnesium from gasoline additives and oil that reach the engine generate metallic ash. In a diesel particle filter, soot collects on the walls of the ceramic or metal filter. When the soot is oxidized or burned off to regenerate the filter, any accumulated ash also flakes off, Henry says. But GDI engines produce less soot than diesel engines, so instead of ash combining with the soot and flaking off, Henry wonders if it would deposit on the walls, clog the filter, and cause back pressure that increases the load on the engine and reduces efficiency.



A porous zeolite made of silicon (yellow), oxygen (red), and aluminum (green) contains copper (silver) atoms that catalyze the reduction of nitrogen oxides to nitrogen gas. Credit: Christopher Paolucci.

William F. Northrop, a mechanical engineer at the University of Minnesota, and his colleagues are testing filters and working to better understand particle emissions from lean-burn GDI engines. In diesel engines, filters keep particulate emissions to about one-tenth of the limit, Northrop says, and he thinks appropriately designed filters could do the same for GDI cars. "I really do think filters are going to come. It's just a matter of when and how."

History suggests he's right. While emissions control problems for NO_x or particles seem difficult to conquer, so were the first attempts to control the belching emissions from tailpipes beginning in the 1980s. Since then, better engines and emissions controls have already cut emissions from heavy duty trucks by at least 90%. And they've managed to do it while also dramatically improving fuel economy and vehicle performance. Even amidst the Volkswagen scandal, Jim Parks, a physicist at Oak Ridge National Laboratory, says the vast majority of diesel vehicles made since 2007 are clean and fuel efficient: "Clean diesel technology is not a myth."

Melissae Fellet is a freelance contributor to Chemical & Engineering News, the weekly newsmagazine of the American Chemical Society.

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