

Supercritical fuel

A new process transforms diesel fuel in a way that reduces emissions and increases brake thermal efficiency.

KEY CONCEPTS

- A fourth state known as supercritical is reached when a substance exhibits temperature and pressure values above the critical point.
- Deficiencies in the diesel engine can be overcome by moving the fuel into a supercritical state.
- CFD modeling shows that a supercritical fluid based on a mixture of diesel fuel and an EGR stream has the potential to lead to reduced emissions and increased brake thermal efficiency in a diesel engine.

A wide range of approaches have been undertaken to determine how to reduce emissions from automotive engines. In a previous TLT article, the development of the homogeneous charge compression ignition (HCCI) engine was discussed.¹

When used in place of a conventional gasoline engine, an HCCI engine can produce a 15% to 20% improvement in fuel economy and a significant reduction in NO_x emissions. The HCCI process relies on spontaneous ignition of the gasoline, air mixture similar to the auto-ignition process in a diesel engine.

As we all know, three specific states of matter (solid, liquid and gas) exist, and most substances can be found in one of these states at any given combination of temperature and pressure. When the temperature and pressure is increased above a value known as the critical point, the substance reaches a fourth state known as supercritical.

A supercritical fluid exhibits properties somewhere between a liquid and a gas. It is a homogeneous fluid that is maintained in a single phase. Dr. George Anitescu, research scientist in the department of biomedical and chemical engineering at Syracuse University, in Syracuse, N.Y., says, “A supercritical fluid cannot be turned into a liquid solely by compression/expansion (e.g., air in the engine cylinders).”

Two supercritical fluids also mix easily with one another. They exhibit molecular diffusivities and no surface tension, which facilitates the mixing process. Supercritical fluids are used in applications such as decaffeination and power generation.

Anitescu says, “The diesel engine displays greater efficiency than the gasoline engine. The air-fuel mixture in the latter, although homogeneous, needs a spark to ignite due to low reactivity. In contrast, the mixing of air and fuel in a diesel engine is not uniform. Diesel fuel, which is composed of heavier hydrocarbons, is more viscous and less volatile than gasoline. The resulting incomplete combustion usually leads to the generation of undesirable levels of particulate matter, while high-temperatures at the flame front generate NO_x.”

These deficiencies in the diesel engine can be overcome if the diesel fuel is moved into a supercritical state. Anitescu says, “Enabling diesel fuel to become supercritical will allow for mixing with air in a homogeneous phase upon injection, in a similar fashion to a gasoline engine.”

An approach has now been devised to use diesel fuel in a supercritical state.

FUEL-EGR FUEL MIXTURES

Anitescu has developed a process for making diesel fuel supercritical. He says, “We need to mix diesel fuel with a diluent to prevent coking, which is the formation of carbon deposits. Coking of pure diesel fuel can occur at temperatures above 200 C. The logical diluents to use are water and carbon dioxide. Both are readily available, relatively inert at the temperatures where fuel combustion occurs and environmentally acceptable.”

'An independent assessment showed that an 80% reduction in both NO_x and particulate matter can be achieved by the combustion of supercritical fuel-air mixtures.'

A mixture of diesel fuel and carbon dioxide is shown at various points on the way to a supercritical state in Figure 1. The first image shows a blend of the two at a temperature well below critical. In the second image, the blend is seen just below the critical temperature.

The two phases, as they transition to a supercritical state, are shown in the third image. Finally, the fourth image shows a uniform mixture in a supercritical state. Note there is no sign of a meniscus between the two liquids.

Anitescu determined that the logical source of the water and carbon dioxide is the exhaust gas recycled (EGR) stream that is already generated by a diesel engine. He conducted a series of experiments in mixing diesel fuel No. 2 or hexadecane (cetane) with a blend of nitrogen, carbon dioxide and water meant to be comparable to EGR. The composition of the blend is 74% nitrogen, 13.5% carbon dioxide and 12.5% water.

Tests to evaluate the feasibility of preparing a supercritical fluid mixture were conducted using a bench-top laboratory apparatus. The mole fraction of the fuel was varied between 0.100 and 0.786. Experimental conditions to produce diesel fuel-EGR mixtures ranged up to a pressure of 600 bar and a temperature of 450 C. Anitescu found that a mixture of either diesel fuel No. 2 or hexadecane and the synthetic EGR can be heated up to a supercritical state without coking.

Promising results have been found in initial CFD modeling for both emissions reduction and brake thermal efficiency. Anitescu says, "An independent assessment showed that an 80% reduction in both NO_x and particulate matter can be achieved by the combustion of supercritical fuel-air mixtures. In fact, in laboratory combustion experiments almost no particulate matter and NO_x were observed, as the emission stream captured in hexane was as clean as the pure solvent." The reason for the lower NO_x result is that combustion was achieved at a lower temperature than a conventional diesel engine.

Brake thermal efficiency represents the percentage of fuel converted into useful work. Anitescu found that this figure could be increased for the diesel engine from approximately 40% to 50%.

Anitescu believes that the EGR stream should be mixed with diesel fuel at a temperature between 100 C and 200 C. But the EGR stream leaves the engine manifold at a temperature of approximately 500 C.

Anitescu envisions that a portion of the EGR stream should initially be sent through an existing heat exchanger to be cooled down prior to mixing with the diesel fuel. From there, the mixture is heated up to approximately 400 C by the hot EGR to a supercritical state prior to injection into the combustion chamber.

One of the biggest problems facing Anitescu is the need for development of a suitable injector that can handle the fuel-EGR mixture. This remains an objective as the process is optimized for use in a diesel engine. The Achilles' heel here is the low lubricity of supercritical fuel-diluent mixtures. One idea is to keep the mixture in a liquid form below the critical point since liquids can be handled better by current injectors. The fuel will then rapidly transition to a supercritical state upon injection.

Anitescu says, "We now know that a supercritical fluid blend can

be prepared, but we need to find out experimentally how it performs in the combustion chamber. The spraying of the supercritical fuel mixture into a view cell is currently being studied. Finally, we need to find out what are the performance differences between conventional fuel and supercritical fuel in the diesel engine."

Additional information can be found in a recent paper² and patent³ or by contacting Anitescu at ganitesc@sy.edu.

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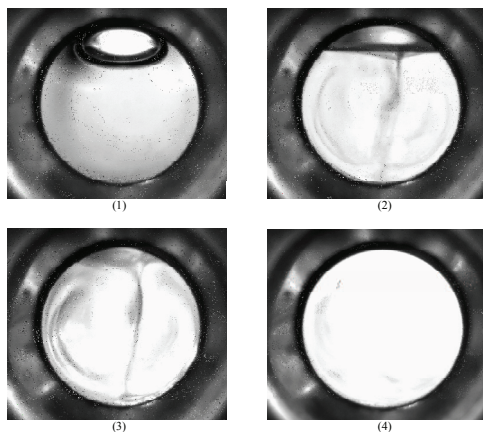


Figure 1 | Image 1 shows a blend of diesel fuel and carbon dioxide well below the critical temperature. The mixture in Image 2 is just below the critical temperature. Image 3 shows the two phases as they transition to a supercritical state. The uniform mixture of two components in a supercritical state is seen in Image 4. (Courtesy of Syracuse University)

Early corrosion detector

Researchers have developed a 'smart' epoxy coating that can detect early steel corrosion.

With the challenges of stopping corrosion, a number of technologies have emerged to deal with it through a stimulus-generated response. This means that an external mechanism impinges on the specific area suspected to be corroding, and a response is generated to assist with retarding the process.

In a previous TLT article, the concept of self-healing coatings was discussed.¹ A new approach to fix an epoxy coating on a metal substrate was described that involved incorporation of microcapsules of a monomer and catalyst into the coating. These capsules open when the coating is ruptured and exposes the substrate. The monomer and catalyst react to form a self-healing coating that provides protection to the section of substrate exposed.

Dr. John Tsvalas of the Nanostructured Polymers Research Center at the University of New Hampshire, in Durham, N.H., says, "Self-healing polymers is just one of several techniques that are in the field of stimuli response. Other approaches include ion sequestration technology and release of rust inhibitors. Missing from these technologies is a way to detect corrosion at a very early stage."

Corrosion is a process that initially starts on the molecular level and is very difficult to identify at an early stage. Before this electrochemical process makes a major impact in destabilizing a specific substrate, detection at an early stage enables maintenance to be conducted to minimize further damage.

One strategy that has been looked at is to use a pH-triggered mechanism in which a specific substance is incorporated into a coating and changes either color or fluorescence. Tsavalas says, "Compounds sensitive to changes in pH have worked with acrylic and polyurethane coatings. But a compound sensitive to pH changes has not worked well in epoxy coatings."

The reason for the problem with epoxy coatings is the raw materials used in their preparation. One of the precursors used to prepare epoxies is an amine that exhibits basic pH values. Residual amines in epoxy coatings tend to prematurely trigger the currently known pH indicators, leading to misleading results.

Epoxy-based coatings are widely used to protect steel substrates. A new approach is needed to develop early detection technology that will not prematurely activate. According to UNH researcher Dr. Weihua "Marshall" Ming and Tsavalas, "Key characteristics that are required for a fluorescence indicator include no premature reaction with the coating during application; ability to remain in a dormant, non-fluorescence state when no corrosion is present; effectiveness to fluoresce at low concentrations when corrosion is taking place and to maintain effectiveness, even in the presence of other ingredients such as pigments."

Such a technology has just become available. Drs. Tsavalas and Ming along with fellow UNH researcher Anita Augustyniak have developed a "smart" epoxy coating that can detect early steel corrosion.

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KEY CONCEPTS

- Early detection of corrosion can be achieved through activation of a fluorescence probe in a process known as chelation-enhanced fluorescence.
- A probe based on spiro lactam has been found to fluoresce reversibly with ferric ions.
- This probe can detect corrosion at an earlier stage than seen with the naked eye.

'The key performance feature of FD1 is that we can detect fluorescence at a very early stage before it can be seen with the naked eye.'

FLUORESCENCE INDICATOR

In looking through the literature, the researchers noted that a number of fluorescence probes have been developed for use in bioimaging. In particular, a series of probes could be activated in the presence of specific metal cations in a process known as chelation-enhanced fluorescence (CHEF).

They focused their interest on a probe based on a spiro-lactam that fluoresces reversibly when chelating ferric ions. This molecule is known as FD1 and has appeal as a corrosion detector because it fluoresces selectively with ferric ions.

The researchers initially worked with the CHEF in a solution environment where ion mobility is high. They found that it worked well and then embedded FD1 into epoxy coating films to check its efficacy through titration with ferric ions.

A laser scanning confocal microscope was utilized to image the fluorescence, which is observed between wavelengths of 520 and 660 nanometers with the maximum emission near 580 nanometers. The coating thickness ranged from 30 to 40 microns.

These experiments went well, and the researchers finally incorporated FD1 into an epoxy coating placed on a 1018 steel substrate. Two procedures were used to evaluate the effectiveness of FD1. Augustyniak first scribed a coated panel with a razor blade and placed the coating on top of a beaker containing a 0.5 molar sodium chloride solution for 40 hours. The coating was then placed in deionized water for 22 hours and submerged in the sodium chloride solution for an additional 30 minutes.

Fluorescence generated by the CHEF was observed at the end of this procedure. More important, no corrosion was observed with the naked eye until the coated steel was left in the sodium chloride solution for an additional 90 minutes.

A second evaluation technique used was to deliberately generate a defect in the coating to see if FD1 can detect un-

dercoat corrosion. The researchers generated the defect by applying a silicone oil on the steel substrate prior to application of the FD1-incorporated epoxy coating.

The defective part of the coating was then exposed to a 5% sodium chloride solution at ambient temperature to accelerate the corrosive response. Fluorescence was detected after two days, but corrosion was not seen by the naked eye

until after three days. Figure 2 shows the difference in using fluorescence vs. the naked eye.

Ming says, "The key performance feature of FD1 is that we can detect fluorescence at a very early stage before it can be seen with the naked eye. Initial work with FD1 was done at a concentration in the coating of 0.5% by weight. We

believe that FD1 is sensitive at lower treat rates, and we will evaluate its efficacy in the future."

The CHEF technique also has been found to be more sensitive than pH detection. FD1 does not appear to leach out of the coating and exhibits stability for at least one year in a dormant state prior to the onset of corrosion, according to Tsavalas and Ming.

Future work will involve learning more about how broadly FD1 can be used as a fluorescence detector. The researchers indicate that they will look into other steel alloys and nonferrous metals.

Additional information can be found in a recent article² or by contacting Ming at w.ming@unh.edu.

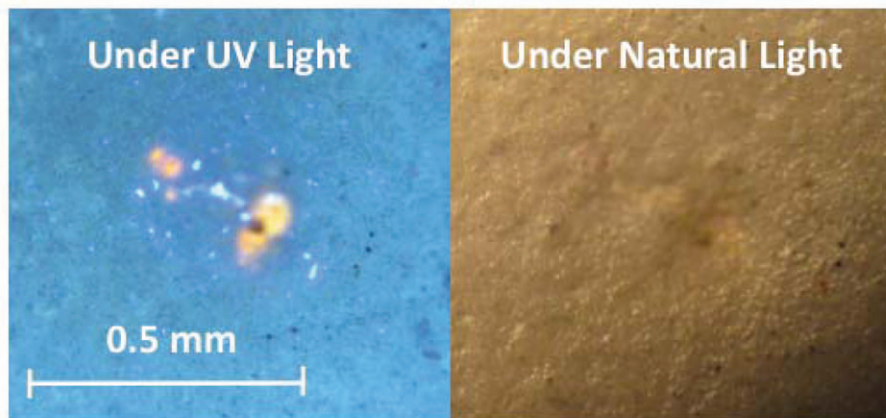


Figure 2 | A fluorescence probe detected corrosion on a surface (left) two days after exposure to a 5% sodium chloride solution. Corrosion on the same surface (right) by the naked eye after three days. (Courtesy of the University of New Hampshire)

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Catalyst effectiveness: Size does matter

The size of palladium atom catalyst clusters can affect the conversion of carbon monoxide to carbon dioxide.

KEY CONCEPTS

- The size of palladium atom catalyst clusters affects the rate of conversion of carbon monoxide to carbon dioxide.
- Differences in the binding energy of electrons in palladium atoms also affect catalyst performance because more tightly bound valence electrons are less likely to participate in bond-making processes.
- Catalyst activity increases as the size of palladium atom clusters increases up to 20 atoms before dropping when 25 atom clusters are reached.

Catalysts play an important role in a number of different processes that involve lubricants. The first application that comes to mind for many of us is in reduction of automotive emissions. A three-way catalyst based on precious metals (palladium, platinum and rhodium) is used to simultaneously remove carbon monoxide, hydrocarbons and NO_x .

In a previous TLT article, a new approach was discussed to maximize the performance of the three-way catalyst.¹ The precious metal used is transformed into fine nanoparticles that exhibit comparable performance to conventional three-way catalysts but are effective over a longer operating period and at a lower treat rate.

A second application that we are familiar with is the use of catalysts in the preparation of mineral oil basestocks. Group II and Group III base oils are mainly produced through the use of hydrocracking. In a previous TLT article, a new approach to prepare higher molecular weight hydrocarbons from lower molecular weight hydrocarbons can be carried out through the process of metathesis.²

The work done showing the increased effectiveness of nanoparticles of a specific catalyst vs. micrometer-sized particles of the same material means that particle size can have an impact on performance. Bill Kaden, a chemistry doctoral student at the University of Utah, in Salt Lake City, Utah, says, “Researchers have taken stabs at determining the size of active catalyst particles currently used in the chemical industry. But typical preparation methods and analytical tools used have been insufficient to provide this information.”

One other factor that has been seen is that after large particles are removed from a catalyst, reasonable activity is still seen with smaller particles. This suggests that work is needed to determine how catalyst particles on the atomic-scale function.

Such work has not been conducted until now.

CLUSTER SIZE

Kaden and his fellow researchers set out to evaluate the differences in catalyst performance as a function of size. He says, “We decided to evaluate the effectiveness of palladium metal deposited in various cluster sizes on a titanium dioxide surface. The process studied is the conversion of carbon monoxide to carbon dioxide.”

The clusters represent palladium atoms in sizes ranging from one atom up to 25 atoms. Kaden adds, “A 30-atom palladium cluster is less than one nanometer in size.”

The catalyst is prepared by laser vaporizing palladium metal in a flow of helium. An electric field and a quadruple mass filter were used to isolate clusters of specific sizes, which were then deposited onto a titanium dioxide crystal of the (110) orientation. In all cases, the number of palladium atoms was maintained at 1.53×10^{14} per square centimeter.

The researchers evaluated catalyst effectiveness by conducting a temperature programmed reaction. Initially, the palladium catalyst was treated with 10 Langmuirs ($1\text{L} = 1 \times 10^{-6}$ Torr partial pressure for 1 second) of oxygen at a temperature

It is very apparent that the orientation of atoms at this sub-nanometer level influences catalyst performance.

of 127 C and 5 L of carbon monoxide at -93 C. The temperature of the catalyst was then increased from -143 C to 257 C at a rate of 3 C/second.

Concurrently, a mass spectrometer was used to monitor the concentration of carbon monoxide and carbon dioxide present during the reaction. Kaden says, “We found that the size of the cluster influenced the performance of the catalyst.”

Data produced shows that a single palladium atom does not generate any activity. When the cluster size is increased, catalyst activity increases up to two palladium atoms and then declines as the number of atoms is increased to seven. From there, activity increases linearly up to 20 atoms before dropping when 25 atom clusters were reached.

At the atomic level, Kaden indicates that differences in the binding energy of electrons within the core levels of the palladium atoms significantly impacts catalyst performance. He says, “We measured the shifts in the binding energy of the 3d orbitals of palladium atoms and used the results to indirectly reflect what the valence orbitals are doing. We found that higher-than-expected binding energies led to lower levels of catalytic activity because the valence electrons are more tightly bound and less likely to participate in bond-making processes.”

Kaden further explained that this binding energy is very important because it impacts the activation of the bond palladium atoms have with oxygen atoms during the reaction with carbon monoxide. He adds, “Activation of the palladium-oxygen bond is the limiting step in the conversion of carbon monoxide to carbon dioxide.”

One other consideration evaluated by the researchers is the composition of the palladium atom clusters on the titanium dioxide surface. As the clusters increase in size, helium ion scattering shows that a second layer of palladium layers starts to form above a cluster size of 10. The appearance of this second layer occurs as catalytic activity increases from 10 to 20 palladium atoms but then declines to 25 palladium atoms.

The complex apparatus used to prepare the catalyst, conduct and analyze the reaction results is shown in Figure 3. Kaden says, “The structure of the palladium atom clusters is very important in determining catalytic performance. A

particular number of atoms present in specific clusters lead to geometries that dictate catalyst performance.”

It is very apparent that the orientation of atoms at this sub-nanometer level influences catalyst performance. Differences in size and orbital binding energies are major considerations in predicting how well a specific number of palladium atoms perform.

Future development of catalysts should benefit from this work, which will hopefully lead to more effective

approaches to reduce emissions, produce mineral oil basestocks and generate the wide variety of additives used in the lubricant industry.

Additional information on this research can be found in a recent article³ or by contacting Kaden at kaden@chem.utah.edu. **TLT**

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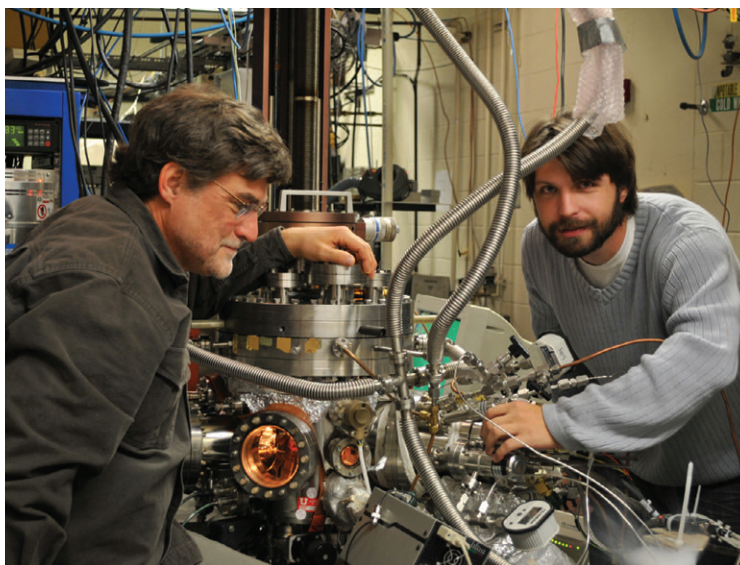


Figure 3 | The apparatus used to prepare the catalyst, conduct and analyze the reaction results is quite complex as shown above. [Courtesy of the University of Utah]



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