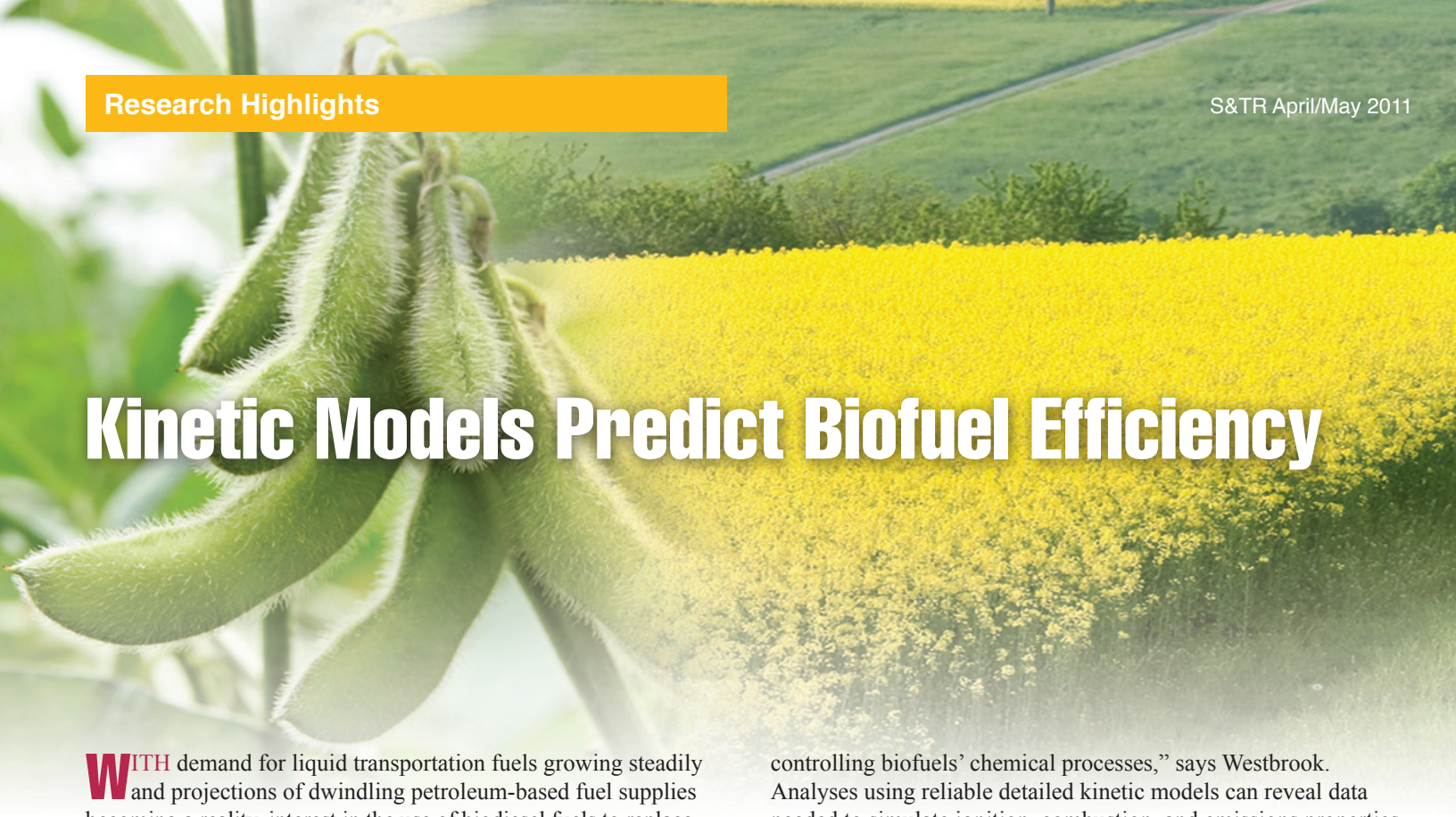


Kinetic Models Predict Biofuel Efficiency

WITH demand for liquid transportation fuels growing steadily and projections of dwindling petroleum-based fuel supplies becoming a reality, interest in the use of biodiesel fuels to replace or blend with conventional fuels for aircraft and automotive applications is on the rise. Because plants consume carbon dioxide via photosynthesis, these renewable fuels offer the potential to be carbon neutral. Biomass products, such as ethanol and n-butanol produced from fermentation of plant materials, may replace or supplement gasoline in spark-ignition engines and in conventional jet and diesel fuels.

Biodiesel fuel is produced from oils in soy, canola, coconuts, linseed, jojoba, olives, peanuts, and other plants as well as from beef tallow and other animal fats. Another source with great promise is bioengineered algae that can be grown in large vats, a practice that does not compete for fertile soil. Biodiesel fuels are produced by esterification, the process of combining oil with methanol to produce methyl esters. These fuels can be used in diesel engines without significant engine modification. In fact, the original engine that Rudolph Diesel demonstrated at the 1898 Exhibition Fair in Paris, France, ran on biodiesel produced from peanut oil.

Bio-derived fuels have important chemical differences from petroleum-based fuels, which affect their performance, efficiency, and pollutant emissions. The Livermore combustion chemistry group, led by Bill Pitz and Charlie Westbrook, has spent years developing computer modeling capabilities that provide information about biofuels' combustive behavior. The team has used kinetic modeling to study methyl esters ranging from 1 to 20 carbon atoms in length as well as carbon chains with varying numbers of carbon double bonds. "The resulting chemical kinetic reaction mechanisms present a predictive computational tool that can be used to explain, for the first time, the basic chemistry controlling biofuels' chemical processes," says Westbrook. Analyses using reliable detailed kinetic models can reveal data needed to simulate ignition, combustion, and emissions properties of these fuels.

Kinetic models based on elementary reactions offer the best accuracy and reliability, and the knowledge of a specific elementary reaction can be reapplied for completely different operating conditions and in different species mixtures. Detailed kinetic models represent the molecular interactions that occur when chemical bonds are broken and reformed into new chemical compounds. Much of the value of kinetic modeling lies in how dynamic simulations can reveal information about inherently complex chemical systems. In contrast, more approximate modeling methods have parameters determined strictly by fitting to experimental measurements, which limits their applicability. Much more information is contained in chemically reacting systems than can be extracted from simple inspection.

"The resulting chemical kinetic reaction mechanisms present a predictive computational tool that can be used to explain, for the first time, the basic chemistry controlling biofuels' chemical processes."

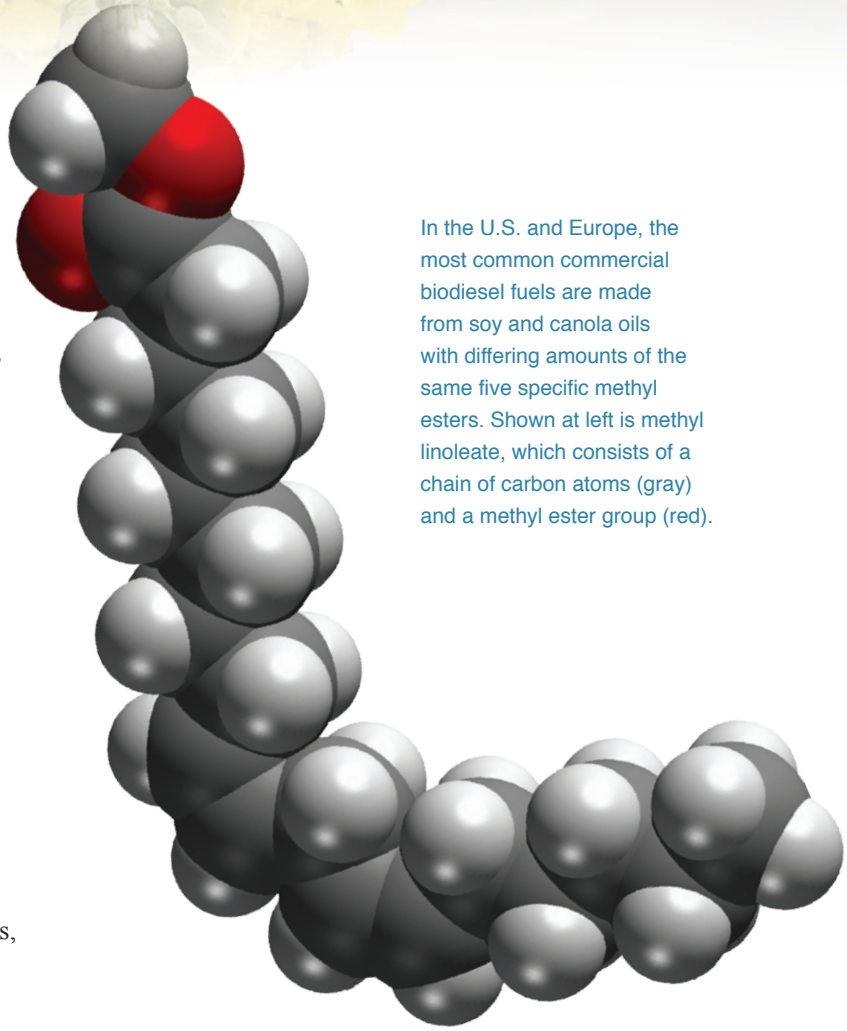
Chemical kinetic modeling codes are rule-based computations that predict how the composition of fuel affects energy conversion

performance and pollutant emissions. Kinetics refers to the study of physicochemical (including biological) systems that change with time. The Livermore model, which emulates how real-life systems operate, uses a large set of differential equations to represent physical and chemical processes known or hypothesized to occur in biological systems.

Burning Questions

Westbrook and Pitz spent five years developing models for methyl esters that include all pertinent species, reactions, rate coefficients, and related thermochemical and transport parameters as functions of temperature and pressure. Westbrook says, "The process was lengthy because the varied chemical compositions, such as carbon–carbon bonds, create differences in how each one burns." Kinetic mechanisms for this family of fuels had not been previously available.

Unlike the hundreds of chemical compounds in gasoline or diesel, biodiesel fuels contain a limited number of compounds. In the U.S. and Europe, the most common biodiesel fuels are made from soy and canola oils with differing amounts of the same five specific methyl esters: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. Each biodiesel fuel consists of large fuel molecules, with chain lengths of 16 to 18 carbon atoms plus a methyl ester group at one end. (See the figure at right.) The numerical models for biodiesel fuels are therefore complex, with systems of coupled nonlinear differential equations that may have as many as 5,000 chemical species and 20,000 elementary chemical reactions. Because of the Laboratory's supercomputing facilities, the Livermore team is one of the few groups that can apply these complex models in simulations of realistic, practical combustion problems.



In the U.S. and Europe, the most common commercial biodiesel fuels are made from soy and canola oils with differing amounts of the same five specific methyl esters. Shown at left is methyl linoleate, which consists of a chain of carbon atoms (gray) and a methyl ester group (red).

Biodiesel stations such as this one in Berkeley, California, may one day be as common as those selling petroleum gas. The Biofuel Oasis is a worker-owned cooperative. (Courtesy of Biofuel Oasis.)

The combustion chemistry team found that the methyl ester group in biodiesel fuel weakens some of the bonds between carbon and hydrogen atoms. This effect makes the hydrogen atoms easier to remove, which sets the combustion process in motion. The critical metric of diesel fuel performance is its ease of ignition, as measured by its cetane number. The methyl ester group increases the cetane number of the fuel.

Phenomenal Insight

According to Westbrook and Pitz, oxygen atoms present in biodiesel fuel molecules have a beneficial property. A pollution problem with diesel engines has historically been their tendency to produce soot and smoke, but oxygen in the methyl ester group leads to lower soot emissions from diesel engines when using biodiesel fuel. When oxygen-containing compounds are blended with conventional diesel fuel, soot production can be sharply reduced. Although this effect of oxygen had been observed experimentally in the early 1990s, the Livermore chemical kinetics models provide the first fundamental understanding of chemical processes responsible for the phenomena.

Combustion modeling results are validated with experiments and the relatively small body of existing experimental literature before being used in simulation codes that optimize engine design for maximum efficiency and minimal pollutant emissions. Understanding the kinetics of the reactions occurring in biodiesel fuels at both high and low temperatures is necessary to reliably simulate ignition, combustion, and emissions in diesel and homogenous charge-compression ignition engines. The Laboratory provides data to many university researchers worldwide who are performing experiments.

"As a rite of passage, many postdocs from these universities spend a year at Livermore working with our group," Westbrook says. "Over the years, an international family has developed, all of us engaged in the pursuit of petrochemical alternatives." Westbrook and Pitz are studying other plant and animal fat mixtures in an effort to develop and evaluate future transportation fuels.

—Kris Fury

Key Words: biodiesel, biofuel, chemical kinetic model, combustion, diesel fuel, gasoline, methyl ester.

For further information contact Charlie Westbrook (925) 422-4108 (westbrook1@llnl.gov).