Next-Generation Fuels—What's Old Is New Again

In the search for new biofuels, NREL is reviving its research into biomass pyrolysis and gasification, as well as techniques for converting algae into biodiesel.

Al Darzins has been at NREL for less than 2 years, but finds himself spending a lot of time these days looking at research results from some of the laboratory's earliest research. As group manager for the National Bioenergy Center's Applied Sciences Group, he is overseeing several "new" research efforts that build on some very old ones. His efforts are aimed at converting biomass—plants and plant-derived materials—into fuels.

"Previous biofuels work performed at NREL under various programs has provided a strong foundation for our current efforts to kick-start that research again, ten years later," says Darzins.

When the laboratory first opened in 1977, the Arab Oil Embargo of 1974 was still fresh in people's minds. Early research included several different potential technologies for making liquid transportation fuel from biomass. Some of those, while promising, were subsequently set aside to focus on other research.

Today, with reducing dependence on imported oil a high presidential priority, three of these technologies—the production of pyrolysis oil, liquefied synthesis gas, and microalgal oil—are once again attracting a lot of attention. Darzins and his NREL colleagues are excited about moving forward with them, taking advantage of both our past research efforts and of applying new research capabilities to them.

Borrowing a "Clean Coal" Technology for Ethanol Production

Coal was once the transportation fuel of choice for the United States, powering our trains and even fueling an early automobile, the Stanley Steamer. But liquids and gases burn faster than solids, have high energy densities, and are more convenient to use in vehicles, all of which are reasons why gasoline and diesel fuel became the dominant transportation fuels.

Because of these advantages, it can be well worth expending energy to convert solid fuels—whether they be biomass or coal—to liquids. By heating biomass to very high temperature with limited or no oxygen, researchers can either liquefy or gasify it. When biomass is liquefied, the resulting pyrolysis oil can be used as a feedstock for conventional oil refining. When it is gasified, the synthesis gas can be catalytically converted to liquid fuels that substitute well for diesel or gasoline.

In fact, the pyrolysis and gasification technologies used for converting biomass to liquids were initially applied to coal to produce petroleum substitutes. With a strong utility interest in integrated gasification and combined-cycle technologies for coal power (so-called "clean coal" technologies), gasifier technology has advanced significantly.

While the core technology has advanced, biomass pyrolysis and gasification are gaining renewed interest in part because of the emphasis on producing ethanol from cellulosic biomass, such as wood chips and plant leaves and stalks. Cellulosic biomass is made up of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are plant-derived, sugar-based polymers, and biological biomass conversion technology can ferment the sugars to ethanol. But lignin, the third major component of biomass—making up 15% to 25% of biomass by weight—does not contain sugars.

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Biomass pyrolysis involves heating the biomass to high temperature in the absence of oxygen. The process yields vapors that are condensed to form an oily liquid.

Until recently, NREL's process designs for ethanol production called for burning the lignin to provide heat and power for the ethanol plant. But with transportation fuels as a top priority, the new thought is to use multiple technologies to produce fuels. Because thermochemical processing can produce fuels from any biomass source, not just sugars, researchers can use it to convert the lignin and any other residue from biological processing to additional ethanol or other liquid fuels within the same biorefinery.

Also, biological processing is currently focused on agricultural residues such as cornstalks and husks. Other biomass—particularly softwoods, which may become extensively available from forest thinning operations—is more challenging for fermentation and may be more suitable for pyrolysis or gasification.

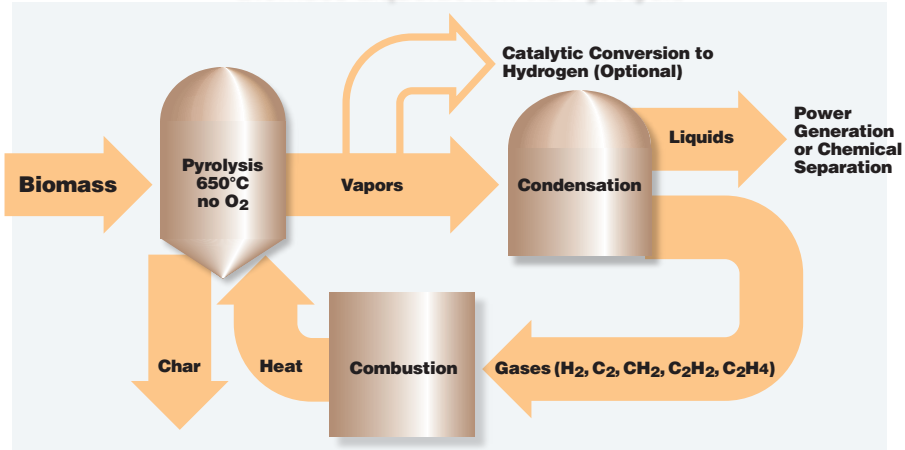
NREL Goes Full Circle on Pyrolysis Research

NREL's research on biomass pyrolysis has returned to its roots. Pyrolysis involves liquefying biomass by first heating it to about 550°C in the absence of oxygen and then condensing the vapors. The resulting pyrolysis oil is a complex mixture analogous to crude oil (except that it contains oxygen) and can be burned as fuel or used as a feedstock for conventional oil refineries.

NREL's original pyrolysis research had that direct product as its objective, but in the late 1980s, the laboratory turned its focus to making specific fuel additives or other petrochemicals from pyrolysis vapors before they condensed. NREL researchers worked on cracking the vapors to ethylene for gasoline production and then on catalytically converting them to aromatics and other liquid hydrocarbons.

In the 1990s, when Scientist Stefan Czernik joined NREL as a thermal and catalytic conversion specialist, the emphasis changed to producing chemical products other than fuels. One effort, for example, sought to develop wood adhesives from pyrolysis oil, a natural fit for reducing petrochemical use by an industry with ready access to biomass resources. Another effort sought to regenerate base chemicals for plastics production by pyrolyzing polymers, specifically from discarded carpeting. Now Czernik is heading up efforts to use

Biomass Liquefaction via Pyrolysis



Biomass pyrolysis involves heating the biomass to high temperature in the absence of oxygen. The process yields vapors that are condensed to form an oily liquid.

the whole pyrolysis oil along the lines of NREL's original pyrolysis work.

"The goal is to make pyrolysis oil a standard petroleum refinery feedstock," says Czernik.

One project is exploring the suitability of pyrolysis oil derived from lignin for such a feedstock. NREL produces the pyrolysis oil and research partners at DOE's PNNL and UOP LLC, a private petroleum research company, hydrotreat it, that is, they upgrade it by removing impurities. Among other things, the process removes oxygen, which is the primary difference between pyrolysis oil and crude petroleum.

NREL is conducting techno-economic and life-cycle analyses of the biorefinery pathway involving lignin pyrolysis and hydrotreating to determine how profitable it will be, what kinds of energy and environmental impacts it would have, and what changes could be made to most effectively improve that profitability and impact.

A second project seeks to upgrade pyrolysis oil during its production by reacting either the condensed oil or the oil vapors with ethanol. Researchers expect this process to reduce the acidity of the pyrolysis oil and make it more stable, both of which would improve its suitability as an oil refinery feedstock.

Because of the potential for either hydrotreating or ethanol upgrading, or a combination of both, the future for pyrolysis oil appears bright.

"We think pyrolysis is a powerful technology and are eager to use it to help meet transportation fuel needs," says Czernik.

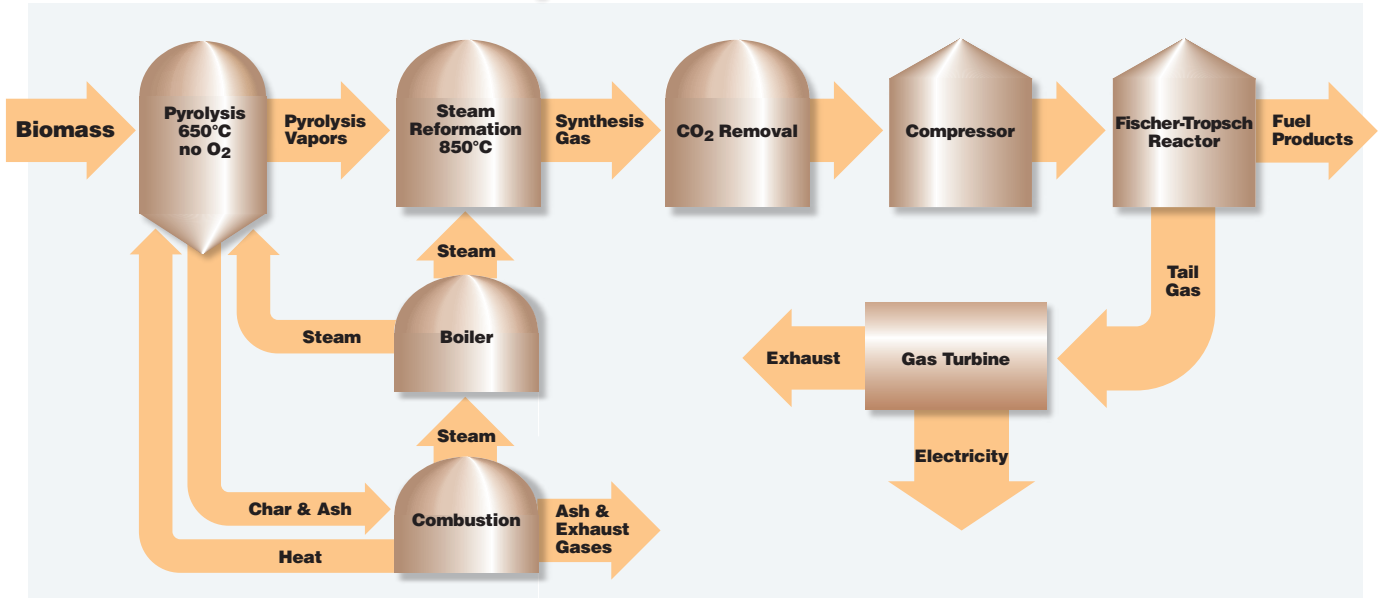
The Three-Phase Approach to Fuels: From Solid to Gas to Liquid

Another approach to converting solid biomass into a liquid fuel is to first convert it into a gas. NREL scientists gasify biomass to a mixture of carbon monoxide and hydrogen known as synthesis gas or syngas by taking the pyrolysis process a step further, heating to about 850°C with about one-third the oxygen needed for efficient combustion.

In the 1990s, syngas was envisioned primarily as a fuel for electrical power generation, with a focus first on large utility systems and then on smaller distributed generation systems. The shift from electricity production back to liquid fuels is in large measure a tribute to the great gains made by wind turbines, solar cells, and other renewable energy technologies for power generation. When it comes to liquid transportation fuels, however, biomass is the only renewable game in town.

Conversion of syngas to liquids also has a colorful and somewhat dark history. Franz Fischer and Hans Tropsch first studied conversion of syngas into larger, useful organic compounds in 1923. Using syngas made from coal and metal catalysts, they were able to produce liquid hydrocarbons. Fischer-Tropsch systems were used successfully in Germany during World War II and South Africa during apartheid embargoes when each faced limited oil supplies. Several commercial Fischer-Tropsch operations continue today, and the term Fischer-

Biomass Gasification via Staged Steam Reformation with a Fluidized Bed Gasifier



Biomass gasification is a multi-step process that starts with pyrolysis, followed by a high-temperature steam treatment that converts the pyrolysis products into a mixture of gases, called synthesis gas. After a treatment step, the gas is compressed and fed into a catalytic reactor to produce a liquid fuel. A byproduct from the process can be used to generate electricity.

Tropsch has come to be applied to any catalytic conversion of syngas to liquid fuel.

The NREL syngas-to-liquid system bubbles the gas through an oil slurry under high pressure, with the catalyst suspended in the liquid. While traditional Fischer-Tropsch processes seek to produce non-oxygenated hydrocarbons, NREL's objective is to produce ethanol or perhaps "higher alcohols"—a mixture of ethanol and larger-molecule alcohols.

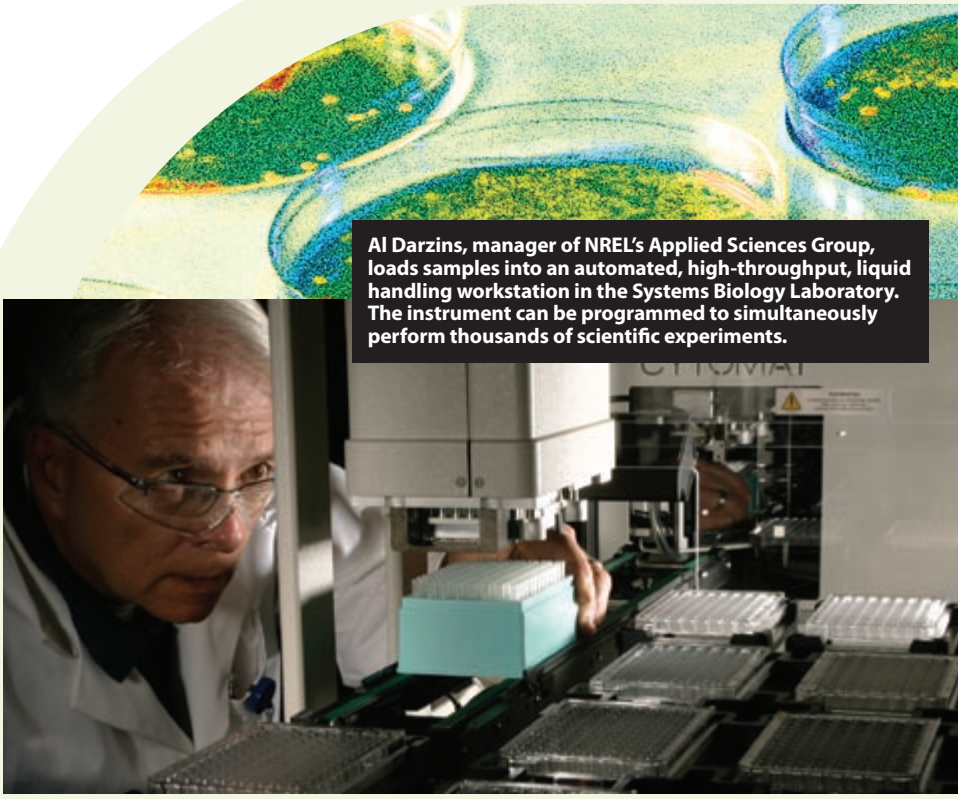
"The process is similar to Fischer-Tropsch or methanol reformation," says NREL Scientist Steve Deutch, "but we stop it at an earlier stage."

Producing ethanol from syngas would be an ideal companion technology for a biorefinery that ferments biomass into ethanol because the syngas process would produce ethanol from material that cannot be fermented, such as lignin. Because both processes would produce ethanol, the approach would avoid the need for additional infrastructure to deliver another product, such as a lignin-derived chemical.

NREL is currently working with DOE's PNNL on a joint effort to produce alcohols from syngas. PNNL is working to improve the catalyst, while NREL is focusing on improving the process conditions and testing the catalyst and process against a wide range of operating conditions, using actual syngas derived from biomass.

Microalgal Lipids—An Aquatic Approach to Future Fuels

Yet another early biofuel research area that is back in the spotlight is the conversion of algae to fuels. Although small in size compared to cellulosic ethanol efforts, the NREL research effort on fuels from algae involved extensive research through the 1980s and early 1990s. NREL's biomass researchers led the way in developing technology for growing



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Al Darzins, manager of NREL's Applied Sciences Group, loads samples into an automated, high-throughput, liquid handling workstation in the Systems Biology Laboratory. The instrument can be programmed to simultaneously perform thousands of scientific experiments.

New Lab Provides Powerful Tools for Biocatalyst Development

Be it microscopic algae for oil production, fungi for enzyme production or yeast or bacteria for sugar fermentation, the advanced biological technology for converting biomass to fuel is all about developing organisms that produce better biochemical agents or better perform desired functions themselves. NREL's bioconversion research capabilities have been greatly enhanced by opening of a major new facility. Applied Sciences Group Manager Al Darzins says the new Systems Biology Laboratory has three main components.

"New X-ray crystallography equipment allows us to determine the three-dimensional structure of enzymes, a key parameter required in understanding how they work," says Darzins. "This information also allows us to make them perform better. High-throughput robotics capabilities allow us to rapidly test large numbers of genetic variants or simultaneously conduct hundreds and even thousands of 'miniature experiments' in a single day.

"And 'omics' tools provide a three-part fundamental 'cataloguing' of the capabilities of a particular biocatalyst organism. Genomics allows one to identify all of the genes that are expressed within an organism. Proteomics identifies all of the enzymes or other proteins that an organism produces and metabolomics identifies all of the small molecule metabolites that an organism produces during growth. With these research tools, our researchers now have dramatically enhanced capabilities from just a few years ago for developing new strains to carry out desired biomass conversions."

NREL has been acquiring some of the new equipment over the last couple years and now has it all set up in a superb facility in two new laboratories in the Field Test Laboratory Building. The new Biology Systems Laboratory is a great complement to the recently opened Biomass Surface Characterization Laboratory.

"Together they arm NREL biomass conversion research efforts with the best tools available, and we look forward to using them to making key advances in the biofuels area," says Darzins. ■

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NREL researchers were able to draw on the laboratory's extensive culture collection to develop strains of algae with high levels of lipids.

microalgae that produce high levels of lipids (oils) for processing into biodiesel. NREL developed an extensive microalgae culture collection as well as a toolkit for the genetic engineering of these organisms. NREL Analyst John Sheehan, who managed the last few years of the microalgae program, cited economic factors for its being set aside.

"In addition to having to compete with 57-cent-per-gallon diesel at the time, one of the main reasons for dropping the microalgae program was realizing that even using simple outdoor ponds, the capital cost of facilities for growing the microalgae would always keep the technology relatively expensive," says Sheehan. "Today, however—in addition to dramatically higher petroleum diesel cost—low plastic container cost makes the possibility of growing the algae in closed systems such as transparent tubular reactors a very realistic possibility and is making the technology much more attractive again."

NREL Scientist Eric Jarvis, a genetic engineering specialist, is especially excited about the possibility of restarting microalgae research because of new capabilities developed since the mid-1990s.

"The metabolic engineering we did to try to make microalgae produce more lipids was cutting edge at the time," says Jarvis, "but the whole field of genetic engineering has advanced so dramatically since then that we will now have far greater ability to improve the organisms' performance." (see "New Lab" sidebar on page 23).

Another exciting reason for reestablishing microalgae research is the possibility of developing a new end product. Rather than converting the microalgal oil to biodiesel, it is possible to chemically convert it to jet fuel. The same hydrotreating process that could make pyrolysis oil a good oil refinery feedstock could also convert microalgal oil into kerosene, the basic component of jet fuel.

Jet fuel now accounts for about 8% of our petroleum use and no renewable alternative has been developed to this point. Ethanol is not dense enough, having only about half the energy per volume of jet fuel. Biodiesel has about 80% the energy density of kerosene, but can solidify at the low temperatures of high altitude flight.

Industry is very interested in this process because it could utilize existing hydrotreaters in the nation's oil refineries. A likely R&D participant is the U.S. Department of Defense, which is seeking a non-petroleum replacement for military jet fuel.

Darzins likes to characterize all of these research efforts as developing "next-generation fuels."

"They will probably never be as large as our ethanol or hydrogen research programs, but they could lay groundwork for key contributions to meeting our transportation energy needs," says Darzins. "Knowing that NREL has a running head start on them because of our past research says a lot about the value of our broad and continuing commitment to meeting transportation and other energy needs with renewable energy." ■