Making Ethanol from Cellulose

For each of us, this photo to the right may represent something very different—a summer walk or picnic in the country, that unfinished yard work you've been avoiding, or simply the beauty and variety of nature. But for a group of collaborating scientists from the University of Toledo and Los Alamos National Laboratory, this picture represents the most abundant renewable resource on earth, cellulose. Cellulose is what keeps trees standing and gives form to plants and their foliage. It shapes most of the natural living world around us. And if scientists can figure out an efficient way to convert it into ethanol, cellulose may also shape the direction of our energy future. A Los Alamos scientist is using novel neutron and X-ray diffraction techniques to peer into the nanostructure of cellulose to help engineer compounds that could unleash the potential of this vast energy resource (continued on page 6).

The Dawn of a New Era for Solar Energy

A nanotechnology breakthrough could double the efficiency of solar panels

The promise of clean, abundant solar energy has yet to be fulfilled largely because of inefficiencies in photovoltaic technology. Earth-bound cells have never exceeded 24.7% efficiency when converting the sun's photons into electrical current. But what if we could increase that efficiency by twice as much, or even more? Los Alamos researchers may have found a way to break the conversion efficiency barrier that has limited the widespread adoption of photovoltaics for decades. In addition to increasing the electrical output of solar cells, this breakthrough may also enable hydrogen production via photo-catalysis (continued on page 4).
Cellulosic Bioethanol

A Los Alamos scientist is helping to unlock the potential of this abundant, domestic, renewable energy resource.

One of the most important energy security and environmental goals over the next few years will be to develop biomass as a raw material for bioethanol fuels. A recent report prepared by Oak Ridge National Laboratory found that land resources in the United States could produce over a billion tons of biomass per year. That’s enough to displace 30 percent of the nation’s present petroleum consumption. The U.S. ethanol industry is growing rapidly, but the majority of ethanol is made from the starch (that is, the edible parts) of grains such as corn and sorghum. Starches are only a minute fraction of biomass resources. The far greater share, cellulosic biomass, is currently unused because it resists industrial attempts to break it down to a simple sugar—a necessary first step in the fermentation of bioethanol (see box on facing page).

Ionic Liquids

A team of researchers from the University of Toledo and Los Alamos National Laboratory are trying to solve this problem through the use of ionic liquids. Ionic liquids are salts that are liquid near room temperature. Salts can be formed by mixing acids and bases together so that they form a compound between two atoms or two chemical groups, one negatively charged called an anion, and another positively charged called a cation. Because ionic liquids have a low melting point and are made of electrically charged cations and anions, they are better than more common liquids, such as water, at pulling apart and dissolving solids. Ionic liquids don’t emit vapors as do common organic solvents, so they are more environmentally friendly. They are versatile solvents because their chemical structures can
be engineered or tuned to dissolve a variety of compounds. In groundbreaking experiments, two members of the team, Connie Schall and Sasidhar Varanasi from the Chemical Engineering Department at Toledo, have found that pre-treating cellulose with certain ionic liquids can break down the crystal structure into individual chains allowing them to degrade into sugar molecules more easily with subsequent use of enzymes called cellulases. In fact, the rate of glucose production in the pre-treated cellulose increased by a factor of almost 100. Now, with the help of Jared Anderson from Toledo’s Chemistry Department, Schall and Varanasi are working to engineer the chemical structure of the ionic liquids to efficiently convert cellulose into simple sugars for bioethanol production. However, to understand how the cations and anions affect the biomass, they must be able to “see” at the atomic and molecular level.

Neutron and X-ray Diffraction at Los Alamos National Laboratory

That’s where Paul Langan, a scientist in Los Alamos’ Bioscience Division, is helping. Langan has been developing novel neutron and X-ray diffraction techniques for studying the structures of fibrous materials, and it looks like those techniques may play an important part in the development of ionic liquids. The structure and properties of cellulose biomass are incredibly complex. Cellulose is perhaps the most studied polymer in the world, and researchers have been trying to see its structure using X-ray diffraction methods for almost a century. Two decades ago, scientists with the U.S. Department of Agriculture surprised the research community when they discovered that cellulose is composed of not one but two crystal forms which they called I_α, and I_β. That means cellulose chains can densely pack together in two very different ways. We now know that the amount of I_α and I_β vary from species to species. Langan, together with researchers from the Centre de Recherches sur les Macromolécules Végétales in Grenoble, France, the University of Tokyo, and Kyoto University, isolated samples of the I_α and I_β forms and determined their detailed atomic structures using state-of-the-art neutron and synchrotron X-ray radiation facilities. The results were important enough to warrant a review in the leading scientific journal, Nature. The team also used these diffraction techniques, together with a number of other spectroscopic techniques, to characterize the structure of cellulose during and after various industrial processes that change I_α and I_β to even more complex crystal forms such as cellulose II and cellulose III. The insight gained by these and future experiments will be critical to engineering ionic liquids that degrade cellulose biomass.

With demand for transportation fuels rising and political instability in

continued on page 13

Starch vs. Cellulose

Today, most ethanol is made from starch, the edible portion of grains such as corn, wheat, and sorghum (left). Cellulose is the fibrous, woody, and generally inedible portion of plant matter. As such, it is usually a farm waste, like cornstalks, but also includes fast-growing trees, grasses, and waste products like paper and wood chips (right). So why use valuable food to produce fuel when we could do it with useless bio-junk? It turns out that the ethanol industry hasn’t been much more efficient than our human digestive systems when it comes to breaking down the huge polymer chains that give cellulose its structure. To derive fuels from biomass, the raw material must first be broken down into simple sugars which are fed to microorganisms (yeast or bacteria) that convert the sugars into ethanol. The cellulose, hemicellulose, and lignin that make up cellulose biomass consist of complex, closely packed polymer chains of molecules that don’t easily break down into simple sugars. Starch, like cellulose, is a polymer of glucose but the glucose rings are linked differently and the polymer chains are packed into crystalline granules that readily break down into usable sugars. But corn and other starches and sugars represent only a small fraction of biomass. The challenge is to find a way to break the much larger, unused share of plant resources—cellulose biomass—into simple sugars without using more energy than the resulting ethanol would yield.
Microdrilling, continued from page 9

electronics and sensor miniaturization in the past decade have made new instrument packages with small diameters possible and increasingly affordable. These instrument packages, however, are poorly suited for large boreholes. Without microdrilling, it would be difficult to deploy sufficient instrumentation to monitor sequestration processes.

Los Alamos National Laboratory is currently collaborating with Lawrence Berkeley National Laboratory to use time-lapse vertical seismic imaging to characterize fluid migration during CO₂ injection. Last year, Berkeley deployed a 20-level hydrophone and geophone string in a 750-ft microhole drilled by Los Alamos at the Rocky Mountain Oil Testing Center at Teapot Dome, Wyoming. The DOE’s National Energy Technology Laboratory funds this work. Los Alamos’ microdrilling system, which can now drill to 1,500 feet, also serves as a test platform for new technologies that may advance microdrilling even further and lead to a sea-change in the way U.S. industry approaches the fossil fuel cycle, from exploration to containment of CO₂ emissions.

— Anthony Mancino

Cellulosic Bioethanol, continued from page 7

petroleum producing regions, it’s hard to overstate the importance of cellulosic bioethanol to the environment and to our energy security. We are inundated with the necessary resources to make it right here at home. With agricultural wastes assuming a new value, farmers could now sell two cash crops where before there was only one. And while all bioethanol burns cleaner than fossil fuels, studies have shown that cellulosic bioethanol is even cleaner than grain-based ethanol. The multidisciplinary expertise and unique facilities at Los Alamos and collaborating institutions are helping to unlock the potential of this vast energy resource.

— Paul Langan and Anthony Mancino

ITER, continued from page 11

faster. These scale-up considerations are perhaps the largest technical risks associated with the project. These risks will be addressed with state-of-the-art computer modeling and system testing at the end of the project.

Los Alamos’ ITER-related chemical processing work will primarily be performed in the Chemistry Division’s Chemical Sciences and Engineering group. Scott Willms, Craig Taylor, Bryan Carlson, David Dogruel, and Matt Caver will be the key technical staff.

The international agreement to build ITER is scheduled to be formalized in November 2006. Partners include the U.S., Europe, Japan, South Korea, China, Russia, and India. ITER will be a big step in demonstrating that fusion can one day safely and cleanly meet the world’s increasing energy needs.

— Scott Willms