SPECIAL REPORT

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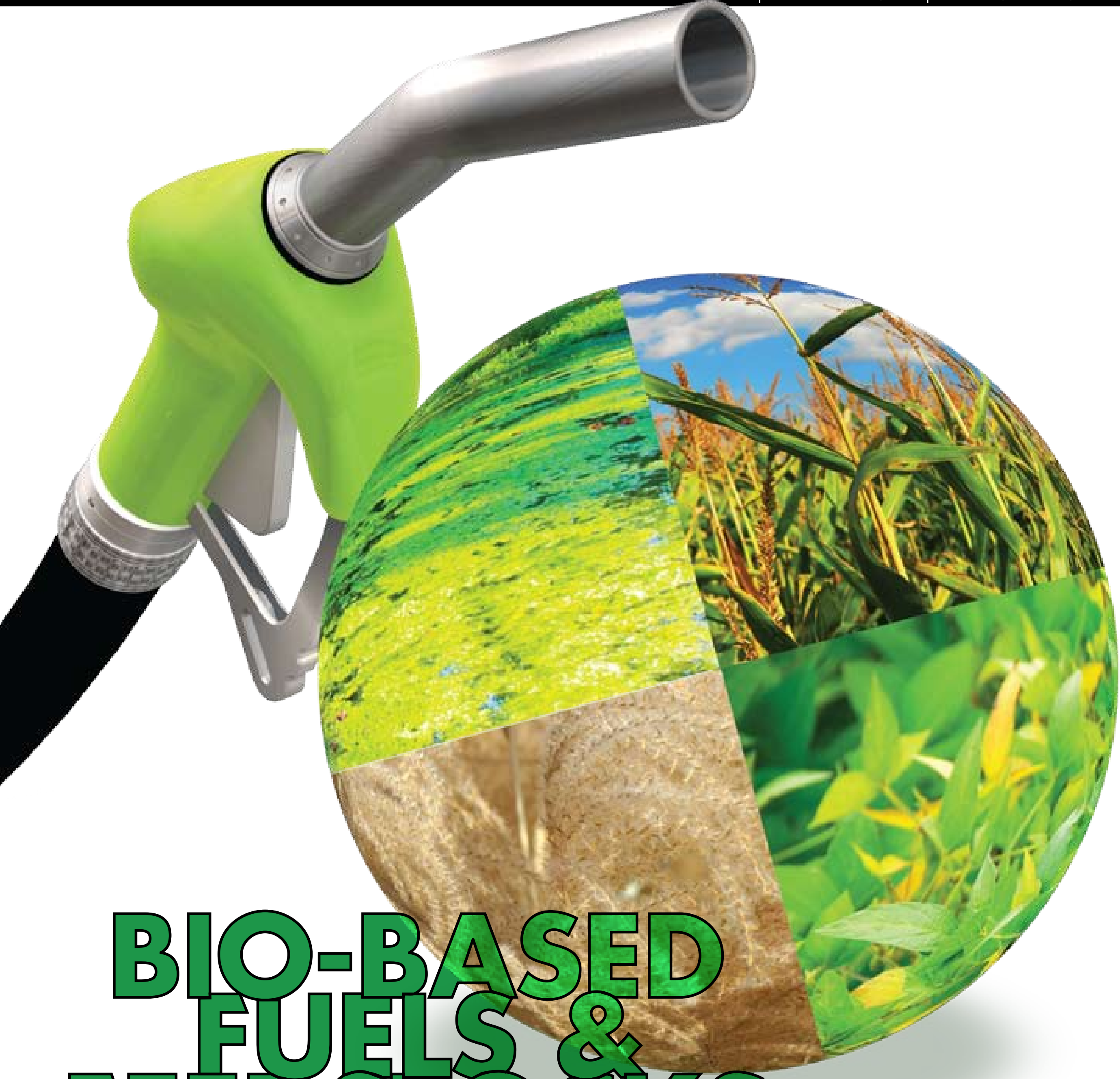

BIO-BASED FUELS & FEEDSTOCKS

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For years the industry has been "talking green." But what real strides have been made? Will a Presidential Executive Order compel the industry to speed up efforts to actually go green? While pollution prevention was the original goal of green chemistry, today's efforts promise to have a substantial economic impact. This Special Report will bring you up to speed on fruitful efforts to "go green" including an update on the growing interest in bio-based feedstocks.

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CHEMICAL INDUSTRY SEES GREEN

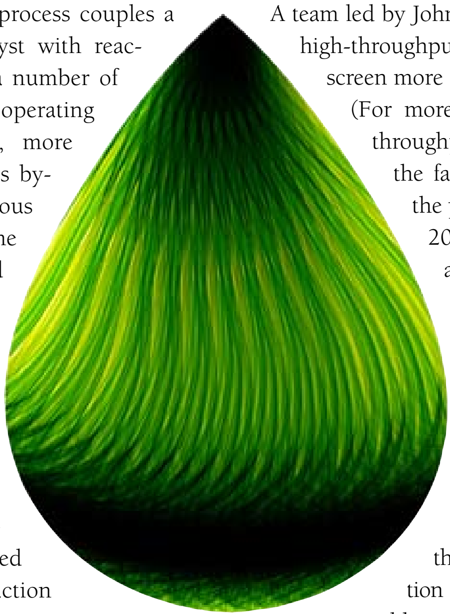
"We have made tremendous strides over the past decade-and-a-half in reversing the psychology of industry and government on the matter of pollution prevention," says Paul Anastas, "and yet we have barely scratched the surface of what the promise of green chemistry holds." Indeed, beneath that surface may lie the future for whole swathes of the chemical industry, as the drive to "go green" grows more persuasive and pervasive.

As director of the Green Chemistry Institute of the American Chemical Society, Washington, D.C., and former assistant director for the environment in the White House Office of Science and Technology Policy, Anastas has been one of the champions of green technology and was one of the prime movers behind the 1997 establishment of the U.S. Environmental Protection Agency's Presidential Green Chemistry Challenge Awards. Moving on this month to head up the new Center for Green Chemistry and Green Engineering at Yale University, New Haven, Conn., he has defined green chemistry as "the design of new products and processes that reduce or eliminate the use and generation of hazardous substances … we're really talking about the chemistry of sustainability."

But if pollution prevention was the original goal of green chemistry, the efforts of Anastas and researchers like him have seen the philosophy develop into one that promises as much economic as environmental benefit. The 2006 Presidential Award winners, for example, include Galen Suppes, professor of chemical engineering at the University of Missouri - Columbia, whose catalytic process for converting glycerol (glycerin) into propylene glycol could change the economics of the burgeoning biodiesel industry.

Byproduct upgrade

Biodiesel economics strongly depend on the market for glycerol, biodiesel's byproduct from the transesterification of vegetable oils. The U.S. biodiesel industry is expected to introduce 1 billion pounds of additional glycerol into a market that currently only has an annual demand for 600 million pounds. So, the industry clearly needs to find a high-value use for its glycerol. Propylene glycol (PG), a less toxic alternative to ethylene glycol for antifreeze and many other uses, could be the answer. Producing it from glycerol, says Suppes, can reduce the cost of biodiesel manufacture by as much as $0.40/gal.



Suppes' award-winning process couples a new copper-chromite catalyst with reactive distillation and offers a number of advantages, such as lower operating temperature and pressure, more efficient conversion and less by-product, compared to previous conversion routes. The same technology also can be used to convert glycerol to acetol or hydroxyacetone, an intermediate and monomer used in the production of polyols. When made from petroleum, acetol costs around $5/lb, which limits its widespread use. However, using biomass-sourced glycerol could cut production cost to as little as $0.50/lb, opening up more markets for glycerol and so benefiting biodiesel production.

Other researchers also are investigating ways of catalytically upgrading glycerol to PG. Under the auspices of the Office of Energy Efficiency and Renewable Energy of the U.S. Department of Energy (DOE), Washington, D.C., researchers at Michigan State University, East Lansing, Mich., and the Pacific Northwest National Laboratory (PNNL), Richland, Wash., are collaborating with Archer Daniels Midland, Decatur, Ill., and UOP, Des Plaines, Ill., on the development of catalysts for an integrated process.

A team led by John Holladay at PNNL has used high-throughput combinatorial techniques to screen more than 4,000 possible catalysts. (For more on developments in high-throughput methods, see R&D takes the fast track.) The next stages in the program, which runs through 2008, involve reaction evaluation and pilot scale testing and finally a conceptual design for a commercial unit.

Meanwhile, food and agricultural giant Cargill, Minneapolis, Minn., is forming a new company to make PG from renewable feedstocks using a proprietary process that is said to increase production efficiency by providing better yields and fewer byproducts than other renewable and non-renewable routes. "Cargill already sells glycerin from its biodiesel plants and has ready access through its supply chain and other sources to produce enough glycerin for world-scale production of PG," says Jim Stoppert, Cargill's senior director of industrial bioproducts. "We are confident that our approach to manufacturing price-competitive, renewable PG on a large commercial scale will be highly desired by the chemical industry." Initial indications are that the product won't require reformulation prior to downstream use. Cargill expects "market rollout to occur quickly."

"Top 12" building blocks

The DOE considers the following chemicals, which can be produced from sugars via biological or chemical conversion, particularly promising for making high-value bio-based chemicals or materials:

- **four carbon 1,4 di-acids (succinic, fumaric, and malic)**
- **2,5 furan dicarboxylic acid**
- **3-hydroxy propionic acid**
- **aspartic acid**
- **glucaric acid**
- **glutamic acid**
- **itaconic acid**
- **levulinic acid**
- **3-hydroxy-butyrolactone**
- **glycerol**
- **sorbitol**
- **xylitol and arabinitol**

Source: "Top Value Added Chemicals from Biomass, Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas," U.S. Department of Energy Biomass Program (2004).

Bioethanol boom

Despite the boost that such developments might give to the biodiesel industry, the biggest impact of green fuel technology will almost certainly come from bioethanol as a gasoline replacement. Current U.S. production totals around 4 billion gal/yr, mostly from corn, but there is rapidly growing interest in developing biorefineries able to process a range of feedstocks including non-foodstuff renewable biomass materials.

With biotechnology processes currently available that use enzymes to convert biomass to fermentable sugars, the U.S. could produce more than 70 billion gallons of cellulosic ethanol (as opposed to the conventional grain-derived bioethanols) per year from crop residues such as corn stover and stalks, sugar cane bagasse, wheat straw and rice straw, according to the Biotechnology Industry Organization, Washington, D.C. Jim Greenwood, the organization's president and CEO, says 25% of the nation's transportation fuel could be supplied from biorefineries by 2015 if development were dramatically ramped up.

It's still very much a fledging industry but the first seeds have already taken root around the world. A demonstration plant in Ottawa, Ont., started up in 2004 by Iogen of Ottawa, provided the first pre-commercial-scale output of cellulosic ethanol. Designed to produce up to 3 million liters/yr, the plant can handle up to 40 metric tons/d of raw material feedstock such as wheat, oat and barley straw, enzymatically converting the cellulose fiber into glucose for fermentation to ethanol.

The first true commercial-scale plant, however, was scheduled for start-up in December in Babilfuente, Spain, at the BCyl cereal ethanol plant of Abengoa Bioenergy, Seville, Spain, and St Louis, Mo. The ethanol-from-biomass plant, which has a 5-million-liter/yr capacity from a feed of 70 metric tons/d of agricultural residue, has been constructed alongside a far larger (195-million-liter/yr) cereal ethanol plant to benefit from its infrastructure. Abengoa, the world's second largest bioethanol producer, is utilizing some of the latest technologies in the new plant, including a continuous biomass pretreatment system from SunOpta, Toronto, Ont., and new enzymes from Novozymes A/S, Bagsvaerd, Denmark, and Franklinton, N.C., developed in conjunction with the DOE's National Renewable Energy Laboratory, Golden, Colo.

Researcher Liz Hill withdraws a sample from a high-pressure reactor being used for making specialty chemicals from ethanol feedstocks.

In June 2006, both SunOpta and Novozymes signed a contract with China Resource Alcohol Corp. (CRAC) for a cellulosic-ethanol demonstration plant in ZhaoDong City, China. CRAC's goal is to install 1.7-million-gal/yr capacity by the end of this year and 330 million gal/yr by 2012.

Another major cellulosic-ethanol project in the works is a 30-million-liter/yr unit in Orange County, Calif., that will use process technology from Arkenol, Irvine, Calif. The plant, being engineered by JGC Corp., Yokohama, Japan, and Houston, Texas, is due for start-up early in 2009.

Going beyond fuels

For biorefineries to fulfill their promise, however, downstream markets other than those for fuels also need attention. "It seems unlikely that fuel from a biorefinery — at least in the beginning — is going to be as cost-effective as fuel from traditional fossil sources. To make the biorefinery sustainable, we must therefore do everything we can to help the economics," says Charles Eckert, a professor in the school of chemical and biomolecular engineering at the Georgia Institute of Technology, Atlanta, Ga., and another Presidential Green Chemistry Challenge award winner.

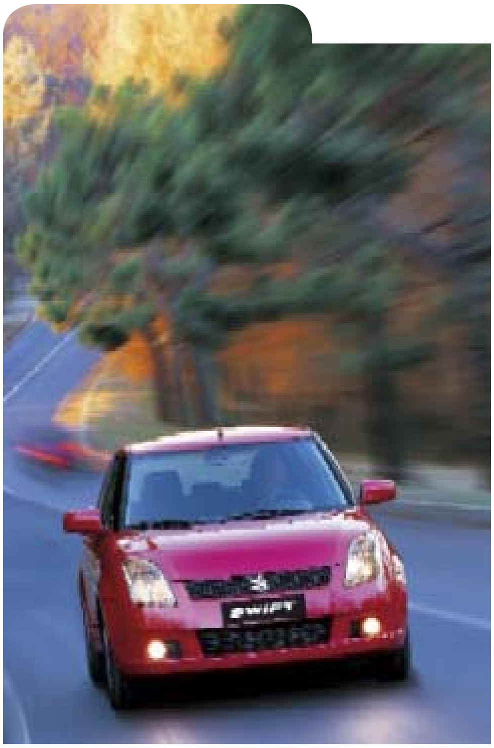
Eckert and a colleague, Charles Liotta, won the 2004 Presidential award for their development of benign tunable solvents that couple reaction and separation processes. They are now collaborating with other researchers on the potential for producing high-value (up to $25/lb) specialty chemicals, pharmaceutical precursors and flavorings as "side stream" chemicals from the ethanol process.

"These are novel feedstocks for chemical production," Eckert notes. "They are very different from what we've dealt with before. This gives us different challenges and provides a rich area for interdisciplinary research." Working as part of a research alliance with Oak Ridge National Laboratory, Oak Ridge, Tenn., and Imperial College, London, U.K., the team is exploring solvent techniques such as the use of near-critical water (pressurized water at 250°C to 300°C), gas-expanded liquids (such as CO_2 in methanol) and supercritical fluids (CO_2 under high pressure).

Meanwhile at the reaction level, Isis Innovation, Oxford, U.K., a company that promotes commercialization of developments at Oxford University, has licensed its Cytochrome P-450 designer enzyme technology to Industrial Biotechnology Corp. (IBC), Sarasota, Fla. Developed at the university by chemistry professor Luet Wong, the P-450 technology applies specific enzymes as biocatalysts for the conversion, often in a single step, of relatively low value substrates into high value chemicals. IBC says the potential market embraces more than 15,000 commercially available chemicals, including various alcohols, aldehydes, ketones and carboxylic acids.

Plastics' progress

The production of plastics from renewable resources provides another example of how green technologies could change the face of the chemical industry. In 2006, for example, Archer Daniels Midland announced plans to build the first commercial plant to produce PHAs (polyhydroxylalkanoates), a family of biodegradable high-performance plastics that can be used in many applications currently served by petrochemical plastics — e.g., coatings, film and molded goods. Due for completion by the middle of 2008, the 50,000-ton/yr plant at Clinton, Iowa, will serve the joint venture set up between ADM and Metabolix, Cambridge, Mass., the company that developed the proprietary PHA technology and won a Presidential Award in 2004 for its work on commercializing bioplastics through the use of metabolic engineering and molecular biology.



New Xenoy iQ resins, initially aimed at automotive applications, are made using recycled PET.

Commenting on the joint venture, Jim Barber, Metabolix president and CEO, says "a broadly useful family of bio-based, biodegradable natural plastics will be commercially available for the first time." Located next to ADM's existing wet corn mill at Clinton, the PHA plant will take starch from the mill as its raw material.

Cargill subsidiary NatureWorks, Minnetonka, Minn., already offers a biodegradable plastic. Its polylactic acid (PLA) polymer is produced from corn at a 140,000-metric-ton/yr plant in Blair, Neb. PLA already has won a significant place in biodegradable packaging; Wal-Mart switched to PLA packaging for its fruit and herbs in 2005.

Not content with producing an inherently biodegradable product from a renewable feedstock, however, the NatureWorks plant has taken the application of green technology even further. Through the purchase of renewable energy certificates it has effectively replaced all the fossil-based electricity used in the plant with wind power. And, according to the company, by buying additional certificates to offset remaining greenhouse gas emissions, its PLA will be the world's first and only greenhouse-gas-neutral polymer. Strictly speaking, PLA polymers fall more within the definition of compostable rather than biodegradable materials at least in the U.S. (The difference is one of timescale and the ambient conditions required for each.) They can, however, also be recycled, which for the moment is arguably one of the few ways for petrochemical-based plastics to carry a "green" label — a case in point being the new use for recycled polyethylene terephthalate (PET) waste developed by SABIC Innovative Plastics, Pittsfield, Mass.

Plastic-waste feedstock

SABIC has developed a new route to polybutylene terephthalate (PBT) based resins and polyester-based elastomers that uses PET waste — mainly from plastic bottles — as most of its feedstock. According to Vikram Gopal, SABIC Innovative Plastics' program manager for crystalline plastics, the PET is first depolymerized and then chemically upgraded so it can be reacted with butanediol (BDO) — one of the main feedstocks in the conventional process — to produce PBT. The recycled-waste-based material supplants the other conventional feedstocks, either dimethyl terephthalate (DMT) or terephthalic acid (TPA). In all, more than 85% of PBT's usual feedstocks are replaced by this "post-consumer feedstock." The Valox iQ and Xenoy iQ resins made from the new PBT-based polymers are initially targeted at automotive applications.

SABIC says that if all the PBT produced in 2005 had been in the form of Valox iQ and Xenoy iQ, it would have consumed more than 565,000 metric tons of PET waste, the equivalent of 22.5 billion plastic bottles. While those are certainly impressive "green" credentials, the figures also help to put some perspective on the scale of the green chemical industry as it currently stands. For example, the annual global production capacity for biodegradable materials amounts to only around 300,000 metric tons, with the NatureWorks plant accounting for almost half of that, according to industry association European Bioplastics, Berlin, Germany.

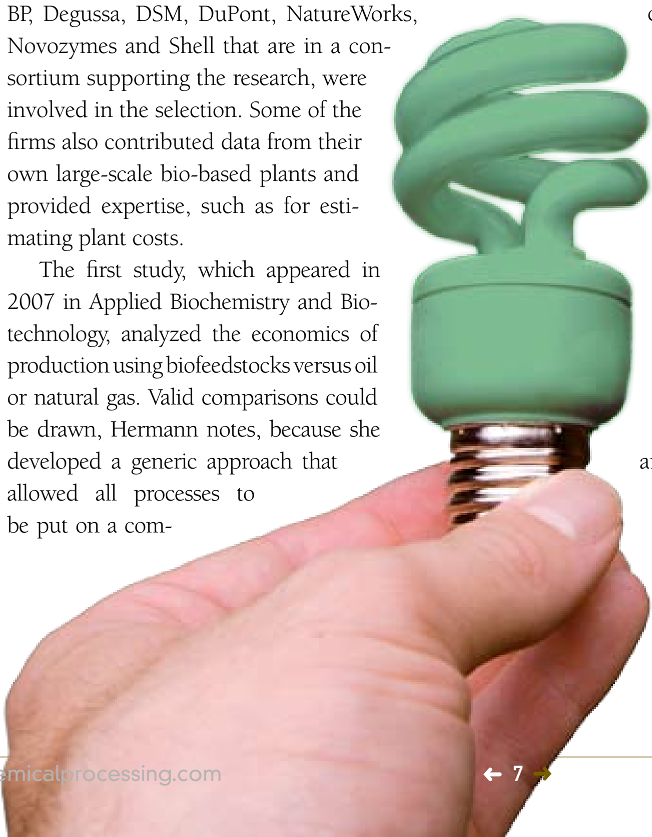
With retail giants like Wal-Mart already in the market for biodegradable packaging, this level of capacity undoubtedly only scratches the surface of the potential for this particular green chemistry.

On a wider front, the chemical industry clearly is starting to unwrap the potential benefits of "going green." ■

BIOFEEDSTOCKS BOAST BULK BENEFITS

Commercialization of renewable-resource-based routes to chemicals is gathering speed, with major players such as Dow and Dupont already actively involved (www.ChemicalProcessing.com/articles/2007/178.html). Now, studies done at Utrecht University, Utrecht, the Netherlands, indicate that biofeedstocks can play a far wider role and offer significant economic and environmental advantages for producing many bulk chemicals.

The studies focused on 15 chemicals — acetic acid, acrylic acid, adipic acid, butanol, caprolactam, ethanol, ethyl lactate (EL), ethylene, lactic acid, lysine, 1,3-propanediol (PDO), polyethylene terephthalate (PTT), polyhydroxyakanoates (PHA), polylactic acid (PLA) and succinic acid — that realistically could be produced via fermentation and that have substantial potential consumption, at least 200,000 metric tons/year in Western Europe, explains Barbara G. Hermann of the school's Department of Science, Technology and Society. An industrial panel, drawn from companies including BP, Degussa, DSM, DuPont, NatureWorks, Novozymes and Shell that are in a consortium supporting the research, were involved in the selection. Some of the firms also contributed data from their own large-scale bio-based plants and provided expertise, such as for estimating plant costs.



The first study, which appeared in 2007 in Applied Biochemistry and Biotechnology, analyzed the economics of production using biofeedstocks versus oil or natural gas. Valid comparisons could be drawn, Hermann notes, because she developed a generic approach that allowed all processes to be put on a common basis. Fermentation-based routes included both current technology and what may be possible in the future (assuming continuous fermentation and higher yields, 90 mol.% of the theoretical maximum, because of better genetically engineered micro-organisms).

The analyses, based on constructing a new 100,000-mt/y plant in Western Europe, gave a profited production cost, akin to a market price, for each chemical for each route. She evaluated its sensitivity to varying prices for sugar (70€/mt, 135€/mt, 200€/mt and 400€/mt) and crude oil ($25/bbl and $50/bbl), the nature of the sugar source (sugar cane, lignocellulosics and corn starch), as well as plant size (100,000 mt/y, as well as 200,000 mt/y and 400,000 mt/y for some of the products). The results showed that making many of the chemicals with biofeedstocks was already economically viable.

A second study focused on using a common methodology to assess the environmental impact — namely, greenhouse gas emissions and non-renewable-energy use — for the same 15 bulk chemicals over their entire life cycle. The results, recently published in Environmental Science & Technology, indicate that biofeedstocks provide significant savings compared to conventional petrochemical-based routes for most of the products — fermentation now doesn't offer benefits only for adipic acid and acetic acid but eventually should (Figure 1). Indeed, Hermann adds that future fermentation technology may reduce greenhouse gas emissions by more than 100% when energy credits are considered.

Since the studies came out, Hermann has updated the results — to consider less optimistic scenarios for the performance of future fermentation technology and to account for higher prices of both crude oil and sugar.

As far as productivity, for example, she tested future performance for ethanol using 10 g/Lh instead of 50 g/Lh (versus current actual values of about 2.2 g/Lh for starch feedstock). This impacted investment, primary energy consumption and profited product cost by less than 5%. So, the general conclusions still hold, Hermann stresses.

"We actually recently looked at updated numbers for a crude-oil price of $70/bbl for a slightly reduced number of bulk chemicals… The outlook can be summarized as 'the picture improves' — even at the highest sugar price of 400€/mt, ethanol, succinic acid, PDO/PTT, PLA and ethyl lactate are economically viable," she notes. "At 200€/mt, the list also includes acetone/butanol/ethanol and ethylene."

The Utrecht University team now has evaluated economic viability, market size and environmental improvement together. "The results show that ethylene is best, followed by PHA, PLA and PTT (the latter three are on the same level). Market size is an important factor here, as the market for ethylene is very large, whereas the market may be much smaller for other chemicals."

Prospects for biofeedstock-based bulk chemicals are favorable but Hermann raises a caution: "We have seen a coupling of sugar and oil prices, with both prices increasing significantly in the past year." Several factors have contributed to this, including recent crop failures, economic growth in China and India, and competition with biofuels, she explains. "There are ambitious policy goals [for biofuels], whereas policies for biochemicals are still missing… policy action by governments can lead to improvements for biochemicals," she stresses.

Isobutanol beckons as biofuel

Genetically modified bacteria promise to provide a low-cost way to produce isobutanol from sugar — opening up the prospect of the alcohol displacing ethanol as a biofuel, say developers at the University of California, Los Angeles. The bio-based route should halve the cost of making isobutanol, believes Pat Gruber, CEO of Gevo, Inc., Pasadena, Calif., which holds the exclusive license for the technology from UCLA.

Isobutanol boasts a higher energy density and octane number than ethanol as well as lower hygroscopicity, notes James C. Liao, professor of chemical and biomolecular engineering at the school. However, bacteria ordinarily won't synthesize higher alcohols like isobutanol. Liao and his team overcame this through genetic modification of E. coli — shunting intermediates from amino-acid biosynthesis pathways to alcohol production. This results in conversion of glucose with high specificity and at high yield to isobutanol.

A reactor is seeded with the modified E. coli and glucose. Reaction over the next 40+ hours converts all the sugar into isobutanol and carbon dioxide, he notes. Yields, now 0.35 g of alcohol/g of sugar, already approach 90% of theoretical, without optimization of the bacteria and the process, says Liao.

Gevo now is working on the optimizations. A 1,500–2,000 L/batch pilot plant should be operating within six months, says Gruber, adding that the process should be ready for commercialization by the end of 2009 or early 2010.

The first installation likely will be a retrofit of a North American ethanol plant, he says. This involves using the new bacteria and adding a skid for product separation. Conversion of a 100-million-gal/yr plant should run about $20 million, Gruber reckons.

Gevo also plans to offer another skid that will convert the isobutanol to materials comparable in makeup to conventional jet fuel and biodiesel. This will make economic sense at a crude oil price of $75/bbl, he says.

Meanwhile, Liao is developing modified bacteria that would work on cellulose instead of glucose, and hopes to finish constructing the strains this year. ■

CATALYSTS STREAMLINE BIODIESEL PROCESS

Researchers at Oak Ridge National Laboratory, Oak Ridge, Tenn., have developed a series of solid acid nanocatalysts that promise to avoid some post-reaction steps in the production of biodiesel. The catalytic transesterification of vegetable oils or animal fats is central to the production of biodiesel, which is attracting increasing interest.

Conventional processes yield a biodiesel that contains some catalyst, which could corrode engines. Removal of the catalyst adds several steps such as neutralization and washing to the production process, consumes chemicals, water and energy, and invariably leads to some loss of biodiesel.

The new sulfonated mesoporous carbon-based heterogeneous catalysts can be fixed inside a column, retained and reused, notes Oak Ridge's Chengdu Liang. They boast pore sizes of five to 10 nanometers to provide improved catalytic performance, and an average surface area of 400 m2/g, which is about 20 times higher than that of other heterogeneous catalysts, he adds. ■

http://www.chemicalprocessing.com/industrynews/2007/018.html

FEEDSTOCK CHANGE IS HOT AND POPPING

A year that raised the public's awareness of oil price trends, global warming, and other environmental sustainability issues also may prove to have been a turning point for the chemical industry. In 2005, the outlines of a substantially different industry, shifting gradually from petroleum-based feedstocks to renewable resources, gained clarity amid talk of a new generation of biorefineries and other initiatives involving new products, processes and partnerships.

Some of the news was about progress that already has been made by companies and consortia which, often with help from U.S. government grants, are exploring new pathways from plants, crop oils, and biomass waste to basic building blocks, chemical intermediates and fuels. Much of the buzz came from executives' ambitious projections about the potential technological leaps, although there were also reminders that economic hurdles could slow change.

Growing momentum

DuPont, Wilmington, Del., was a leader in [2005's] consciousness-raising. In a November briefing, Thomas M. Connelly, chief science and technology officer, pledged a 30% acceleration in science-based innovation, and cited bio-based materials as "the right science at the right time." Components of DuPont's bio-based materials pipeline have an estimated net present value exceeding $3 billion, he said.

The company has a joint venture with Tate & Lyle to build a $100-million plant at Loudon, Tenn., that will use corn to produce 1,3 propanediol (PDO) (see CP, October, p. 11). This building block, which DuPont has trademarked Bio-PDO, is a key ingredient in its Sorona polymer. The plant is expected to start up in mid-2006. DuPont also said in November that it would invest $55 million to expand its Sorona plant at Lenoir County, N.C.

A 100-million-lb/yr-capacity 1,3 propanediol plant in Loudon, Tenn.

Sorona is now made from petroleum-based PDO. The company estimates that production of Bio-PDO from corn will consume 30% to 40% less energy. “The corn fields of today will be the oilfields of the future,” said Tate & Lyle chief executive Iain Ferguson.

DuPont’s growing interest in bio-based feedstocks was also accentuated by the announcement of progress in another of its partnerships — a consortium behind a $38-million project to develop an integrated biorefinery that will convert corn and other biomass into sugars for production of fuel ethanol as well as Bio-PDO and other chemicals. The consortium, which includes Diversa, Deere & Co., the National Renewable Energy Laboratory, and Michigan State University, backed by U.S. Department of Energy (DOE) funding, aims to demonstrate the feasibility of a biorefinery by the end of 2007.

Diversa, San Diego, Calif., announced in July that it had delivered a set of candidate enzymes that exceed DOE’s initial performance targets. Diversa says these enzymatic “cocktails” can break down a variety of crude plant materials — potentially including switchgrass, wood and corn stover as well as corn — into sugars ready for fermentation.

The biorefinery

“I like to think of this as very similar to an oil refinery, taking a very crude material, breaking it down into its smallest components and then making multiple business products out of it,” says Patrick McCroskey, Diversa’s vice president of business development.

Many facilities are already described as biorefineries, but this “integrated biorefinery” is different because it represents integration on so many different levels, McCroskey says. It requires the combination of biological, chemical and other expertise. It envisions multiple inflows of feedstocks and multiple outputs of fuels and other products. It recognizes the need to match modified cocktails of high-performing enzymes with different feedstocks and fermentation suited to different products. Perhaps most importantly, it recognizes the need to combine technologies in a way that meets business imperatives.

Conversion of lignocellulosic biomass into its component sugars is already technically feasible, says Mark Burk, Diversa’s senior vice president of chemical and industrial R&D. But the cost of conversion is too high, especially when one of the outputs is relatively low-cost ethanol. “It’s going to take a step change in the activity of the enzymes in order to get to where we need to be for economic viability.”

For Diversa, which also has biotech collaborations with other chemical companies including Syngenta, DSM, Cargill, and BASF, bio-based products have become a focus area, says McCroskey. But the speed with which the DuPont consortium has progressed should not imply that the path ahead is easy, he cautions, adding that government funding — which has averaged $100 million to $300 million annually for bio-based research in recent years — will still be necessary perhaps for a decade.

Chemical companies will face their own challenges, including the “dramatically different” processing that may be needed when a fermentation paradigm replaces a continuous production paradigm, McCroskey says. One key to success will be continued smart partnering between chemical companies and enzyme makers, so that the right, cost-effective technologies are developed in tandem. He is optimistic about the success of the DuPont-led consortium: "We may not be the first biorefinery, but we'll be the first one that can make money."

Other drivers

The profit motive, coupled with the desire to reduce reliance on oil with its growing price and supply uncertainties, is certainly important to the future of bio-based chemistry, but it's not the only driver. Companies also are attracted to the trio of economic, social, and environmental benefits.

BIO, the Biotechnolgy Industry Organization, Washington, D.C., notes that the benefits could include: new consumer products; new markets for the agricultural sector; the possibility of smaller, regional processing facilities around the country and around the world; energy savings; and reduced carbon dioxide emissions. A wide array of companies apparently find this combination appealing. "We've had quite a few new members lately" from the chemical sector, says Brent Erickson, vice president for BIO's industrial and environmental section.

Carbon dioxide reductions will be especially attractive if woody biomass becomes an important feedstock, notes David Shonnard, a chemical engineering professor at Michigan Technical University, Houghton, Mich., and co-author of the book "Green Engineering: Environmentally Conscious Design of Chemical Processes." Today's reliance on fossil fuels, he says, acts "like a giant carbon pump working on a global scale," bringing carbon from beneath the ground and sending it into the air, but the multiplication of plants and trees as feedstocks would "close the loop on carbon," because such processes embrace the power of photosynthesis to remove carbon dioxide from the air while sending less of it back.

But Shonnard acknowledges several challenges that must be overcome. Wood is naturally resistant to degradation, so the enzymes and microorganisms needed to break it down are of a different order than those for corn kernels or some other renewable resources. The Natural Resources Defense Council, New York, in a 2004 report noted that "large scale penetration of cellulosic biofuels will require growing millions of acres of dedicated energy crops," so early adoption of bio-based materials will rely more on agricultural and forest residues.

Shonnard also cites the chemical industry's existing infrastructure as a possible obstacle to progress, partly because "the processes for converting these bio-based raw materials into products are different from the processes for converting fossil fuel materials into products." Economic judgments justifying the changeover are complicated by the fact that environmental costs being paid by society under today's fossil fuel regime are not well captured in the calculations watched by investors, he adds.

Different directions

Dow Chemical, Midland, Mich., took several steps assessing the costs and benefits of bio-based materials in 2005. It sold its stake in the Cargill Dow joint venture that produces polylactic acid (PLA) at Blair, Neb., from lactic acid derived from corn. But the company plans to retain bioprocessing in its toolbox, noting it "continues to make significant progress in its development of natural-oil-based polyols that can be used in lieu of a significant percentage of hydrocarbon-based polyols in urethane formulations." Dow, which began research on such bio-based polyols in 2001, says it started product sampling with select manufacturers of flexible urethane slab in the U.S. and Europe in autumn 2005 and plans to continue the effort at least through this year.

The process for the "new family of vegetable-oil-based polyol products" developed and patented by Dow involves the disassembly of soybean or other natural oil feedstocks using a selective modification of the resultant fatty acids and the reassembly of the molecules into the desired product. "This process offers a number of advantages to both the manufacturer and the end-user," Dow said in a statement to *Chemical Processing*. The ability to precisely tailor the degree of conversion of soy esters "allows for on-the-spot adjustment in the production of the bio-based polyols to compensate for the variation in the feedstocks." The process also produces primary hydroxyl groups, yielding fast-reacting polyols that significantly enhance polyurethane foam's processibility. Moreover, Dow says, a foam manufacturer can eliminate additional processing steps ordinarily needed to remove olefins — because the new process involves the complete hydrogenation of residual olefins, which helps to remove at their source odor-forming chemistries, which are common in natural-based polyols.

This development of natural oil polyols "is consistent with Dow's effort to explore options to hydrocarbon-based feedstock challenges and opportunities, as well as supporting a sustainable environment," Dow said in its statement.

Other initiatives include a production agreement announced early last year between Dow Haltermann Custom Processing and World Energy, Chelsea, Mass., a leading producer of biodiesel fuel.

Meanwhile, Cargill, Minneapolis, Minn., which has a number of active and planned investments and joint ventures for biodiesel and ethanol production in both the U.S. and Europe, has expressed wide-ranging interest in developing bio-based materials for the chemical industry. The company bought the Dow stake in their joint venture for PLA, which it calls the world's first greenhouse-gas-neutral polymer made from corn. The PLA business, renamed NatureWorks in early 2005, now is focusing on the packaging market and has captured big customers like Wal-Mart, which currently uses NatureWorks PLA in some of its food packaging. Sales last year were projected to be more than 170% ahead of the 2004 level, a spokeswoman said.

Cargill says it made its first commercial sales of bio-based urethane polyols in the summer of 2005. The company also announced earlier last year that it had expanded a development agreement to use the proprietary olefin metathesis technology of catalysts company Materia, Pasadena, Calif. The aim is to convert bio-based oils to industrial chemicals, feedstocks and consumer products. Cargill sums up its bio-based enthusiasm with the estimate that "more than two thirds of the $1.5 trillion global industrial chemicals and plastics business could potentially be served by renewable materials."

Biodiesel beckons

Another major player in agricultural feedstocks, Archer Daniels Midland, Decatur, Ill., announced plans in October to build its first wholly owned biodiesel production facility in the U.S. The 50-million-gallon plant at Velva, N.D., will use canola oil as its primary input. ADM, already active in the biodiesel market in Europe and a leader in U.S. ethanol production, also revealed in September that it plans to expand ethanol capacity by 500 million gallons.

Ethanol and biodiesel fuel might be among the products from a next generation of biorefineries, but much of the chemical industry's — and DOE's — interest is focused on other potential biorefinery products, and how these would become building blocks for plastics or a variety of value-added platforms. ADM, for its part, announced in November a plan to build a polyols facility that will use renewable carbohydrate- or glycerol-based feedstocks. The plant, whose location has not yet been disclosed, will produce propylene glycol and ethylene glycol. The company also is in a strategic alliance with Metabolix, Cambridge, Mass., to commercialize a new generation of high-performance plastics based on renewable resources.

Key criteria

The economic justification for plants based on bio-based feedstocks first and foremost depends upon what the materials bring to the value-added products. Discerning the right mix of operations to achieve profitability at different sites "is both the promise and the danger of designing these plants," says Chuck McCleskey, Atlanta, Ga.-based leader of the bioprocessing strategic initiative at engineering and construction firm CH2M Hill Lockwood Greene. The configuration must be based on a degree of certainty about what the plant will produce, how many products it will make, and in what volumes, and it must allow for flexibility, he says.

Plant location is also an important factor; proximity to feedstocks might offer sufficient logistical savings to justify construction of a new plant, but at other times the retrofitting of an existing plant might make more sense. Despite these uncertainties, the bio-based sector is "growing every day and gaining momentum," McCleskey says. "A lot more of these projects are moving forward now," he stresses.

"We're looking for opportunities to use bio-based materials where the advantage is either performance or cost competitiveness," says Tom Kauffman, technical manager of adhesives and sealants at Rohm and Haas, Spring House, Pa. The company is in a partnership with Eastman Chemical, Kingsport, Tenn., and Virginia Tech, Blacksburg, Va., backed by a grant from DOE and the U.S. Department of Agriculture.

Rohm and Haas has met an aggressive timetable to develop prototypes of adhesive components that meet performance requirements, says technology partnerships leader Katie Hunt. Thus it is starting to supply some of the answers to crucial questions such as: What building blocks would chemical companies want to use? Which of the competitive

routes to those building blocks would be most economical? What would be the optimal team of organizations to work on the bio-based pathways of the future? It's crucial for research to proceed simultaneously at both ends of the pipeline before new biorefineries are built, she says. After all, Hunt cautions: "You could make all these building blocks, but what if nobody uses them?"

The company's monomers group is involved with Engelhard, Iselin, N.J., and the University of Delaware, Newark, Del., in another DOE effort to develop new sustainable catalyst chemistries, seeking "a template for going from alkanes to higher products," Hunt says. A separate DOE effort has allied the company with ADM and the University of Minnesota, Twin Cities, to pursue sustainable coatings chemistries, using bio-based materials in a new process to generate binders for paints. She calls this initiative, which has been trimmed back because of government budget cuts, an example of the need for continued government support in risky endeavors that have long time horizons. Such funding could have big payoffs because new processing pathways could save "trillions of BTUs" of energy, use less raw materials, and capture maximum performance from building-block chemicals.

Process challenges

In general, companies hope to be able to shift from

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petroleum-based to bio-based feedstocks with the same manufacturing infrastructure, says Kauffman, but some new pathways may have important differences. "Certain building blocks are inherently more variable" than their petroleum-based predecessors and may be more limited in their utility or reliability, or may require more purification or additional processing steps, even if they have otherwise desirable characteristics, he notes.

The work already done by Rohm and Haas has found "very promising" signs that the pathways developed for adhesives could be applicable to other product platforms, hugely multiplying the volume of chemicals that might become bio-based, says Kauffman. Hunt adds that the possibilities are "compelling."

Research in all these areas must continue, and has gotten "a good kick" from the 2005 spike in oil prices, says Hunt, although companies like Rohm and Haas were looking at bio-based chemistry before that.

Among the companies that have been working on pieces of the complex puzzle, with assistance from DOE funds, are enzyme companies Genencor International, Palo Alto, Calif., and Novozymes, Bagsvaerd, Denmark. They both reported last year significant reductions in the cost of cellulase enzymes for converting biomass to ethanol, acknowledging that this is just one step toward their increased involvement in biorefining. Genencor announced in 2005 a new enzyme technology that increases energy efficiency and reduces processing steps in ethanol production. Novozymes recently launched three new enzymes that make the production of ethanol from wheat, rye, and barley up to 20% more efficient.

The DOE, for its part, in 2004 issued a "top 12" list of high-potential, value-added building blocks that might be produced from biomass-derived sugars (see sidebar). Among these are four-carbon di-acids such as succinic acid.

DSM, Heerlen, the Netherlands, formed in late 2003 a partnership with Diversified Natural Products (DNP) of East Lansing, Mich., for commercializing succinic-acid-based products derived through fermentation. DNP announced last August a joint venture with Agro-Industrie Recherches et Developpements, Pomacle, France, to produce succinic acid from corn. Also last summer, AgRenew Inc., Manhattan, Kan., began testing the use of grain sorghum as food for bacteria that make succinate, which is a key ingredient in drugs, food additives, solvents and plastics.

BASF, Ludwigshafen, Germany, says its long-range strategy for sustainable development includes "eco-efficiency analysis" of its products, which includes assessing alternative production processes by their consumption of raw materials and energy and generation of emissions.

Other companies, universities, and research institutions have made various announcements about initiatives in bio-based materials. All told, the news of the past year not only suggests a critical mass of interest, funding, and projects, but also powerfully illustrates the depth and breadth of expertise that must come together, from all sorts of organizations, for continuing progress.

The arena of these initiatives is nothing less than a "new frontier," says Kauffman of Rohm and Haas. "Chemical processing, biotransformation, and enzymatic transformation are all converging to give us a new future chemistry." ■

World Energy and Siemens Help Fuel America's Quest to Lessen its Dependency on Petroleum

In 2006, the U.S. will spend more than $500 billion on the 21 million barrels of petroleum that it consumes each day. Approximately $300 billion will be spent to procure crude from outside the U.S. with the cost per barrel of the crude having essentially tripled over the last five years. This cost-per-barrel figure represents the OPEC prices and does not even begin to figure in the cost of refining, distribution, taxes, and environmental impact. The price of petroleum oil dependency has become staggering.

Americans have experienced huge price swings at the gas station as evidence of the financial impact of this dependency, where the cost of gasoline has gone from an average price of $1.85 per gallon nationwide in July of 2004 to an average of $3.10 per gallon in July of 2006. It has become increasingly urgent for America to find practical alternatives to its dependency on fossil-based fuels. As a result, a long list of alternative energy sources is being researched and tried.

One of the most promising alternative fuels, "biodiesel," has already begun to decrease America's dependency on fossil-based fuels. Manufactured from oils derived from plant and animal feedstocks such as soybean oil and animal fat that are extremely abundant in the U.S., biodiesel is an extremely clean burning and efficient fuel. Even recycled cooking oils and "yellow" grease feedstocks can be used to produce biodiesel.

At the forefront of this rapidly emerging industry, is a company called World Energy Alternatives, which has a Biodiesel production facility located in Lakeland, Florida. The bulk of the hardware and software for the overall process control at the Lakeland biodiesel facility is provided by Siemens Energy & Automation, Inc. Continually working to improve its process, the Lakeland facility recently migrated to Siemens PCS7 OS/APACS human machine interface (HMI) from a legacy Mycroadvantage and Process-

Suite HMI solution that was originally installed by Moore Process Automation Solutions. Siemens purchased Moore in early 2000 and added the APACS technology to its total process automation portfolio.

The Biodiesel Process

World Energy's Production Facility, like may others in the biofuel industry, produce biodiesel through the transesterification of vegetable oils or animal fats used as the feedstock. These oils and fats are composed of molecules called triglyceride, which contain fatty acids connected to a chemical backbone known as glycerol. Transesterification is the process of separating the fatty acids from the glycerol into the commercial products of biodiesel and glycerin.

The fatty acids are broken down into a monoester by the process; and thus become the biodiesel that is suitable for combustion in a diesel engine. The separated bottoms, which contain glycerine, fatty acid, soaps, and excess methanol, can be further processed into a high-grade refined glycerin product. At the Lakeland complex, there are actually two facilities—one for producing the high-quality biodiesel fuel and the other for further producing the high-grade refined glycerin. The Siemens process control system controls the processes at both of these facilities, and as such are interconnected. World Energy's is one of the few facilities in the U.S. that has its own glycerin refinery; and in addition to refining its own by-product, it also refines crude glycerin on a contract basis from outside companies.

Biodiesel feedstock is classified according to its free fatty acid (FFA) content as follows:

- Refined oils, such as soybean or refined canola oil (FFA<1.5%)
- Low free fatty acid yellow greases and animal fats (FFA<4%)
- High free fatty acid greases and animal fats (FFA <20%)

World Energy's facility has the capability to produce biodiesel from any of these types of feedstocks. Feedstock with the lowest FFA, below 1.5%, is the most ideal for producing biodiesel because it does require pre-processing, which involves higher than atmospheric pressures (approaching 250 psi), at least a 98% strength sulfuric acid, and high temperatures to convert the fatty acids into methyl esters prior to conventional transesterification. Additionally, pre-processing requires strict safety precautions, higher costs for processing, and creates a corrosive atmosphere that can damage or certainly shorten the life of hardware and machinery in a facility.

World Energy's biodiesel facility has both acid-base, two-stage esterification capabilities for handling the higher FFA feedstock, as well as the preferred base catalyzed transesterification process

configuration for the low FFA content refined oils. The bulk of its current biodiesel output is from refined oil feedstock (e.g. RBD soybean oil). All things considered (time, labor, reactive chemicals and feedstock), almost 80% of the total cost of production is in the cost of the feedstock selected. Having multiple feedstock capability gives the facility the flexibility to produce its products at the lowest possible cost while still meeting the strict standards of the industry (ASTMD6751: Standard Specification for Biodiesel Fuel).

Process Control

The process batch recipes at World Energy's facility for any feedstock-to-biodiesel conversion involve precise automated valve timing, temperature and pressure regulation, and level and flow control. Batch and recipe logic is configured and stored directly in the APACS controllers. The process at the Lakeland facility has been described as a "batch continuous" operation because as one batch is moved forward in the process, another batch is put in place behind it continuously throughout the production day. All pre- and post-batch processing takes place in a continuous fashion. The facility manufactures approximately 18-million gallons per year of biodiesel fuel using this hybrid process.

The pump and agitator motors are controlled by Variable Frequency Drives (VFDs) that receive commands from the Siemens APACS Advanced Controller Modules (ACM's) and the associated rack-mounted IO modules of the system. The World Energy facility utilizes controller redundancy so that if one ACM goes down, another can replace the same functionality without interruption of the process. Configuration of the ACM's is handled through the APACS 4-mation software.

The HMI Upgrade Project of 2005

The original process control system used the ProcessSuite Vision HMI (human machine interface) for the interactive graphic screens of the biodiesel side of the operation, which was implemented on a Windows NT platform, while the screens on the glycerin side of the operation were developed using Mycroadvantage, an earlier HMI of Moore.

When the computer having the ProcessSuite screen graphics went down last year, all of the interface graphics for the biodiesel operation were lost. Fortunately, this only resulted in a short outage while some screens that were formerly developed for the biodiesel process using Mycroadvantage were retrieved elsewhere and used temporarily to get things running again. In the meantime, Siemens proposed upgrading to the PCS 7/APACS OS HMI, which runs on the Windows XP operating system. The proposal also included the conversion of all the existing HMI screens over to Siemens PCS 7 OS.

Siemens engineers developed six replacement screens for the biodiesel process and two for the glycerin refining process offsite, working closely with input from World Energy. The controller configuration code from the original HMI

station, which are stored in the controller and backed up by battery, provided the starting point for the World Energy/Siemens team to upgrade the system. New graphics were created to minimize change on the operators while incorporating the powerful new features of PCS 7 OS, such as zoom and pan capability, HMI alarming, built-in historian, and tool tips. The Database Automation Tool performed dynamic linking of the HMI symbols to the control strategy automatically enabling the new graphics to be created in a shorter period than the originals.

The open architecture of the Siemens PCS 7 platform made the commissioning an easy task. The working team relationship between Siemens and World Energy resulted in a smooth transition, taking just a little more than three months from a signed order to being fully commissioned.

"The migration was nearly seamless," said Lucas Altic, Engineering Project Manager and in-house controls specialist, for World Energy. "It took one weekend to completely install and troubleshoot the new system. Siemens developed most of the initial graphics and converted the 4-mation code in-house before performing the tie-in on-site. Migrating to PCS 7 required little more than a few code tweaks, which improved the system performance."

"When I went back to modify a few of the graphics to fit the Lakeland facility's specific operational needs, I found the graphics building process simple and intuitive," said Altic. "It is a far cry from the limited functionality of older products. DBA seamlessly and automatically adds controller faceplates to the screens and links them back to the appropriate tags with almost shameful ease."

The new architecture includes an engineering workstation as well as a single workstation for additional integrations. The engineering station operates as a client and contains the APACS 4-mation toolset allowing World Energy to update, troubleshoot and maintain the APACS hardware configuration from the same station that is used to view the process. The single station includes a 512-tag SQL historian for the archiving of process variables, alarms and events.

The Future of Biodiesel

While the role biodiesel will play in supplying the world's future energy needs is unknown, demand is growing every year. With the changing economics relative to fossil fuels, it is becoming increasingly attractive for a wider range of uses. Additionally, it burns cleaner than gasoline or regular diesel and can be used in diesel engines without any modifications. In just six years, biodiesel usage in the U.S. has grown from 500,000 gallons to more than 25-million gallons in 2005.

As demand for biodiesel continues to grow, each new advancement means the ability to produce more gallons out of the same facility. Additionally, with each new piece of equipment, the process becomes more effective and more economical.

"To implement a new change with the older systems, it meant hours spent in development and, shutting down the facility for days" said Altic. "With the new PCS 7 architecture, engineering time is minimal. If a new system goes in, it takes less than an hour to code the controllers and link them to the HMI. That directly translates into greater productivity."

World Energy is now launching a multi-million dollar Capital Expansion program. With the new process control system from Siemens, it now has the flexibility it needs to implement complex controls applications with minimal in-house development time. This shifts the focus away from controls engineering to plant engineering.

With each new advancement, more gallons can be squeezed out of the same sized facility. With each new piece of equipment, the process becomes more effective, more economical.

"Whatever future role biodiesel might have, World Energy stands poised and ready to help fulfill those needs," said Altic. "With a platform like PCS 7, Siemens enables current and future facilities to easily expand their production needs as the demand for biodiesel and alternative fuels continues to grow."

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About World Energy and Siemens…

Founded in 1998, World Energy Alternatives is the nation's premier supplier of biodiesel, biodiesel blends, and biofuels. They operate the largest, most comprehensive biodiesel distribution network in the U.S. With multiple distribution points across the country, World Energy has developed the largest multi-plant, multi-region, multi-feedstock supply network in the nation. The Lakeland facility is it's only wholly owned production plant, however their business model includes plans to expand their production interests into various parts of the world. The facility's feedstock adaptability and glycerin margin optimization are second to none. It has become the nation's largest multi-feedstock biodiesel producer in the U.S.

Siemens AG is a leading global electronics and engineering company. Siemens Energy & Automation, Inc. is one of Siemens operating companies in the U.S. manufacturing and marketing the world's broadest range of electrical and electronic products, systems and services to industrial and construction market customers. Its technologies range from circuit protection and energy management systems to process control, industrial software and totally integrated automation solutions. ■

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Siemens delivers comprehensive automation solutions to the ethanol industry that decrease time to production, risk, and total cost of ownership.

Siemens helps reduce time to production by creating the following advantages:

- Decrease the engineering and commissioning time by reducing the amount of cabling, termination points, and plant space required through integrated software solutions for Profibus fieldbus technology in electrical, automation, and instrumentation
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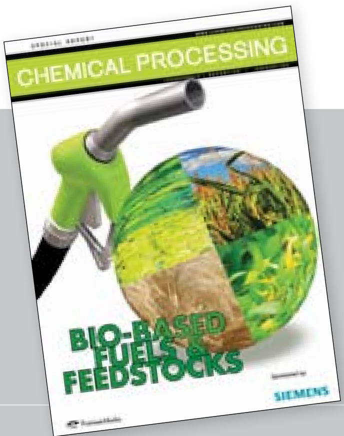
- Products and services that provide an integrated water treatment system with guaranteed water quality for plants of any size

Siemens helps reduce total cost of ownership (TCO) by including the following cost-saving elements:

- One software system for configuration, parameterization, operation, expansion and maintenance for safety, instrumentation, automation, water, and electrical systems, thereby reducing engineering, operational and training requirements
- Online diagnostics, alarming, and asset management solutions that alert operators to operational information, allowing preventative action before there is a problem

National Support – Global Support

The Siemens biofuels national team meets regularly to discuss ways to better serve biofuels customers. The results include development of comprehensive strategies that provide best-practice sharing and quicker response times for customer issues. This national team works with the Siemens global biofuels center of competence and has executive sponsorship to support the continuation of its mission.



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