PROCESS TECHNOLOGY

Engelhard Catalyst Mobilized for Diesel-Emission Control

Before cars can be approved for sale in the European Union, they must meet the Euro IV standards for emissions (particulate matter < 25 mg/km and nitrogen oxides < 0.25 g/km), which became effective in January. A platinum/palladium (Pt/Pd) diesel oxidation catalyst (DOC) that replaces one-third of the Pt with Pd, is being rolled out in serial production this month on new Euro IV model platforms from two European automakers, and it promises not only to enable cars burning low-sulfur diesel fuel to meet Euro IV regulations, but also reduce manufacturers' precious metal costs.

This technology has been honed by a handful of companies for several years, but it is Engelhard Corp.'s (Iselin, NJ; www.engelhard.com) platform that made it to the end-users' first. Each vehicle features Engelhard's three-catalyst emission control system. One of the catalysts offers the lower Pt formulation. "Until now, DOCs for European cars were based exclusively on Pt, due to the sensitivity of Pd to sulfur poisoning," says Engelhard's commercial director, Dave Kuzy. "When Engelhard added Pd to the Pt, we wanted it to enhance the performance of the DOC catalyst and not just be a cost-saving substitute." One benefit is that Pd has twice the number atoms per gram as Pt, and therefore, offers more active sites for sulfur removal (although, gram per gram, Pd is not as active as Pt). Pd also thermally stabilizes Pt and prevents it from sintering at the high temperatures required for sulfur removal.

"Conversely, Pd can sulfate more readily than Pt, and this effect had to be mitigated," says Engelhard's Joe Dettling, a senior research scientist. "With the deployment of lower sulfur fuels and the option to place the catalyst in higher temperature locations in the system, the Pt/Pd DOC could survive very nicely," he says.

Engelhard plans to extend the application of Pt/Pd technologies to other diesel-emission control applications. The next generation of fuel-exhaust standards for diesel cars (known as Euro V) are currently under discussion and are expected to reduce emissions of particulate matter and nitrogen oxides to 2.5 mg/km and 0.08 g/km, respectively. The European Commission is expected to present its proposal for Euro V in autumn 2005. If approved, the new standards will be enforced in 2010.

Automating the Electrospark Deposition Process

Researchers at Pacific Northwest National Laboratory (PNNL; Richland, WA; www.pnl.gov) have developed the first computer-based automation system for the electrospark deposition (ESD), a microwelding process. During ESD, an electrode uses short-duration, high-current electrical pulses with frequencies in the 0.1–4 Khz range to deposits small amounts of metal onto a substrate that needs a protective coating. "Pulsing allows the substrate to dissipate heat during a duty cycle, which avoids the high temperatures associated with conventional welding processes," says John Kelley, vice president R&D at Advanced Surfaces and

DISPOSABLE CHROMATOGRAPHY MEMBRANE RIVALS RESIN-BASED SYSTEMS

Pall Corp. (East Hills, NY; www.pall.com) leveraged the drawing power of Interphex 2005 (New York; Apr. 26–28) to launch what is said to be the largest disposable chromatography capsule available to customers in the life sciences marketplace. Designated the Mustang XT5000, it boasts a membrane (column) volume of 5 L and a maximum throughput of 50 L/min, or 30 times that achieved with resin-based columns (RBCs), when used in large molecule capture and contaminant removal. It also extends the disposability feature to primary capture (when the target molecule is bound, while contaminants flow through), and to new applications (*e.g.*, recovery of blood plasma fractions and drug molecules that use recombinant proteins) that traditionally require RBCs.

The Mustang XT5000 comprises a polyethersulfone membrane with a pore size of 0.8 μm that is coated with polymers bearing anion or cation functionality. Sixteen layers of the membrane are assembled into a capsule format via a laid-over pleating technique that maximizes membrane area (vs. fan pleating methods). "Due to the membrane's large pore size, the target molecules — even those in the hundreds of thousands of Daltons range — have easy access to the surface chemistry (*i.e.*, their movement is not diffusion limited), which results in high flowrates and binding capacities," says John Jenco, a senior staff scientist at Pall. For example, a plasmid DNA exhibited a 20 mg/mL binding capacity on Mustang XT5000, but only a 0.5 mg/mL on a conventional resin. Elution was achieved with solvent volumes of only 15–20 L. "Further, we achieved good resolution with differentially complex mixtures, and sharp breakthrough with high yields," adds Jenco.

To simplify validation and process development for the Mustang XT5000 capsule, Pall also introduced the Mustang XT5 capsule. It uses small volumes and scales up directly to the XT5000, which can handle higher throughputs by configuring the capsules in series or manifolded in parallel (photo). "At 50 L/min, the pressure drops are only 8–10 psi/capsule, which is much lower than seen in chromatography," notes Jenco. "Given that the chromatography step accounts for 40% of the overall process cost, Mustang XT5000 capsule can make a significant cost impact," says Holly Haughney, vice president of biopharmaceuticals marketing. A case study comparing the documented performance of a 50-L RBC column with the actual performance of the 5-L Mustang XT5000 membrane during the recovery of albumin from 1,000 L of feed indicates a solvent savings of 1,150 L or $4,600 for the Mustang configuration, reports Pall. Processing time was cut from 8 h to 50 min, resulting in a cost savings of $5,150/run (assuming a labor rate of $75/h).

Mustang XT5000 chromatography capsules can be arranged in parallel to facilitate scaleup without excessive pressure drops.

Process, Inc. (Cornelius, OR; www.advanced-surfaces.com), which has licensed the automation technology for integration with its equipment.

The ESD setup includes a capacitor-based power supply, an electrode and an applicator, which either vibrates or rotates the electrode pneumatically or electrically. In the automated system, for which a patent is pending, a sensor measures the amplitude of the spark current, which indicates the contact force of the electrode, and sends the signal to a computer that correlates the amplitude to a delivered power. “The software compares this measured power to a desired power and adjusts the equipment to maintain the optimum contact force,” explains PNNL automation team leader Jeff Bailey. The control technology enabled the probe pressure to be controlled to within ±10 g of a target pressure,” he says

“ESD targets applications where the cost of replacing a part is very high (*e.g.*, a $430,000 control valve) or where conventional welding techniques are not suitable,” says Kelley The equipment costs about $35,000, including a power supply, two torches and supply of electrodes and accessories. Bailey says PNNL has bid to duplicate the automated system for a client at $180,000. “We have also bid to build a computer-operated application from scratch at $500,000,” he adds. The automated ESD systems will be commercially available in 3–6 mo.

Elastomer with Nanocrystalline Structure Boasts Better Overall Performance

Mitsui Chemicals, Inc. (MCI; Tokyo, Japan; www.mitsui-chem.co.jp) has developed a new line of alpha-olefin-based elastomers based on metallocene catalyst technology that, for the first time, feature a nanocrystalline structure. Typically, metallocene-based elastomers feature a crystalline structure on the order of 1 µm. Designated Notio, the polymers will become commercially available in November 2005.

Notio has demonstrated better performance with respect to transparency, heat resistance (70°C higher softening point), flexibility and rubber elasticity than their non-nanocrystalline counterparts, says the firm. Its target applications will be protective films for electronic and optical parts, impact modifiers for propylene, and additives for a variety of sealing materials, such as food packaging films.

BIOTECHNOLOGY

This Protein Has an Affinity for Lead

A new fluorescent sensor based on a protein from a bacterium that thrives in a brew of heavy toxic metals has revealed its potential as a lead detector. The protein could be used to develop more selective chelating agents for treating lead poisoning (*Angew. Chem. Int. Ed. 2005*, **44**,pp. 2). “Current treatments also strip away beneficial metals, such as iron and zinc, which results in serious side effects,” says biologist Daniel (Niels) van der Lelie, a scientist at Brookhaven National Laboratory (Upton, NY; www.bnl.gov).

Fellow researchers the Univ. of Chicago (IL; www.uchicago.edu) led by Chuan He demonstrated the affinity of the protein for lead using *Ralstonia metallidurans*, a bacterium that produces a DNA-binding protein Pbr-R, which allows the bacterium to survive in a lead-rich environment. The group prepared a short segment of double-stranded DNA containing the Pbr-R-binding sequence and a fluorescent base. In the absence of lead, the two strands of the DNA double helix stay “zipped,” and there is no fluorescence. However, when the Pb(II) ion and Pbr-R are added, the protein complexes with Pb and binds to the DNA duplex, causing the DNA to distort (unzip) and the fluorescent base to fluoresce. The scientists found the protein binds Pb about 1,000 times more strongly than other heavy metals, such as mercury or copper. Thus, the fluorescence method converted the protein into a Pb(II)-ion probe that could be used for rapid on-the-spot lead detection in homes, say the scientists. They will also attempt to optimize the DNA-probe method so that the probe emits visible light, which would simplify detection.

Microbial Fuel Cell Yields “Practical” Hydrogen

Using a new electrically-assisted anaerobic microbial fuel cell (MFC), Pennsylvannia State Univ. (PSU; University Park; www.psu.edu) environmental engineers and a scientist at Ion Power Inc. (New Castle DE;

www.ion-power.com) have developed a process that enables bacteria to produce four times as much hydrogen directly out of biomass than can be generated by fermentation alone. "This technology demonstrates, for the first time, the potential to capture hydrogen for fuel from renewable sources for clean transportation," says Bruce Logan, professor of environmental engineering and co-inventor of the technology, which has been designated the bioelectrochemically-assisted microbial reactor (BEAMR).

In earlier MFC research, Logan's group and others have demonstrated that when bacteria in a conventional microbial is fed foodstuffs, such as glucose and acetate, or even organic compounds in wastewater, electricity is generated. These MFCs can be used to generate hydrogen by breaking down water, but this approach requires substantially more power than what is currently provided by the MFC in order to be commercially viable. An alternative to making electricity using bacteria is to make hydrogen using bacteria that can ferment glucose. However, there is a "fermentation barrier" because bacteria cannot produce more than 4 moles of hydrogen per mole of glucose. The rest of the hydrogen is tied up in fermentation end products, such as acetate (2 mol/mol glucose) and butyrate, that the bacteria lack the energy to metabolize.

Logan's group found that by augmenting the electrochemical potential (achieved by bacteria) in a completely anaerobic MFC circuit with a voltage of 250 mV or more, they gave the bacteria enough energy to break down the fermentation byproducts at the anode. More than 95% of the acetate was consumed, with a concomitant recovery of 90% of the electrons as hydrogen gas in a completely oxygen-free cell," reports Logan. "Including the energy expended to provide the boost (1.2 mol H_2/mol glucose), the BEAMR process could net 8–9 mol of H_2/mol glucose, which is much closer to the 10–12 mol of hydrogen that the U.S. Dept. of Energy says is required to make the production of biohydrogen from corn economically feasible," he says.

In the bench-scale prototype, bacteria consume biomass and transfer electrons to an anode. They also release protons, which go into solution. The electrons at the anode migrate via a wire to the cathode, where they are electrochemically assisted to combine with the protons and produce hydrogen gas. A voltage (250 mV or more) is applied to the circuit by connecting the positive pole of a programmable power supply to the anode and the negative pole to the cathode.

Logan notes that the BEAMR process is not limited to carbohydrate-based biomass feedstocks like conventional fermentation processes. "We can theoretically use any biodegradable, dissolved, organic matter — agricultural or industrial wastewater, for example — and simultaneously clean the wastewater," he says. Further, the process uses 10% of the voltage needed for electrolysis, with comparable yields of hydrogen, which could be a boon for this emerging fuel. However, other MFC researchers contend that the net energy yield from the BEAMR process will be less than that when just electricity is made, because of the added boost needed to produce hydrogen.

BACTERIA-BASED BIOMASS-TO-ETHANOL PROCESS IS OPTIMIZED

At the World Congress on Industrial Biotechnology and Bioprocessing in Orlando, FL (Apr. 19–22, 2005), Univ. of Florida (UFL; Gainesville; www.ufl.edu) microbiology professor Lonnie Ingram unveiled a new technology that can be used to produce ethanol for about $1.30/gal — genetically engineered *E. coli* bacteria that convert biomass and other farm wastes into fuel ethanol at yields of 90–95%.

The organisms were created by cloning two genes from *Zymomonas mobilis* (*Z. mobilis*) and inserting them into the *E. coli*. "The gene *adhB* encodes for alcohol dehydrogenase B (ADHB), while *pdc* encodes for pyruvate decarboxylase (PDC)," explains Ingram. "This replaces the fermentation-acid producing pathways in *E. coli* with the alcohol-producing pathway in *Z. mobilis*," he adds. PDC converts pyruvic acid, the common intermediate in all sugar metabolism, to carbon dioxide and acetaldehyde. ADH converts the acetaldehyde to ethanol. Like yeast, *Z. mobilis* is limited in the types of sugars it can metabolize, but is ideal for making ethanol. *E coli* is able to metabolize all plant sugars, but normally makes a mixture of acids as products. "Our work combined the best of both organisms," says Ingram.

This bioconversion technology, selected by the U.S. Dept. of Commerce to become Landmark Patent No. 5,000,000, is being commercialized with help from the U.S. Dept. of Energy (DOE; Washington, DC; www.doe.gov). BC International Corp. (BCI; Dedham, MA; www.bcintlcorp. com), which holds exclusive rights to use and license the UFL-engineered bacteria, plans to build a 30-million gal/yr biomass-to-ethanol plant in Jennings, LA, based on Ingram's microbial platform. Slated to start up in late 2006, the facility will process wastes from Louisiana's sugarcane industry and produce ethanol for industrial chemical and clean-burning fuel applications, according to Greg Luli, vice president of research for BC International's laboratory in Alachua, FL. "Other potential feedstocks include rice hulls, forestry and wood wastes," adds Ingram.

"To date, all of the world's fuel ethanol has been produced from high-value materials such as cornstarch and cane syrup using yeast fermentations," says Ingram. "The chemical makeup of biomass prevented it from being used to make ethanol economically, until now. "Ingram underscores the impact of his bioengineering innovation with a report by the U.S. Dept. of Agriculture and DOE, which states that more than 1 billion ton/y of biomass can be produced on a sustainable basis. "Converting this to fuel ethanol, now a very real possibility, could replace half of all imported petroleum in the U.S."