SONOCHEMISTRY MAKES ITS MARK

Once considered a novelty for niche applications, sonochemistry has blossomed into many CPI sectors

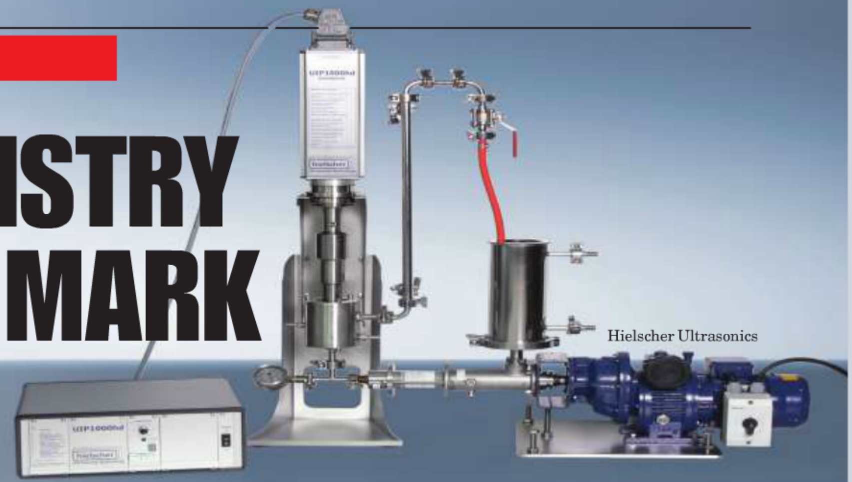

FIGURE 1. The UIP1000 processor from Hielscher Ultrasonics has a power of 1,000 W and operates at 20 kHz

Industrial uses of high-intensity ultrasound have grown tremendously over the past 25 years, says Kenneth Suslick, professor of chemistry at the University of Illinois at Urbana-Champaign and one of the pioneers in the field. Ultrasonic welding of plastics is universal, ultrasonic cleaning of equipment has replaced most solvent and vapor degreasing, and it is even routine for homes to have ultrasonic humidifiers, either built-in or portable. The use of ultrasound for chemical processing, too, has found a permanent niche in industrial applications, including sonocrystallization of pharmaceuticals, enhancement of high-value-added chemical reactions, well-water purification, and preparation of ultrafine emulsions for cosmetics. Many other large-scale applications are developing as well in the food industry, says Suslick.

Thirty years ago, sonochemistry was a black art, unknown to nearly all chemists, and understood by no one. Today we understand in detail the nature of acoustic cavitation and most of the mechanisms responsible for sonochemical reactions, Suslick continues. "Our understanding of the extraordinary conditions produced during cavitation, created by the implosive collapse of microscopic gas bubbles in liquids, is thorough. We can measure and control the temperatures and pressures of cavitation that drive sonochemical reactions."

In fact, biodiesel production, water and wastewater purification, and sonocrystallization of pharmaceuticals, are among the most successful applications of sonochemistry.

Biodiesel production

Making biodiesel fuel from vegetable oils — such as soy, canola, Jatropha or sunflower seed — or animal fats, involves the base-catalyzed transesterification of fatty acids with methanol or ethanol to obtain either methyl or ethyl esters. Glycerin is a byproduct of those reactions. The heavier glycerin will sink to the bottom and the biodiesel fuel floats on top and can be separated by decanters or centrifuges.

The traditional esterification reaction in batch processing tends to be slow, and separation of the glycerin can take several hours. The batch process mixes various chemicals together mechanically.

When ultrasound is used, however, the ensuing cavitation provides the kinetic energy needed for faster and more complete esterification. Cavitational shear also reduces the size of methanol or ethanol droplets, resulting in improved methanol and catalyst utilization. Thus, less methanol and catalyst are required.

As opposed to batch operations, ultrasonic biodiesel processing allows for continuous inline processing and ultrasonic reactors reduce the processing time from the conventional 1–4 h to less than 30 s. Ultrasonication also reduces the separation time from the 5–10 h required for conventional agitation, to less than 60 min, says Scott Weis, owner of Wisconsin Fluid Systems LLC (Union Grove, Wisconsin www.wisconsinfuels.com).

Ultrasound also allows a reduction in the use of heat and pressure, two of the largest energy costs of batch plants.

"We've had good experiences with ultrasound for continuous-flow biodiesel production," says Weis. "The best advantages are that it is a faster reaction, less energy is used, it requires a smaller process area, and requires less material with a flammable mixture of methanol," he says.

"The setup process was purely trial and error [with batch reactors]. With a continuous flow system it is fast and easy to make adjustments."

The throughput for most of the company's systems is 450 to 600 L/h. The frequency and flowrate vary, depending on the feedstock.

Genuine Bio-Fuel Inc. (Indiantown, Fla; www.genuinefuel.com) has had a similar experience. "Batch reactors are too cumbersome and limiting," says the company's executive vice-president Jeff Longo. "The batch process is time-consuming, taking anywhere from a couple of hours to days to complete. Plus, it is not conducive to using a variety of alternative feedstocks of variable quality," he says. Using ultrasonics allows the company to produce greater quantities of finer-quality biodiesel fuel, while reducing costs and enabling the company to use a wide variety of feedstocks.

Genuine Bio-Fuel spent 18 months procuring proprietary data, which gives the proper flowrates, catalyst percentage, and injection rates along with the proper frequencies to be applied.

Genuine Bio-Fuel has used the UIP1000hd – 1 kW, 20 kHz industrial ultrasonic processor (Figure 1) from Hielscher Ultrasonics GmbH (Teltow, Germany; www.hielscher.com), designed for continuous processing at high flowrates.

Wastewater treatment

While ultrasound in biodiesel fuel processing works mainly by providing the shearing forces that greatly speed up the chemical reactions, additional effects are involved in ultrasonic wastewater treatment. Here the aim is to reduce the amounts of pollutants, including nutrients and potentially pathogenic micro-organisms. Low frequency, high-intensity ultrasound can break up various pollutants, and even break up bacteria. The ultrasound destroys bacterial cells, causing them to spill out their contents and endo-enzymes, which are then consumed by other bacteria that become more effective at degrading the organic pollutants. The pollutants, having been broken down by the ultrasound, become easier to degrade.

The ultrasonic treatment allows the disintegrated sludge to be used as an internal electron donor to fuel the denitrification stage. A sufficient carbon concentration is needed to remove nutrients from wastewater through the biological nutrient-removal process.

Several wastewater treatment plants have installed ultrasonic treatment. One of the latest is the wastewater treatment plant at Schleswig, Germany, which had an ultrasound system installed in March 2011 by Ultrawaves GmbH (www.ultrawaves.de). The company has its roots in the R&D work pursued in Germany at the Northern Institute of Technology, situated on the campus of the Hamburg-Harburg University of Technology. It was founded by professor Uwe Neis and Klaus Nickel.

The company's reactor for sludge disintegration is a compact machine with a volume of 28 L. The standard model is normally fitted with five oscillating units that can be supplied with up to 2 kW each. This reactor is capable of treating a sludge flow of up to 30 m^3/d.

The company says the reactor decreases digestion time by up to 60%, reduces the digested sludge mass by up to 30% and produces up to 50% more biogas.

The plant at Schleswig has a design capacity of 75,000 PE (persons equivalent). The system has a power of 5 kW. About 30% of total thickened, waste-activated sludge flow is treated with ultrasound. Compared with the start-up phase of the ultrasound application, the volatile solids degradation was increased from 57% to 66%. From May 2011 to March 2012, the specific biogas yield has also been improved by 32%.

A more recent wastewater-treatment plant is in the town of Maroochydore, in the Sunshine Coast of Queensland, Australia. There, the ultrasonic units were installed by Royce Water Technologies Pty Ltd. (Albion, Queensland; www.roycewater.com.au), the Australian representative of Ultrawaves.

The plant has "A" and "B" bioreactors. The methanol dosing to "A" plant was turned off in February while plant "B" continued dosing. The sonicated, thickened sludge has been successful in maintaining low nitrate levels in plant "A" effluent without the addition of methanol as a carbon source.

The trial will continue for another two months to assess what effects sonication has on sludge drying and disposal volume.

Food processing

Another effect of acoustic cavitation that has been successfully exploited is particle size reduction in food processing. One of the most recent breakthroughs was achieved by a team from Dairy Innovation Australia Ltd. (Werribee, Victoria; www.dairyinnovation.com.au), and the School of Chemistry, University of Melbourne (www.unimelb.edu.au), led by professor Muthupandian Ashokkumar. The team has used a continuous sonication process at 20 kHz that is capable of delivering up to 4 kW of power with a flow-through reactor design to treat dairy ingredients at flowrates from 200 to 6,000 mL/min. Dairy ingredients that have been treated include reconstituted whey protein concentrate, whey protein and milk protein retentates and calcium caseinate.

Sonication of solutions with a contact time between 1 and 2.4 min led to a significant reduction in the vis-

ULTRASOUND SOURCES

The following companies offer equipment and services related to the use of ultrasound:

1. **Ultrawaves GmbH** (Hamburg, Germany; www.ultrawaves.de); reactors systems and consulting for treatment of water, wastewater and biomass
2. **Hielscher Ultrasonics GmbH** (Teltow, Germany; www.hielscher.com); ultrasonic reactors for applications such as biodiesel production, and wastewater and biomass treatment.
3. **Meinhardt Ultraschalltechnik** (Leipzig, Germany; www.meinhardt-ultraschall.de); ultrasonic transducer/generator systems
4. **Ultrawave Ltd.** (Cardiff, U.K. www.ultrawave.co.uk); precision ultrasonic cleaning equipment
5. **Branson Ultrasonics** (Danbury, Conn.; www.emersonindustrial.com); precision cleaners
6. **Honda Electronics Co.** (Tokyo, Japan; www.honda-el.co.jp); ultrasonic reactors
7. **Industrial Sonomechanics, LLC** (New York, N.Y.; www.sonomechanics.com); nanocrystallization of pharmaceuticals
8. **Stoelting Ultrasonics** (Kiel, Wisconsin; www.stoeltingcleaning.com); custom cleaning
9. **Telsonic AG** (Bronschhofen, Switzerland; www.telsonic.com); generators, tube resonators, transducers, cleaning
10. **Ultrasonics Australasia Pty Ltd.** (Sydney, Australia; www.ultrasonicsaustralasia.com.au); ultrasonic cleaning
11. **Unisonics Australia Pty Ltd.** (Sydney, Australia; www.unisonics.com.au); ultrasonic cleaning
12. **U&Star Ultrasonic Technology** (Hangzhou, China; www.ustar-ultrasonic.com); ultrasonic accessories and reactors, consulting

Industrial Sonomechanics

FIGURE 2. The BSP-1200 ultrasonic processor from Industrial Sonomechanics is designed for batch and flow-through processes and pilot-scale production. The processor outputs up to 1,200 W of acoustic power and operates at 20kHz

Professor Kenneth Suslick

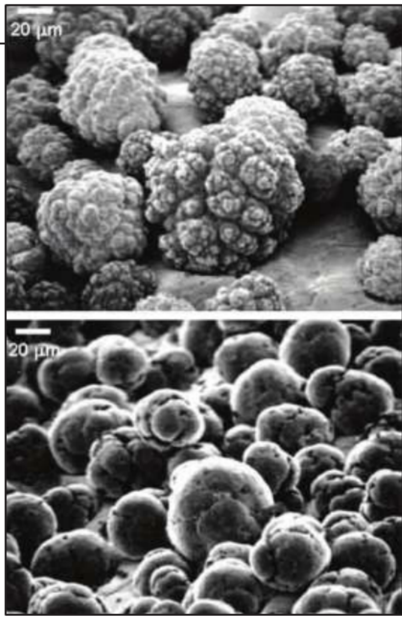

FIGURE 3. This scanning electron micrograph shows the effect of ultrasonic irradiation on the surface morphology and particle size of nickel powder. Upper image is before ultrasound and lower is after irradition of a slurry in decane. High-velocity interparticle collisions caused by ultrasound are responsible for the smoothing and removal of a passivating oxide coating

cosity of materials containing 18 to 54% (w/w) of solids. The viscosity of aqueous dairy ingredients was reduced by between 6 and 50% depending on the composition, processing history, acoustic power and contact time, says Ashokkumar.

The team also noticed an improvement in the gel strength of sonicated and heat-coagulated dairy systems. When sonication was combined with a heat treatment, the heat stability of dairy ingredients containing whey proteins was improved. The gelling properties and heat stability were maintained during spray drying and upon reconstitution.

Ashokkumar says: "The financial viability of the Australian dairy industry relies heavily on the manufacture and export of milk powders and dairy protein concentrates. The acoustically generated chemical and physical effects were used to modify the functional properties of dairy proteins. Transformation of the sulfur-containing proteins by this means may overcome many of the difficulties currently encountered in thermal processing of whole milk and whey proteins. Further, the resulting dairy products can be marketed as specialty hydrogel-based dietary products, microcapsules, and medical ultrasound contrast agents."

Sonocrystallization

Apart from food processing, ultrasonics has become a major tool in particle-size reduction down to the nano-scale (nanocrystallization) in the pharmaceutical industry. High-powered ultrasound can assist the crystallization process by influencing the initiation of crystal nucleation, controlling the rate of crystal growth, ensuring small and even-sized crystals are formed, and preventing fouling of surfaces by newly formed crystals.

A large number of currently available drugs exhibit poor water solubility, leading to reduced bioavailability and increased potential of side effects. Particle-size reduction has been shown to increase the bioavailability and reduce the required dose frequency, decreasing drug side-effects.

The process of nanocrystallization requires the application of very high ultrasonic amplitudes to particle suspensions, which produces extreme shear forces.

Industrial Sonomechanics, LLC (New York, NY; www.sonomechanics.com), offers bench and industrial-scale, high-power ultrasonic processors for the production of nanosized drug crystals (Figure 2). The processors are based on its Barbell Horn Ultrasonic Technology.

The company says the process of ultrasonic nanocrystallization requires extremely high ultrasonic amplitudes to be applied to particle suspensions in order to produce extreme shear forces. Conventional high-power ultrasonic technology forces all processes to run either at a small scale and high amplitude or a large scale and low amplitude, according to Industrial Sonomechanics, which limits the commercial implementation of high-power ultrasound to processes for which low amplitudes are sufficient, such as cleaning, simple deagglomeration, mixing and macro-emulsification. The company says it has overcome this limitation by developing the Barbell technology.

For example, the company said, ultrasonic amplitudes of the order of 100 microns can only be reached by conventional horns when their output tip diameters do not exceed about 20 mm (laboratory scale). Conventional horns with output tip diameters of 40 mm and above (industrial scale) operate at the maximum amplitude of about 25 microns, irrespective of the specified system power.

Barbell horns are able to amplify ultrasonic amplitudes while retaining large output tip diameters.

CONFERENCE NOTE

The 1st meeting of the Asia-Oceania Sonochemical Society will take place at the University of Melbourne on July 10—12. The meeting will be be chaired by Ashokkumar, with participants from China and Japan, as well as from Australia, the U.S. (Suslick), and the U.K. (Mason).

Other applications

In addition to these successful applications of ultrasound, many more are predicted to become important in industry. Another pioneer in the field of sonochemistry, Timothy Mason, professor of chemistry and director of the Sonochemistry Applied Research Center at Coventry University (U.K.; www.coventry.ac.uk.) sums up what he believes will be the main areas of influence of sonochemistry in industry, as follows:

- ***Benefits in synthesis.*** Use of less hazardous chemicals and environmentally friendly solvents; minimizing the energy consumption for chemical transformations; using alternative or renewable feedstocks
- ***Benefits in electrochemistry***. Continuous cleaning and activation of the electrode surfaces; degassing, which limits gas bubble accumulation on the electrode surface; agitation (via cavitation), which disturbs and reduces the thickness of the diffusion layer; agitation, which also stops the depletion of electroactive species in the immediate vicinity of the electrode
- ***Benefits in materials science.*** Improvement in the preparation, modification and coating of nanoparticles; surface modification of materials (Figure 3); improvements to crystallization processes
- ***Environmental protection.*** Cavitation weakens bacterial cell membranes, rendering them more susceptible to biocides; the production of radical species such as hydroxyl radicals provides the essential elements for both the chemical and biological decontamination of water; enhanced advanced oxidation processes, for instance ultraviolet radiation, ozone or chemical oxidants ■

Paul Grad