GREEN CHEMISTRY

CHEMRAWN conference explores the progress and prospects of chemical research and science policy in advancing global sustainable development

STEPHEN K. RITTER, C&EN WASHINGTON

Green is a strong color. Green is the color of chlorophyll, and green is the color of money. Being green has long been a battle cry of environmental activists, and being green has become an important marketing tool for businesses. And for chemists, it is becoming increasingly important to be green by applying the principles of green chemistry to all facets of the chemical sciences: basic and applied research, production, and education.

A BOULDER VISION **The University of Colorado campus provided an ideal setting for CHEMRAWN XIV. PHOTO BY STEVE RITTER**

Green chemistry, also known as sustainable chemistry, is an umbrella concept that has grown substantially since it fully emerged a decade ago. By definition, green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.

Last month, some 200 scientists and policymakers from more than 30 countries gathered on the campus of the University of Colorado, Boulder, to discuss the progress and prospects of green chemistry at CHEMRAWN XIV: Toward Environmentally Benign Processes and Products. The purpose of the conference was to assess the current state of the art in green chemistry and discuss the role of chemical research and science policy in advancing global environmental protection and sustainable development.

"This is an extraordinary opportunity for four important groups in the formation of policy--academia, government, nongovernmental organizations, and industry--to work together through 'constructive engagement' to focus on solutions to many of the world's problems and their effects on the human condition," commented Rohm and Haas President and Chief Operating Officer J. Michael Fitzpatrick, who was chair of the conference organizing committee.

THE CONFERENCE was organized around the premise that chemistry is an important part of the solution, Fitzpatrick said. "Chemistry is an enabling science that will allow economic progress and environmental progress to proceed in harmony. It is our goal to talk about the technologies that are available to us in order to achieve that, but also to have a dialogue about the issues that need to be resolved."

CHEMRAWN (Chemistry Research Applied to World Needs) is a program of the International Union of Pure & Applied Chemistry. Designed to support scientists who have the skills and expertise to address pressing world problems, the program sponsors conferences on specific topics to prioritize needs from a chemical perspective with the aim of disseminating that information as broadly as possible.

The green chemistry conference, which consisted of invited lectures, contributed posters, and discussion groups, was cosponsored by the American Chemical Society and the Green Chemistry Institute (GCI), which formed an alliance with ACS at the beginning of this year. The conference was supported by the University of Colorado, several chemical companies, government agencies, and national chemical societies.

A welcoming plenary session featured remarks by a number of dignitaries, including Fitzpatrick; ACS President Attila E. Pavlath; ACS Immediate Past-President Daryle H. Busch; GCI Director Dennis L. Hjeresen; IUPAC CHEMRAWN Committee Chairman Parry M. Norling; and University of Colorado chemistry professor Robert E. Sievers, who was the conference's local arrangements chair.

The conference covered an ambitious range of topics, which included alternative reaction and separations media, such as supercritical CO_2 and ionic liquids; environmentally benign agricultural practices; emerging biotechnology alternatives, such as enzyme-catalyzed reactions; product life-cycle impacts, from raw materials to recovery and reuse; establishing national green chemistry programs; and green chemistry education.

FITZPATRICK
PHOTO BY PETER CUTTS

"Many of the issues that we are trying to address with green chemistry are global issues," Hjeresen commented. "These are not laboratory curiosities or individual research projects. This is a field aimed at large global problems such as climate change, energy consumption, and management of our water resources."

HJERESEN
PHOTO BY KEVIN MACDERMOTT

Individual disciplines involved in environmental science--atmospheric science, oceanography, chemistry, and others--have reached an "age of understanding" of environmental problems, Hjeresen said. But in many ways, the problems themselves dwarf the purviews of the individual disciplines.

"Much of green chemistry is focused on how we can bring biologists together with chemists, with engineers--with scientists from a range of disciplines," Hjeresen noted. "A lot of the issues that we are dealing with now are so complex and so multivariate that if we don't combine our forces we don't have a chance to solve them."

CRUTZEN
PHOTOS BY STEVE RITTER

SUSTAINABILITY is an issue that is critical now, not 100 years from now, Hjeresen stressed. "We need to compress the time scale of this discussion so that we are talking about real problems in real time."

One purpose of the conference was to identify the scientific gaps and the economic and social issues that need to be addressed for sustainable development. This task was carried out before and during the conference by the CHEMRAWN XIV Future Actions Committee, which was chaired by Paul T. Anastas of the White House Office of Science & Technology Policy (OSTP).

ANASTAS

"The reason green chemistry is being adopted so rapidly around the world is because it is a pathway to ensuring economic and environmental prosperity," Anastas commented. "Green chemistry is powerful because it starts at the molecular level and ultimately delivers more environmentally benign products and processes."

The committee issued a report at the conclusion of the conference that noted key findings and indicated the actions needed to meet the goals of green chemistry. Extensive engagement and commitment of many individuals will be needed in order to make the recommendations a reality, Anastas noted. "Green chemistry requires nothing less than the highest quality science with the broadest possible perspective," he said.

Some of the report's key findings are as follows:

- Many technologies that meet green chemistry objectives already exist and offer immediate opportunities to reduce environmental burdens and enhance economic performance.
- The incorporation of green chemistry and related approaches into the training of current and potential science students increases the effectiveness of recruitment and retention efforts in this crucial field.
- Research investments beyond current "pilot program" levels are needed from both government and industry to empower and enable the development and utilization of green chemistry technologies by the broad spectrum of private-sector interests.
- Key action items include the following:
- National centers for green chemistry should be established or expanded, and these centers should be linked to create an effective worldwide network.
- Educational initiative funding in green chemistry is needed to focus on curriculum materials development, faculty training centers, fellowships, and recruitment and retention activities.
- Increased incentives are needed for the initial implementation of green chemistry technologies by industry to offset investment, policy, and regulatory barriers that may exist.
- Informational outreach is needed to educate industry, public, and environmental groups of the benefits of green chemistry adoption.

CHEMRAWN XIV featured a number of keynote lecturers, including Nobel Laureate Paul J. Crutzen, who is professor emeritus at Max Planck Institute for Chemistry, Mainz, Germany; Rosina Bierbaum, then-acting director of OSTP; and Mary L. Good, president of the American Association for the Advancement of Science.

Crutzen gave an overview of the effects of industrial and agricultural activities on atmospheric chemistry. The impact caused by the rapidly growing population and development in Asia, especially from coal and biomass burning, is a particular point of concern, he emphasized. The environmental effects of human activities over the past 200 years and in the coming centuries, Crutzen suggested, could delineate a new geological time period--the anthropocene, derived from anthropogenic--replacing the current holocene epoch that covers the past 10,000 years.

Several conference speakers commented that green chemistry, while necessary, will not be sufficient by itself to overcome current environmental problems. One of those speakers was Joe Thornton, a member of the department of biological sciences and the Earth Institute at Columbia University. Thornton also is the author of "Pandora's Poison: Chlorine, Health, and a New Environmental Strategy," a book published last year by MIT Press (C&EN, Oct. 9, 2000, page 57).

THE DIFFICULTY doesn't lie in the availability of the necessary green technologies, Thornton said, but in overcoming obstacles to effectively implement them. Inertia--the simple act of getting started--and the cost of implementing new technologies impede progress, he said, but the real obstacle is the current system of regulation and enforcement. Permitting policies that set acceptable limits on emissions perpetuate the current pollution problem rather than eliminate it, he added, because they ignore the global cumulative effect of chemicals in the environment.

SUPERCRITICAL Postgraduate student Eleni Venardou exchanges collection flasks at the supercritical water reactor used to make terephthalic acid at the University of Nottingham. The reactor uses a series of pumps to mix *p*-xylene, oxygen generated from hydrogen peroxide, water, and $MnBr_2$ catalyst, which pass through a high-pressure reactor. The reaction is the first selective oxidation to be carried out as a continuous process in supercritical water.
PHOTO BY ROY SEARCY, UNIVERSITY OF NOTTINGHAM

"Chemistry is an enabling science that will allow economic progress and environmental progress to proceed in harmony."

Instead of micromanaging individual chemicals, Thornton suggested that classes of compounds be macromanaged to achieve the goal of eliminating toxic emissions altogether by systematic phaseout as better and better alternatives are introduced. "The expected result of [this type of program] will be the progressive and gradual reduction in the use of synthetic chemicals except for those designed specifically to be compatible with ecological and biological processes," he said.

The role of biotechnology in agriculture to reduce the reliance on agrochemicals was addressed by several conference speakers. Roger N. Beachy, president of the Donald Danforth Plant Science Center, a nonprofit research institute in St. Louis, discussed the need for pest-resistant and disease-resistant genetically modified crops and gave some examples of recent developments.

Transgenic crops can make an important impact, he said, especially in developing countries, but scientists and regulatory authorities will have to work with consumers and advocacy groups to assure them of the safety of crops and foods developed by green technologies. Beachy emphasized the need to try to avoid emotional debates over these concerns, but rather to use good science as a guide.

Another speaker who addressed agricultural biotechnology was Don S. Doering, a senior associate at the World Resources Institute, a nonprofit research organization that focuses on environmental problems. Doering is working toward developing guiding principles for applying biotechnology to agriculture.

Genetic engineering is a powerful means to achieve sustainable agriculture, Doering said, but it must be carried out in a socially responsible way to preserve biodiversity. Biotech won't be the cure for all of society's needs, he believes, but it is one of many tools in a "design-for-environment" framework to guide the future of green agricultural practices.

The goal of implementing green chemistry into agriculture and manufacturing in developing countries sometimes is overwhelmed by the potential for social impact. Qing-shi Zhu, a physical chemist and president of the University of Science & Technology of China, in Heifei, discussed the problem in his country in convincing government officials of the importance of green chemistry efforts.

Although China has water quality and other environmental problems that need to be addressed, Zhu said, often the impact of green chemistry on improving those problems is outweighed by the potential loss of tens of thousands of jobs. Still, he said, educating people about green chemistry and finding ways to focus attention on enforcement of environmental laws will help.

Among the examples he noted that are being investigated in China include 100% methanol automobile fuel from biomass sources and the use of biomass (straw) to make paper in a process that employs enzymes to break down cellulose rather than chemical or mechanical treatment. China recently held its fourth international symposium on green chemistry as a way to foster its green chemistry efforts.

AT THE HEART of green chemistry are alternative reaction media. They are the basis of many of the cleaner chemical technologies that have reached commercial development. Many conference speakers described chemistry using supercritical carbon dioxide (31.1 °C, 73 atm) and supercritical water (374 °C, 218 atm); room-temperature ionic liquids; biphasic systems; and solvent-free systems that utilize the surfaces or interiors of clays, zeolites, silica, and alumina.

In the case of supercritical fluids, a large degree of control over product selectivity and yield is possible by adjusting the temperature and pressure of the reactor, noted chemistry professor Martyn Poliakoff of the Clean Technology Research Group at the University of Nottingham, in England. In many cases, supercritical fluids allow easy recovery of the product and separation of the catalyst, Poliakoff said, plus they can readily be recovered and reused.

Hydrogenation of organic compounds is one venue where alternative reaction media are expected to play a major role (C&EN, May 28, page 30). The Nottingham group has examined a wide range of continuous supercritical fluid hydrogenations using 5-mL flow-through reactors that it has pioneered. One of the group's efforts reported by Poliakoff and his Nottingham colleague Paul A. Hamley is the commercial development of supercritical fluid-heterogeneous catalyst reactors with British fine chemicals manufacturer Thomas Swan & Co. A 1,000-ton-per-year supercritical CO_2 demonstration plant is under construction in Consett, England, and is expected to be ready in late September.

Another collaboration that is beginning to pay off for the Nottingham group is a continuous flow-through reactor for partial oxidation of organic compounds using a homogeneous catalyst in supercritical water. A test reaction under development is the oxidation of *p*-xylene to terephthalic acid, a feedstock used to make polyethylene terephthalate and polyester fiber. The work originally was a collaboration with ICI, Poliakoff said, but the company sold its polyester business in 1997 to DuPont, and DuPont Polyester Technologies has continued the collaboration.

The traditional synthesis of terephthalic acid uses *p*-xylene and air with acetic acid as the solvent and a manganese/cobalt catalyst system at 190 °C and 20 atm of pressure. The process is highly selective, Poliakoff said, but it can be energy-intensive. In addition, terephthalic acid is insoluble in acetic acid, and some 10% of the acetic acid is oxidized during the reaction.

By contrast, *p*-xylene, oxygen, and terephthalic acid are all soluble in supercritical water, he noted. Thus, the Nottingham team developed a route that uses oxygen from hydrogen peroxide as the oxidant with 1,000 ppm of manganese dibromide as the catalyst. This reaction is the first selective oxidation to be carried out as a continuous process in supercritical water, Poliakoff said. Isolated yields of terephthalic acid are better than 70%, he reported, with selectivity at better than 90%.

The miniature reactor, which can produce about 10 g of terephthalic acid per hour, is being used to optimize the reaction further. Poliakoff emphasized that these projects could not have happened without both industrial and government support.

Ionic liquids have been found useful for a wide range of chemical reactions and processes, including hydrogenation reactions, biocatalysis reactions such as transesterification and perhydrolysis, and electrochemical applications such as battery electrolytes (C&EN, Jan.1, page 21). Another use for ionic liquids is as a medium for separation of biologically produced feedstocks from a fermentation broth, such as acetone, ethanol, or butanol (C&EN, April 2, page 57).

Ionic liquids typically consist of nitrogen- or phosphorus-containing organic cations coupled with inorganic anions. An important property of ionic liquids is that they have essentially no vapor pressure, which makes them optimal replacements for volatile organic compounds traditionally used as industrial solvents, noted Kenneth R. Seddon, a chemistry professor at Queen's University of Belfast, in Northern Ireland. Seddon showed that there is an almost endless number of possible ionic liquids that can be made by combining various anions with a wide range of cations.

Seddon focused his talk on collaborative work with a number of chemical companies to move ionic liquids from the lab to pilot-plant scale through the Queen's University Ionic Liquids Laboratory (QUILL). One example he cited is an effort with BP Chemicals to prepare an isomeric mixture of linear alkylbenzenes in ionic liquids.

THE GOAL of the work is to eliminate the use of organic solvents and sulfuric acid or aluminum trichloride catalysts while maintaining product selectivity. A nice feature of ionic liquids, Seddon noted, is that yields can be optimized by changing anions or properties of the cation. In the alkylation reactions, ionic liquids gave better results than sulfuric acid or aluminum trichloride with the added benefit that the ionic liquid can be recovered and reused.

Although ionic liquids have been shown in the lab to have great potential, there has not yet been any known large-scale industrial application of the solvents, Seddon said. Several observers cited cost and potential toxicity and environmental impact as concerns, but noted that cost will be less important if ionic liquids can be recycled as shown in the lab. The initial work at QUILL and by other groups has created a test bed for studying ionic liquids, Seddon said, which provides chemical engineers a basis for scale-up and optimization.

All of these seemingly competing alternative media systems are going to be needed, Poliakoff pointed out. "I think there is a danger in green chemistry that people who are proponents of one technology or another give the impression that their technology is the best," he stated. "It is my view that green chemical problems are so large and so broad that we need all of the new technologies that are coming and probably quite a few that have not yet been devised.

"One of the important things at this conference is to see how these different technologies can come together," he continued. "And the problem with all of these new technologies is that people still have to build plants and make money from them. Only then will it be clear how useful they will be."

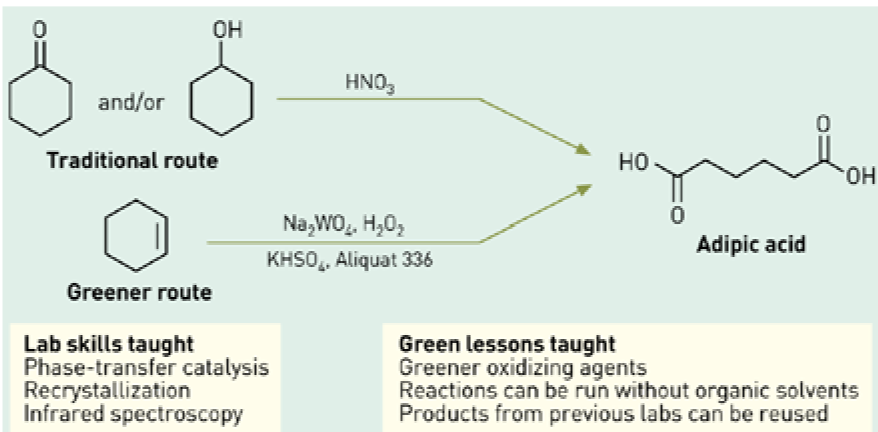
Seddon agreed. "These technologies are part of a toolbox," Seddon said. "Our job is to increase the amount of information so that someone in industry with a specific plant to build or a specific problem can come along and look at the main options available to them and make an informed decision. Right now, you can't necessarily make that decision because the information is not far enough advanced."

There have been commercial success stories using alternative reaction media, and some of them were told at the conference by Joseph M. DeSimone, a professor of chemistry at the University of North Carolina, Chapel Hill, and a professor of chemical engineering at North Carolina State University. DeSimone also is director of the National Science Foundation's Science & Technology Center for Environmentally Responsible Solvents & Processes, a multidisciplinary government-university partnership that is developing some of the technologies he described.

In one example, from research started in the early 1990s with support from DuPont, DeSimone and coworkers found that reactions usually carried out in chlorofluorocarbon solvents can be done in liquid or supercritical CO_2. In one case, the group was able to show the polymerization of tetrafluoroethylene in CO_2 using fluorinated initiators. DuPont recently completed the first phase of an announced total investment of $275 million for a production facility based on the process in Fayetteville, N.C., to make its Teflon polytetrafluoroethylene and copolymers.

DeSimone has further developed CO_2 as a reaction medium through a company he started with two partners in 1995. The company, called Micell Technologies, offers integrated CO_2-based processes for dry cleaning, metal cleaning, and textile processing. One of the company's developments is a dry-cleaning process, called Micare, that uses liquid CO_2 as a solvent rather than perchloroethylene, a groundwater contaminant and possible human carcinogen.

Micell has launched a chain of more than 60 dry-cleaning stores throughout the U.S., called Hangers Cleaners, which use a specially designed washing machine to clean clothes with beverage-grade CO_2 and specialty surfactants. The 60-lb-capacity machine uses a conventional rotating drum to agitate clothes and has a 40-minute cleaning cycle. It can recover the surfactants and about 98% of the CO_2 used, DeSimone noted.



MORE BENIGN One of the green organic lab experiments developed at the University of Oregon is the synthesis of adipic acid, a feedstock used to make nylon. The experiment teaches the same lab skills as a traditional experiment while stressing the principles of green chemistry by avoiding production of nitrous oxide as a by-product and using only water as a solvent [*J. Chem. Ed.,* 77, 1627 (2000)].

A COMPETING LIQUID CO_2 cleaning process, called DryWash, has been developed by Global Technologies, El Segundo, Calif., a subsidiary of Raytheon Environmental Systems. Raytheon collaborated with Los Alamos National Laboratory in the early 1990s to develop its CO_2 technology. Global Technologies has licensed the technology to a consortium of companies that are developing their own dry-cleaning systems and equipment that they in turn are selling to dry cleaners.

"At the end of the day, one of the most important aspects of this technology is that you don't have a contamination issue," DeSimone said. The federal government, which funded the development of both dry-cleaning processes through EPA, would like to eliminate perchloroethylene from dry-cleaning use, he added, but until now there hasn't been a better alternative. The technology has an added economic benefit, he said, because banks will finance new businesses that use CO_2, whereas they have been loathe to finance dry-cleaning businesses for some 20 years because of perchloroethylene ground contamination and worker safety issues.

DeSimone also spoke about potential commercial uses for liquid CO_2 in the microelectronics industry to spin-coat photoresists instead of using traditional organic solvents. Another example he cited is the use of CO_2 to clean integrated circuits and flat-panel displays during manufacturing rather than using large amounts of water and organic solvents.

Education is an important component of green chemistry that was emphasized in many of the CHEMRAWN lectures and at a preconference workshop. The three-day workshop was devoted to training 25 young chemical professionals from 16 nations in the concepts, principles, and methodologies of green chemistry. The goal was to empower workshop participants and provide them with the necessary tools to return to their home region or country to successfully use what they have learned. Expenses for attending the workshop were covered by the conference's sponsors.

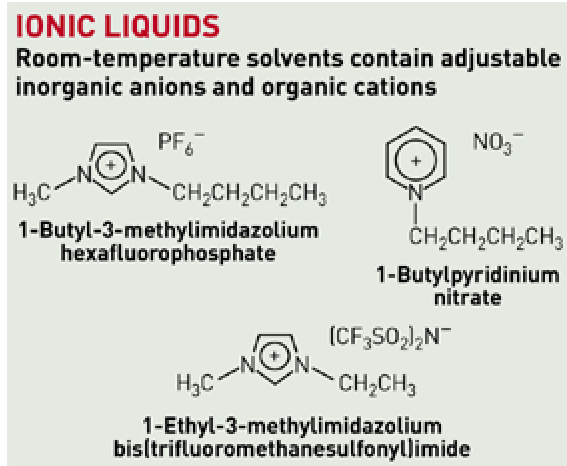
"Education can be enabling and transforming," observed John C. Warner, a chemistry professor at the University of Massachusetts, Boston, and educational chair of the CHEMRAWN conference. "People who go to school to become chemists expect their education to enable them to get a job or to start a career. Environmental problems, while important to them, appear outside their sphere of influence. Green chemistry transforms this perspective. It allows practicing chemists to feel that they themselves can contribute to pollution prevention as individuals. This empowerment is extremely important."

One way Warner is addressing the need for green chemistry education is by developing the first U.S. doctoral program in green chemistry at Massachusetts. "If people start to recognize toxicity and environmental impact as just another physical property of a material, so many problems would be solved. These properties then could be factored in at the design stage of any R&D process."

Some examples of positive outcomes from the workshop are as follows:

- Supawan Tantayanon, an associate professor of chemistry at Chulalongkorn University, in Bangkok, Thailand, was asked last year to become president of the Thailand Chemical Society. She had reservations about ascending to that position, but after the workshop she stated that she now will accept the position.
- Workshop attendees from South America and Mexico plan to organize a Latin American green chemistry collaboration.
- Attendees from Singapore plan to start a website at the National University of Singapore dedicated to green chemistry and how it can help their students.
- Sarah Guy, who started her own environmental consulting firm in Swaziland, will be encouraging her clients to support green chemistry research and development programs.

"The crystallization by Paul Anastas and John Warner of their chemical synthesis experience into the 12 Principles of Green Chemistry is very useful--indeed critical," Guy told C&EN. "The principles are simple, logical, and an essential addition to every chemists' considerations. It is hoped that every chemist and chemical engineer will look far beyond their laboratory or plant in designing and optimizing their processes."



When students are introduced to the ideas of green chemistry, "they get very excited indeed," noted Sylvia A. Ware, director of the ACS Division of Education & International Activities. "It is critical for those who are planning a career in chemistry to see green chemistry as something that is going to be intellectually respectable and exciting."

"The care and skill with which we manage our resources, with which we do our science ... will determine whether our profession and perhaps civilization as we know it will be sustainable."

ACS has been working for several years with EPA's Office of Pollution Prevention & Toxics to develop an evolving toolbox designed to promote green chemistry to various audiences. The materials are by no means comprehensive, Ware added, but they can easily be customized and integrated into existing courses at both the secondary and undergraduate levels.

Among the ACS materials incorporating green chemistry are the latest editions of "Chemistry in the Community" (ChemCom), a high school textbook, and "Chemistry in Context," a textbook for undergraduate nonscience majors. Green chemistry also is being introduced into the ACS magazine for high school students, ChemMatters, and the magazine for undergraduate chemistry majors, in Chemistry.

Another resource is a booklet of 10 case studies presented in a format amenable for undergraduate chemistry classrooms titled "Real-World Cases in Green Chemistry," which was published by ACS last year. The case studies, prepared by chemistry professor Michael C. Cann and undergraduate Marc E. Connelly of the University of Scranton, in Pennsylvania, are based on research that was nominated for or received a Presidential Green Chemistry Challenge Award (C&EN, July 2, page 24). The Green Chemistry Challenge Awards also are the basis of a 20-minute video available from ACS, "Green Chemistry: Innovations for a Cleaner World."

More information about all of the ACS green chemistry education projects is available on the Internet (http://www.chemistry.org/education/greenchem).

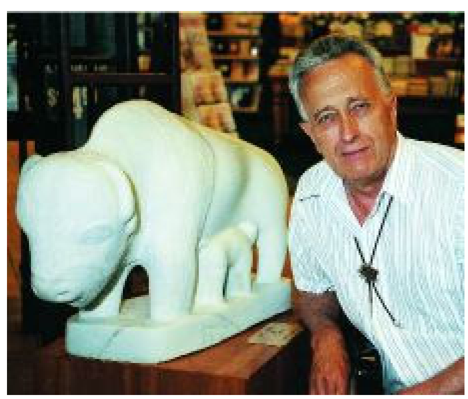
One example of how green chemistry has found solid footing in an undergraduate program is the University of Oregon's green organic chemistry lab course. Over the past few years, associate chemistry professor James E. Hutchison, chemistry professor Kenneth M. Doxsee, and a team of graduate students have developed greener experiments that teach the same principles as a traditional undergraduate organic lab (http://www.uoregon.edu/~hutchlab/greenchem).

The basis for developing the green organic lab, Hutchison noted, is to meet the need for students to comfortably step into an industrial setting now that chemical companies are embracing green chemistry. In the experiments, which focus on the use of less toxic solvents and reagents, students are taught to consider the environmental cost of the chemistry they are doing, he said. The students are regularly required to evaluate the chemical hazards associated with a method and learn to take appropriate precautions, he explained, as opposed to taking the stance that all chemicals are hazardous.

An advantage of the cleaner syntheses is that students can use larger volumes of chemicals in the labs, reversing a 20-year trend toward microscale experiments. Microscale labs use smaller amounts of chemicals to reduce costs and the amount of waste that needs to be treated, but they also require specialized glassware that students aren't likely to see again, Hutchison pointed out.

The success of the Oregon lab program has been enormous: The chemistry department earlier this year received two NSF grants totaling $635,000 to promote its green chemistry efforts, and this fall all organic lab students will follow the green lab procedures. The Oregon chemists also have been working with EPA and ACS to develop new course materials and are writing a green lab course textbook that will be published within the next year.

Teaching students green chemistry early on, Hutchison believes, helps to make them "green ambassadors." When students complete the lab course, he said, the instructor charges them to take their unique skill set and go out into the chemistry community to spread the word about green chemistry.



SUSTAINABILITY **Sievers poses with a marble sculpture he carved, "Nurturing the Young,"**

A QUESTION RAISED during one conference talk was, "Is green chemistry alone powerful enough to lead chemistry to a sustainable future?" The answer turned out to be no, that a little "Verbund" is also needed.

Verbund, loosely translated as integrated systems, is a networking approach that combines isolated company functions with social interests in product development to improve overall efficiency. Verbund was started at BASF's Ludwigshafen, Germany, complex several years ago, and has spread to BASF sites worldwide.

which will go on permanent display in August at the University of Colorado's Alumni Center. The sculpture is a reminder of the sacred role of the buffalo in providing nearly all the needs of the Plains Indians, Sievers said, who were masters of sustainability. The near extinction of the buffalo by overhunting in the 19th century is a further reminder of the need for stewardship of Earth's current natural resources, he added.

"We have to develop better strategies and cleverer ways to improve, and we need a guiding framework," noted Hermann Pütter, BASF's manager for R&D electrochemical processes. "Verbund means looking for better ideas, asking better questions, and finding better solutions--with input from many people and resources."

While green chemistry offers principles to develop greener syntheses, Pütter noted, Verbund checks to see if using the greener synthesis makes sense in a real-life context. One example is BASF's development of the first industrial paired electrosynthesis, an old dream of organic electrochemists. In paired electrosynthesis, one product is generated at the anode and a different product is generated at the cathode.

BASF already used a green anodic process to make aromatic aldehydes, Pütter explained, and was looking at a green process to make phthalide, a fungicide intermediate. But instead of building a new plant to produce phthalide alone by a greener method--catalytic hydrogenation--Verbund suggested in this case that it would be better to use a less green cathodic process to make the compound along with the aromatic aldehyde in the paired electrosynthesis. The overall process turned out better than the two processes alone could have, Pütter said, with 200% electrode efficiency, no by-products, and the savings from not building a chemical plant.

In some ways, Verbund is like the Six Sigma business-improvement process that has made inroads in major U.S. businesses such as Motorola, General Electric, DuPont, and Dow Chemical (C&EN, June 18, page 23). Six Sigma is a companywide effort to reexamine projects to discover the root causes of problems with the idea of optimizing a product to make it better. With Six Sigma, nearly all of the projects have a targeted dollar savings associated with them.

Verbund, Six Sigma, the chemical industry's Responsible Care program, and the triple bottom-line business strategy that combines a commitment to profit, ecology, and social responsibility are all concepts that share the goals of at least some part of the 12 Principles of Green Chemistry. And as several conference attendees commented, all of these concepts are going to be needed to meet the target of global sustainability.

"This is not the time to back away from our responsibility as scientists and engineers," remarked Joseph A. Miller Jr., the former head of DuPont R&D who recently retired after 35 years with the company. "Our approach to dealing with sustainability--green chemistry, green engineering--must be multifaceted. We need to collaborate and cooperate. We need to integrate our disciplines to create the capacity to deal with these challenging issues. We need to find ways to bring science, technology, and policy closer together."

Miller focused his plenary lecture on DuPont's commitment to achieve zero waste generation and to develop new products and processes that have increasing margins of safety for human health and the environment. He added that leadership by citizen-scientists is needed to move forward and deal with the pressing issue of K–12 science and math education, and he urged those in the audience to become involved in classrooms, curriculum development, assessment, and change.

AS A LONGTIME environmental advocate, the University of Colorado's Sievers captured the sentiments of many of the conference attendees in his remarks at the opening plenary session: "I believe we live in a time of great peril as chemists. We are told that the public has a reasonably good impression of the word 'chemistry.' But it has a very bad image of 'chemicals,' and often 'toxic' is coupled to suggest 'toxic chemicals.' Since chemicals are what we work with, our profession has a serious problem.

INTERNATIONAL Young chemical professionals from 16 countries and their instructors spent three days exploring the principles of green chemistry in a workshop prior to the CHEMRAWN conference. PHOTO BY ERIC NEURATH

"We live in an era of progressively poorer scientific literacy," he continued, "and while chemistry and related sciences and industry have brought society lifesaving drugs, more food, better nutrition, mobility, and contributed to a prosperous economy, chemophobia and scare tactics have characterized chemicals as hazardous and unnatural. The critical issue is how chemists can mobilize green chemistry research and education so that it contributes directly to sustainability."

The Plains Indians were masters of sustainability, Sievers noted, and the buffalo was at the center of their stewardship of the Great Plains for centuries. The buffalo provided food, clothing, and shelter--nothing was wasted: bones became tools and droppings were fuel, he added. But the near extinction of the buffalo by overhunting in the 19th century essentially voided that sustainability.

"The care and skill with which we manage our resources, with which we do our science, with which we introduce to our students the appropriate environmental ethic will determine whether our profession and perhaps civilization as we know it will be sustainable," Sievers concluded.

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STRATEGIES

Twelve Principles Of Green Chemistry

Prevention It is better to prevent waste than to treat or clean up waste after it has been created.

Atom Economy Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

Less Hazardous Chemical Syntheses Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Design Safer Chemicals Chemical products should be designed to effect their desired function while minimizing their toxicity.

Safer Solvents and Auxiliaries The use of auxiliary substances--solvents, separation agents, and others--should be made unnecessary wherever possible and innocuous when used.

Design for Energy Efficiency Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Use Renewable Feedstocks A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Reduce Derivatives Unnecessary derivatization--use of blocking groups, protection/deprotection, and temporary modification of physical/chemical processes--should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

Catalysis Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Design for Degradation Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

Real-Time Analysis for Pollution Prevention Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Inherently Safer Chemistry for Accident Prevention Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

SOURCE: "Green Chemistry: Theory and Practice," Paul T. Anastas and John C. Warner. New York: Oxford University Press, 1998.

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HISTORY
Foundations Of Green Chemistry

BREEN
PHOTO BY BETTE HILEMAN

Green chemistry is a science-based, nonregulatory, economically driven approach toward sustainable development that has grown substantially since the concept fully emerged a decade ago. A key event that generated broad interest in sustainable development was the release of the 1987 United Nations report "Our Common Future." In the report, sustainable development is defined as development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

"This statement marked a recognition by environmental activists that economic growth and development are necessary to meet the needs of the world's expanding population," commented J. Michael Fitzpatrick, president and chief operating officer of Rohm and Haas, who spoke at CHEMRAWN XIV last month. "And it also marked the recognition by industry that growth must be accomplished in a way that recognizes the needs of society to conserve resources and the environment for future generations."

In the U.S., interest in green chemistry began in earnest with the passage of the Pollution Prevention Act of 1990, which was the first environmental law to focus on preventing pollution at the source rather than dealing with remediation or capture of pollutants--the so-called end-of-the-pipe solution. The new law led the Environmental Protection Agency to establish its Green Chemistry Program in 1991 within the Office of Pollution Prevention & Toxics. The term "green chemistry" was coined and first defined at that time by EPA's Paul T. Anastas, an organic chemist who is now at the White House Office of Science & Technology Policy.

EPA has since collaborated with academia, industry, and other government agencies to promote the use of chemistry to develop new technologies for pollution prevention. One outcome of these collaborative efforts was the establishment in 1995 of the Presidential Green Chemistry Challenge Awards (C&EN, July 2, page 24). The awards were created as a competitive effort to promote and recognize the development of environmentally benign chemical products and manufacturing processes. National green chemistry awards also have been established in the U.K., Australia, Italy, and Germany.

Another important event that has rallied proponents of green chemistry was the development of the 12 Principles of Green Chemistry by Anastas and chemistry professor John C. Warner of the University of Massachusetts, Boston.

A third key result of early efforts in green chemistry is the Green Chemistry Institute (GCI). The institute was originally organized on the Internet as a virtual nonprofit organization in May 1997 by a group of representatives from industry, academia, national labs, and other organizations. GCI's mission is to facilitate industry-government partnerships with universities and national laboratories to develop economically sustainable clean-production technologies. GCI now has affiliate chapters in 17 countries.

"One of the issues focused on at GCI is the evolution of environmental science," GCI Director Dennis L. Hjeresen noted. "During the past 10 to 15 years, there has been a tremendous growth in understanding in the individual disciplines of environmental science."

But much more work will be needed in the coming years to address growing natural resource needs, Hjeresen pointed out. "A question GCI will try to address is how to put green chemistry higher on the agenda than just in the academic realm to make it a viable tool for everyone."

GCI formed an alliance with the American Chemical Society at the beginning of this year, following efforts by Hjeresen and ACS Immediate Past-President Daryle H. Busch to increase ACS's role in addressing the theme of chemistry and the environment. GCI has established an office at ACS headquarters in Washington, D.C., and ACS is providing core funding for the institute.

One person in the thoughts of many attendees at CHEMRAWN XIV was the late Joseph J. Breen, who died from pancreatic cancer in July 1999. Often referred to as the "heart and soul of green chemistry," Breen had a 20-year career at EPA working in the Office of Pollution Prevention & Toxics before he retired. Breen was the founding director of GCI, and at the time of his death he was serving as the organizing chair of CHEMRAWN XIV.

A number of resources are available on the Internet to learn more about green chemistry: EPA's Green Chemistry Program, http://www.epa.gov/greenchemistry; ACS's green chemistry website, http://www.chemistry.org/education/greenchem; the Green Chemistry Institute, http://www.lanl.gov/greenchemistry; and the Royal Society of Chemistry's Green Chemistry Network, http://www.chemsoc.org/networks/gcn/index.htm.

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