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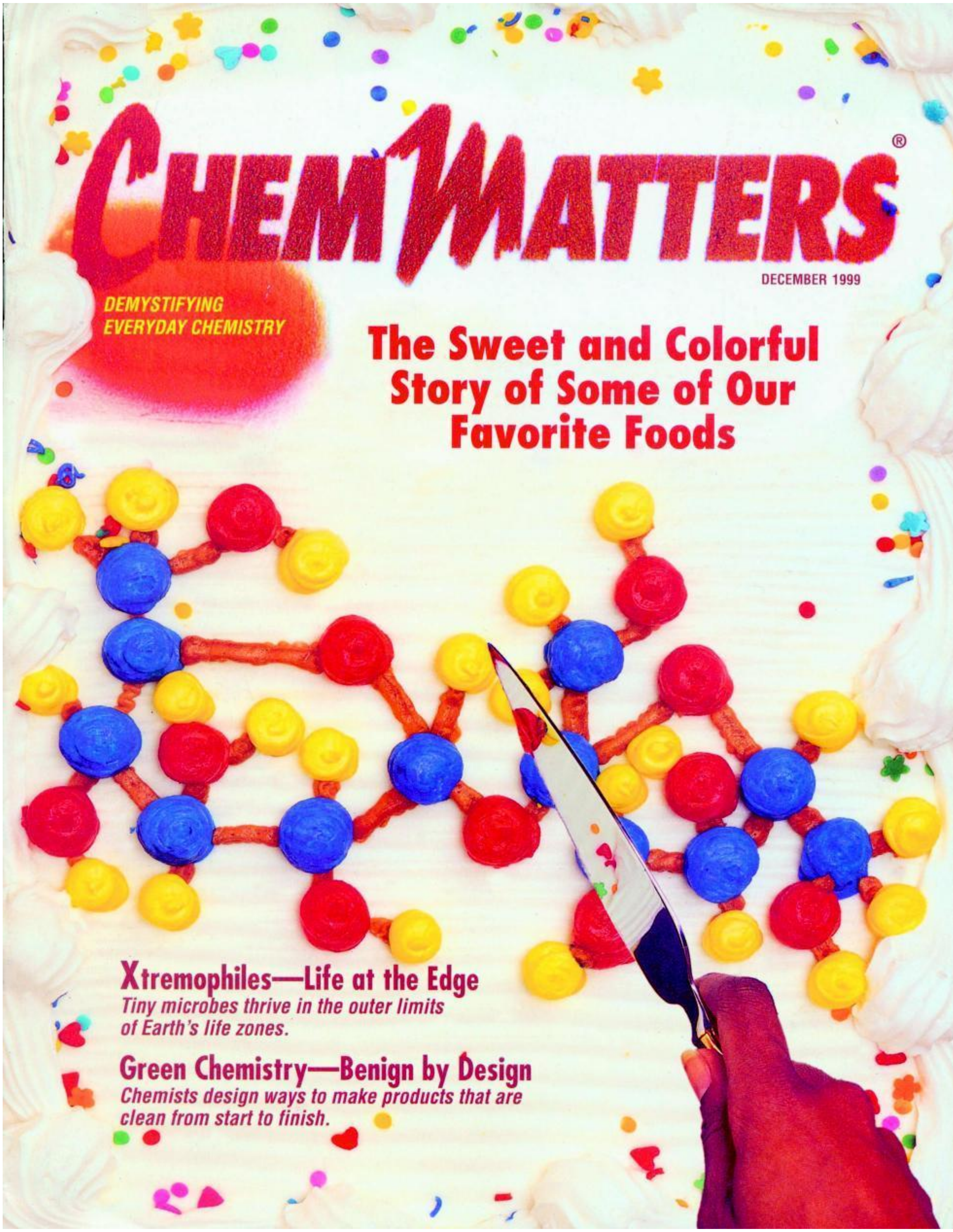

Green Chemistry

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Benign by Design

By Mary Ann Ryan

PHOTO COURTESY OF CANOLA COUNCIL OF CANADA

Chemistry, the source of many of the products we enjoy and take for granted, earns well-deserved credit for the high standard of living we enjoy today. We can thank the efforts of chemists for the gasoline that powers our cars, the pain relievers we take for our headaches, Styrofoam cups that keep our hot drinks hot and our cold drinks cold, and even the paper this magazine is printed on. But it is also true that the production of these and other materials can have undesirable environmental effects. Over the past few decades, news reports have described numerous examples of industrial processes that cause harm by polluting our land, water, and air. Damage to the environment and to human health as a result of chemical manufacturing remains a major global concern.

An effort to ensure a safer, cleaner environment for the 21st century, the green chemistry movement has been gaining momentum in recent years. Basically, green chemistry is an effort toward eliminating pollution by making chemical products that do not harm either our health or the environment, and by using production processes that reduce or eliminate hazardous chemicals. Green chemistry prevents pollution at its source rather than cleaning up the mess later.

Think about it this way. We know it is better to maintain our good health in the first place than to take medicines after we get sick. Chemists are thinking about chemical processes in the same way. They are using their knowledge of chemistry to analyze the current ways of making things. By doing so, they are designing safer and cleaner approaches to manufacturing the products we need.

To promote these efforts and to recognize the most successful ones, President Clinton announced the establishment of the Presidential Green Chemistry Challenge Awards in 1995. On behalf of the President, the Environmental Protection Agency (EPA) has presented awards each year since 1996. As Dr. Paul Anastas of the EPA Office of Pollution Prevention and Toxics explains, "The Green Chemistry Challenge Awards Program provides national recognition for chemistry that incorporates the principles of green chemistry into chemical design, manufacture, and use." Today, these awards are the only Presidential-level recognition of accomplishments in the chemical sciences.

The Pyrocool Award: Putting out fires the green way

At one time, water virtually was the only chemical that firefighters had to put out fires. However, some fires cannot be easily extinguished by using water. When materials like oil ignite, the use of water can actually cause the fire to spread. Consequently, in the 1960s, the U.S. Navy developed fire-blanketing chemical foams to combat fires from oil spills. Other types of foams were designed to put out fires resulting from wood or paper. Halon compounds—chemicals such as bromotrifluoromethane (CF_3Br)—are useful on fires in rooms with electronic equipment, like computer centers, because they leave no residues upon evaporation. All of these new substances have improved fire fighting, but they have also exacted a price on the environment.

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The millions of tons of chemical fire-fighting agents used worldwide have discharged into the environment toxic substances like hydrofluoric acid (HF) and other dangerous fluorine-containing compounds. Sometimes, these chemical foams contaminate water supplies, causing wastewater treatment systems to fail by preventing bacteria from breaking down waste in the water. Some fire-fighting chemicals lead to depletion of the protective layer of ozone in the Earth's stratosphere—a layer that helps to block out harmful ultraviolet radiation that can cause skin cancer and cataracts.

In response to this serious problem, Pyrocool Technologies, Inc., a small company in Lynchburg, VA, invented a foam called Pyrocool F.E.F. (Fire Extinguishing Foam) that includes none of the harmful substances found in other fire-fighting materials. The compounds that make up Pyrocool F.E.F. are rapidly *biodegradable* or easily digested by bacteria in the environment to simpler substances. In addition, they are nontoxic and work faster to put out fires than other extinguishing compounds. And the foam works at a lower concentration than is needed for other substances, so that less is required to do an effective job. For developing this valuable new product for putting out fires without damage to the environment, Pyrocool received a 1998 Presidential Green Chemistry Challenge Award.

Pyrocool Fire Extinguishing Foam puts out fires without releasing harmful gases into the atmosphere that can deplete the planet's protective ozone layer.

COURTESY OF PYROCOOL TECHNOLOGIES, INC.

The Biofine Award: Turning pulpy waste products into something green

The ideal starting material or "feedstock" for large-scale chemical manufacturing of products would be something that is renewable, whose use, therefore, would not deplete valuable natural resources. Yet the vast majority of chemical products made in the United States today are not from such sources, but rather are ultimately derived from petroleum reserves that have taken millions of years to build up in the earth. Realistically, we cannot consider oil reserves to be renewable. Furthermore, some petroleum-based feedstocks are hazardous. Benzene (C_6H_6), for example, is a carcinogen. Consequently, efforts have been under way to identify renewable feedstocks such as those from biological sources. Cellulose, starch, and sugars are examples of plant-based materials that can serve as renewable resources.

COURTESY OF PYROCOOL TECHNOLOGIES, INC.

The Biofine Company of Waltham, MA, recognized the importance of using renewable feedstocks that are needlessly going to waste at present. Biofine received a 1999 Presidential Green Chemistry Award for developing a process that converts waste products containing cellulose into a chemical called levulinic acid ($C_5H_8O_3$). A promising chemical building block that serves as the starting material for a wide variety of commercial chemicals, levulinic acid has already been used to develop a biodegradable herbicide, an economical fuel additive that makes gasoline burn more efficiently, and new biodegradable polymers. The Biofine process produces levulinic acid for a fraction of the cost of alternative methods for making it.

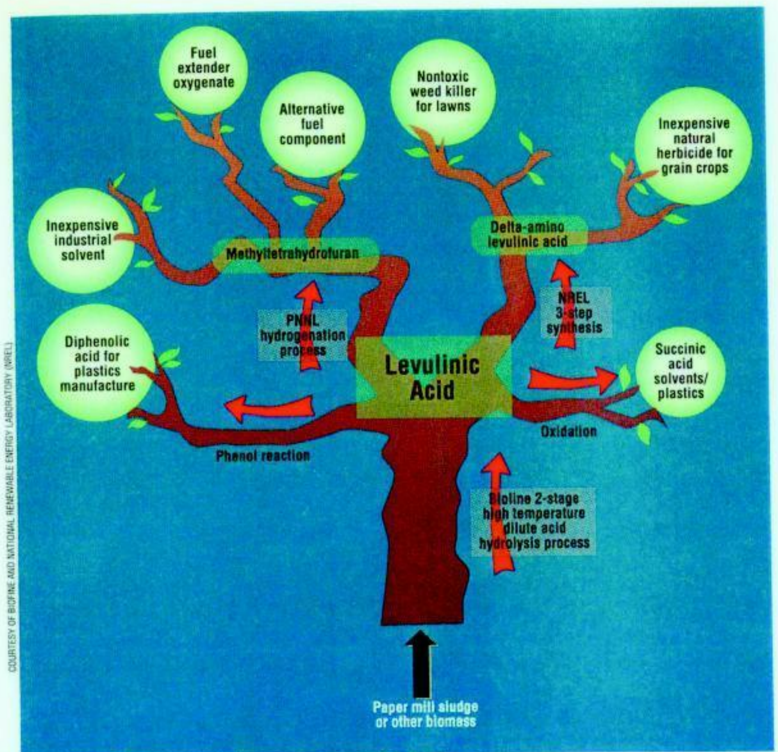
According to the Biofine Company, municipal solid waste consists of 60–70% cellulose in the form of cardboard, paper, and wood, much of which is not recyclable. Such waste is generally dumped in landfills, incinerated, or composted—all methods of disposal that add little value, can be costly, and for the most part, aren't very popular. Who wants a smelly incinerator or a landfill in their neighborhood? Biofine's process converts this waste into valuable products. Conversion of paper mill sludge—cellulose-containing waste that results from the production of paper—into levulinic acid could help paper mills to reduce their waste discharge to nearly zero.

The Dow award: Polystyrene foam goes green

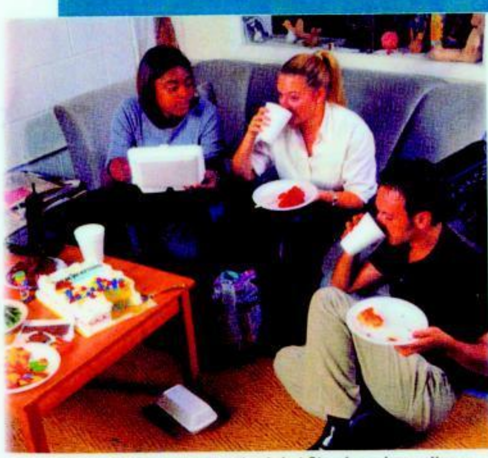
Polystyrene foam, made by the Dow Chemical Company as Styrofoam, is the material that is often used for carry-out coffee cups, meat, and poultry trays, and the molded packaging that surrounds electronic equipment. The foam has good thermal insulation properties, is moisture resistant, and can be recycled.

Before being converted into the foam packaging we know, polystyrene is a hard, brittle, plastic material. The manufacturing process used to transform it requires a *blowing agent*—a substance that is forced through molten polystyrene and then expands to form bubbles or gas pockets in the polystyrene. It is the high percentage of trapped gas in the final, cooled product—about 95% gas and 5% polystyrene—that results in the lightweight foam used to make food trays or containers.

The blowing agents historically used for making polystyrene foam were chlorofluorocarbons (CFCs), in particular, one called



The Biofine Company found a way to turn the sludge from paper manufactuing into a renewable feedstock for a variety of clean products.



You probably haven't noticed, but Styrofoam has gotten a lot greener. Dow chemists have replaced environmentally harmful CFCs with CO_2 to make the foam.

CFC-12, which has the chemical formula CCl_2F_2. These compounds had a number of practical advantages; for example, they were cost-effective, nonflammable, and safe to handle. However, CFCs were found to harm the environment in a manner similar to some of the first fire-fighting foams noted earlier—by causing ozone depletion in the earth's upper atmosphere. Consequently, the production of CFC-12 in the United States was banned in 1995. Several replacement compounds, such as HCFCs (hydrochlorofluorocarbons) or pentane (C_5H_{12}), were found to reduce the environmental risk to some extent, but still were not problem-free.

To eliminate the use of environmentally damaging chemicals, Dow developed a new process for which the company received a Presidential Green Chemistry Award in 1996. This innovative process uses 100% carbon dioxide (CO_2) as a blowing agent. CO_2 is a safe, readily available substance that does not deplete the ozone layer and is cost-effective. Although overproduction of CO_2 can lead to global warming, Dow's process avoids this potential problem by using only CO_2 that is already available—either from natural gas wells or byproducts from plants that produce ammonia. No additional CO_2 is generated to make the polystyrene foam. Dow estimates that the use of CO_2 as a blowing agent has reduced the use of CFCs and other harmful chemical agents by 3.5 million pounds per year.

Toward a greener century

The above examples give only a hint of the many ways in which green chemistry can deliver results that are scientifically sound, cost effective, and safe. Not only is green chemistry the environmentally responsible thing to do, it is also becoming the most practical thing for businesses to do. The costs of cleaning up hazardous wastes have grown substantially as companies grapple with the host of federal, state, and local environmental laws enacted since 1970. If companies can identify cleaner processes that are also cost-effective, they can become more profitable by reducing costs of environmental cleanup. In other words, "green" can be practical, profitable, and protective of the planet.

Editor's Note This article is the first of a series of articles on green chemistry that will appear in futures issues of *ChemMatters*. Watch for more stories about chemists who have designed ways to produce the things we need without polluting the planet. Know some good examples in your community? Write to us at chemmatters@acs.org.

Mary Ann Ryan is a science writer and former chemistry teacher. She serves as coordinator for a project jointly sponsored by the American Chemical Society and EPA to develop educational materials on green chemistry.

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