

# **Appendix A**

## **Descriptions of the 25 Case Studies**

This report is based on 25 case studies of the Next Generation Environmental Technologies (NGETs) listed in Table A1.<sup>1</sup> As described previously, we identified potential case studies from a number of sources, primarily applicants for the U.S. Environmental Protection Agency's (EPA's) Presidential Green Chemistry Challenge Awards Program but also from surveys of the literature and suggestions from persons in the field.<sup>2</sup> We chose cases covering a wide range of technologies, in differing stages of development and commercialization, and in varying economic sectors. We limited our choices to technologies that have near-term application (though some may have long-term benefits as well) and do not include fundamental research. We also focused on cases where appropriate information was available.

Each case study, to the extent possible, describes the underlying chemistry, the short- and potential long-term benefits of the technology, the commercializing firm(s), the incentives that caused those firms to adopt the technology, the government role in the technology's progress, and the barriers that have slowed the technology's adoption. More information is available in some cases than in others. In some cases, our sources do not contain information in all areas we wished to examine. Where information is lacking, we leave blanks under the appropriate heading. A blank under a heading on incentives to adopt given technology or on government's role in diffusing technology does not mean that there are no incentives or any role for government to play; rather, it indicates merely that there is no available information on this, or that the available information is neither definitive or even exemplary.

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<sup>1</sup>Articles and books in the *Green Chemistry General Reference Annotated Bibliography* (<http://center.acs.org/applications/greenchem> or [www.chemistry.org/education/greenchem](http://www.chemistry.org/education/greenchem)) discuss the chemistry of many of these cases.

<sup>2</sup>EPA's Presidential Green Chemistry Challenge Awards represent a significant effort in publicizing green chemistry-based technologies and helping developers of some technologies recognize that they are indeed members of the green chemistry community.

**Table A1. List of Case Studies.**

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Before reporting on each case study, it is useful to consider the range of technologies considered here. Table 2 in the main body of the report arrays the cases according to two key factors relevant to our overall conclusions: the primary benefit provided by the technology and the technology's stage of development. Here it is useful to consider how our case studies span the industries currently benefiting from NGETs and the green chemistry research areas that may help fulfill the promise of green chemistry.<sup>3</sup>

There are a variety of green chemistry areas that aid in fulfilling the promise of green chemistry. The "Twelve Principles of Green Chemistry" are intended for teaching purposes, general guidance, and to represent the spirit of green chemistry. Discussions of the research areas that might lead to green chemistry development often focus on the following seven areas:<sup>4, 5</sup>

### **1. Selection of feedstocks**

Selecting alternative feedstocks can help reduce the hazardous properties of starting materials. This can alleviate health and safety concerns at the same time as eliminating the ability of the materials to enter into the environment. Using preferable sources such as renewable feedstocks helps ensure availability of starting materials into the future.

### **2. Use of natural processes**

- Use of renewable feedstocks
- Fermentation using immobilized cells or free cells
- Use of enzymes as biocatalysts conducting a single reaction
- Use of multicellular organisms (animals or green plants) to process renewable feedstocks

### **3. Selection of reagents and catalysts**

- Reduce the hazardous properties
- Reduce the waste generated
- Improve product selectivity
- Improve reaction efficiency

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<sup>3</sup>For a discussion of the technology opportunities, direction, goals, and potential benefits of "New Process Chemistry," see the Technology Roadmap, [http://www.oit.doe.gov/chemicals/visions\\_new\\_chemistry.shtml](http://www.oit.doe.gov/chemicals/visions_new_chemistry.shtml).

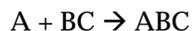
<sup>4</sup>OECD Environmental Health and Safety Publications, Series on Risk Management No. 10, Proceedings of the OECD Workshop on Sustainable Chemistry, Venice, October 15–17, 1998, pp. 204–205.

<sup>5</sup>Pietro Tundo, Paul Anastas, David StC. Black, Joseph Breen, Terrence Collins, Sofia Memoli, Junshi Miyamoto, Martyn Polyakoff, and William Tumas, "Synthetic Pathways and Processes in Green Chemistry: Introductory Overview" *Pure Appl. Chem.* Vol. 72, No. 7, 2000, pp. 1207–1228.

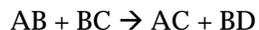
- Reduce quantity needed

#### **4. Alternative synthetic transformations**

- Additions are good:



- Substitutions are not so good:



- Eliminations are probably the worst:



#### **5. Selection of solvents and reaction conditions**

- Five of the top ten chemicals released are solvents (methanol, toluene, xylene, methyl ethyl ketone, and  $\text{MeCl}_2$ ), which account for 27 percent (weight) of total Toxics Release Inventory (TRI) chemicals.
- Reduce general hazards
- Reduce hazards to human health
- Reduce hazards to environment

#### **6. Selection of products and the design of safer chemicals**

- Determine the mechanism of action
- Evaluate structure-activity relationship
- Eliminate toxic functional groups
- Reduce bioavailability
- Design innocuous fate

#### **7. Minimize energy consumption**

- Reduce activation barriers to chemical reactions
- Reduce mechanical, thermal, and other energy inputs

As shown in Table A2, the case studies encompass each of these areas, and each area contributes to several types of benefits either directly or indirectly. The numbers are listed in the boxes to show the primary area and primary benefit described in each case study. This is not meant to be limiting in that some areas may still contribute in some large way to a given benefit that is not yet known or was not considered in this study. The generation of the matrix is merely to illustrate that the seven areas of green chemistry can span multiple benefits, and each benefit can be attained through various different areas of green chemistry research.

The rows categorize technologies by the primary type of benefit provided. All the entries in the “economic” row were (or have the potential to be) adopted because they save the firm money or create new or improved products with greater value to customers. The entries in the other columns provide benefits demanded by society, often through regulations, that cost the firm money to provide. However, the cases here are often the lowest cost means available for the firm to provide these benefits. Although we list each technology only once, many provide benefits in multiple categories, as seen in Table 1 of the main report. This is not meant to be limiting, in that areas may still contribute in some large way to a given benefit that is not yet known or was not considered in this study.

**Table A2. The benefits provided by different green chemistry areas.** Numbers show case studies. Colors show the level of benefit: Green (dark shade): directly affects the benefit; Yellow (medium shade): indirectly affects the benefit; No Color: does not necessarily affect the benefit.

<b>Green Chemistry Area →</b>  <b>Benefit ↓</b>	<b>Alternative Feedstocks</b>	<b>Natural Processes; Biocatalysis, Fermentation</b>	<b>Alternative Reagents; Improved Catalysis</b>	<b>Alternative Synthetic Pathway</b>	<b>Alternative Solvent or Reaction Condition</b>	<b>Selection of Products and the Design of Safer Chemicals</b>	<b>Minimize Energy Consumption</b>
<b>Environmental</b>	3	4- g,m,n,o,p,u,v,w,y,ee, pp,uu,vv	10,15	6,21,22	1,13,14,16, 17,19	18,20	
<b>Security</b>			8				
<b>Health and Safety</b>				5		9	
<b>Economic</b>		4-a,b,c,d,e,f,i,j, k,l,q,r,t,x,z, aa,bb,cc,dd,ff,gg, hh,ii,jj kk,ll,mm,nn, oo,qq,rr,ss,tt	12	2,23,24,25		7	11

Another means of describing the cases in context is to understand the industries affected in each type of green chemistry area. As shown in Table A3, each area has the potential to contribute to a wide variety of industries. Once again, the general areas of green chemistry can span multiple industries, and each industry may have at its disposal a variety of green chemistry techniques and manufacturing processes to affect its business. The case studies used in this study span all major industrial categories. It should be noted that a blank in the matrix does not necessarily mean that that area of green chemistry cannot affect a given industry.

**Table A3. The industries potentially benefiting from different types of provided by Green Chemistry areas.** Numbers show case studies. Colors show the level of benefit: Green (dark shade): directly affects the benefit; Yellow (medium shade): indirectly affects the benefit; No Color: does not necessarily affect the benefit.

<b>Green Chemistry Area →</b>  <b>Industry</b>  ↓	<b>Alternative Feedstocks</b>	<b>Natural Processes, Biocatalysis, Fermentation</b>	<b>Alternative Reagents; Improved Catalysis</b>	<b>Alternative Synthetic Pathway</b>	<b>Alternative Solvent or Reaction Condition</b>	<b>Selection of Products and the Design of Safer Chemicals</b>	<b>Minimize Energy Consumption</b>
<b>Metal Mining</b>		4-n,o,y					
<b>Electric, Oil, Gas, and Sanitary Services</b>		4-q,s	8			7	
<b>Chemicals and Allied Products (pharmaceuticals)</b>	3	4-c,d,e,f,g,i,l,p t,u,v,x,z,aa,bb,cc,ee,gg,ll, nn pp,tt,	10,12	2,5,21,23,24,25	1,16,17	9,18,20	
<b>Primary Metals</b>				22		13	11
<b>Paper and Allied Products</b>		4- m	15	6			
<b>Food and Kindred Products</b>		4-a,j,k,r,dd,ff,hh,ii,jj,kk, mm,oo,qq,rr,ss					

# 1. Supercritical or Liquid CO<sub>2</sub> as Solvent

## Introduction

Carbon dioxide can exist in a variety of states, depending on the conditions—liquid, solid, gaseous, and as a supercritical fluid. Supercritical fluids exist at a temperature and pressure greater than or equal to the critical temperature and pressure of the fluid. The critical pressure for CO<sub>2</sub> is about 1,100 pounds per square inch (psi), and the critical temperature is about 31 degrees C. Supercritical applications using CO<sub>2</sub> typically operate at temperatures between 32 degrees C and 49 degrees C and pressures between 1,100 psi and 3,500 psi. At supercritical temperatures and pressures, CO<sub>2</sub> has properties between those of a liquid and a gas, particularly a lack of surface tension. This means supercritical CO<sub>2</sub> (SCCO<sub>2</sub>) can adapt to intricate molecular geometry to extract oils and other organic contaminants from cracks and crevices or from other materials. Although supercritical fluids were discovered more than 100 years ago, it was not until the 1970s that a commercial application was adopted—decaffeination of coffee. SCCO<sub>2</sub> now is being used in many separation and cleaning applications.<sup>6,7,8</sup>

Carbon dioxide is just beginning to be used in the dry-cleaning industry. There are still few machines (60 from Micell by 2001) using SCCO<sub>2</sub> technology in the roughly 35,000 dry-cleaning establishments in the United States and 150,000 worldwide. Nearly 85 percent of dry cleaners use perchloroethylene (PCE) for their cleaning solvent, and nearly all the rest use other chlorinated solvents such as trichloroethane or trichloroethylene. Replacing these machines with those using SCCO<sub>2</sub> technology could offer immediate benefits for the environment and for worker health and safety and could eliminate nearly 95,000 tons per year of hazardous air pollutants and 51,000 tons per year of petroleum emissions.<sup>9</sup>

Realizing such benefits depends on whether this particular green technology can be adapted on a large scale. The net benefits of such technology must also be considered in light of the energy trade-off between use of CO<sub>2</sub> and other technologies. Using SCCO<sub>2</sub> in dry cleaning, for example, results in a net increase of energy use owing to the power needed for equipment to generate liquid CO<sub>2</sub>. We consider these issues in the use of CO<sub>2</sub> as a cleaning solvent, as a means of decaffeinating coffee, as a solvent in polymerization of amorphous fluoropolymers, and in a number of other growing applications.

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<sup>6</sup>Paul Randall and Douglas Williams, *Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing*, EPA, EPA/625/R-93/016, February 1994.

<sup>7</sup>Donald M. Mattox, "PVD Processes: Cleaning with CO<sub>2</sub>," *Plating and Surface Finishing*, No. 82, May 1995, p. 130.

<sup>8</sup>L. J. Snowden-Swan, *Supercritical Carbon Dioxide Cleaning Market Assessment and Commercialization/Deployment Plan*, Richland, Wash.: Pacific Northwest National Laboratory, PNL-10044, August 1994.

<sup>9</sup>Office of Compliance, EPA, *EPA Office of Compliance Sector Notebook Profile of the Dry Cleaning Industry*, EPA/310-R-95-001, September 1995. Available at <http://es.epa.gov/oeca/sector/sectornote/pdf/dryclng.pdf>.

# Cleaning

## *Chemistry*

More than 34 billion pounds of halogenated and other organic solvents are used worldwide each year in precision cleaning of parts and equipment and in dry cleaning of garments.<sup>10</sup> The market for these solvents has declined as environmental pressures have grown against use of popular volatile organic compounds (VOCs) and chlorinated products. A variety of promising new technologies offer an alternative to these solvents.

There are many benefits to using carbon dioxide as a solvent. Carbon dioxide exists naturally in the atmosphere and is created in a range of industrial processes, including as a by-product in the formation of ammonia, hydrogen, and ethanol plants, as well as during the combustion of carbonaceous fuels for power generation. Recovering and using the large amount of carbon dioxide otherwise released into the atmosphere can be both cost effective and a means of recycling emissions resulting from other uses. Such recycling can also help satisfy environmental regulations; controlling and reducing emissions of greenhouse gases such as carbon dioxide is an objective of emission trading mechanisms, offset rules, as well as many voluntary commitments by industry.

Carbon dioxide is also an attractive solvent because it is environmentally and chemically benign (assuming that the use of CO<sub>2</sub> technology does not result in a net increase of carbon dioxide in the atmosphere). Unlike many halogenated and volatile organic compounds, carbon dioxide does not degrade in the atmosphere and can be completely removed from products.

Carbon dioxide alone can dissolve small molecules, but pure carbon dioxide in either a liquid or supercritical state is a very poor solvent for industrial applications and had few such applications until special surfactants were developed.<sup>11</sup> Compounds that are particularly insoluble in liquid or supercritical carbon dioxide include most polymers, waxes, heavy oils, machine-cutting fluids, solder fluxes, proteins, salts, and metal oxides. Researchers have developed cosolvents and better surfactants to aid in making insoluble CO<sub>2</sub> compounds soluble for such cleaning applications.<sup>12, 13</sup>

These cleaning additives may have to be specially formulated for use with liquid CO<sub>2</sub>. Surfactants designed by Joseph M. DeSimone, for example, have increased the solubility of various materials for

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<sup>10</sup>Kerri A. Walsh, "Oxygenated Products Survive Global Slump," *Markets and Economics*, February 13, 1996, p. 38.

<sup>11</sup>J. B. McClain, D. Londono, J. R. Combes, T. J. Romack, D. A. Canelas, D. E. Betts, E. T. Samulski, G. Wignall, and J. M. DeSimone, "Design of Non-Ionic Surfactants for Carbon Dioxide," *Science*, No. 274, 1996, pp. 2049–2052.

<sup>12</sup>J. M. DeSimone and J. S. Keiper, "Surfactants and Self-assembly in Carbon Dioxide," *Current Opinion in Solid State and Materials Science*, No. 5, 2001, pp. 333–341.

<sup>13</sup>S. L. Wells and J. M. DeSimone, "The Carbon Dioxide Technology Platform: An Important Tool for Environmental Problem Solving," *Angew. Chem.* No. 113, 2001, pp. 518–527.

polymerizing fluoromonomers.<sup>14</sup> The following table summarizes the characteristics of CO<sub>2</sub> and other cleaning solvents.<sup>15</sup>

**Table A4. Cleaning Technology Characteristics of Cleaning Solvents**

<b>Characteristics</b>	<b>Chlorinated solvents</b>	<b>Water</b>	<b>Carbon dioxide microemulsions</b>
<b>Cleaning ability</b>	Good	Poor	Good Performance is similar to CFC performance but without ozone layer damage.
<b>Energy consumption</b>	Moderate	High Drying process (heating of metal parts) in aqueous process leads to largest energy usage.	Moderate
<b>Rusting</b>	No	Yes Flash rusting is a big problem with aqueous systems.	No
<b>Ability to leave protective coating</b>	No	No	Yes
<b>Floor space</b>	Compact	Expansive	Compact
<b>Environmental restrictions</b>	(VOCs, CFCs) Many excellent cleaning solvents were banned by the Montreal Protocol.	Water treatment	Nontoxic, nonhazardous

### ***Immediate Environmental and Economic Impacts***

The immediate impact of liquid and supercritical carbon dioxide as solvents continues to grow as the use in dry cleaning grows. Because there are relatively few dry cleaners currently using CO<sub>2</sub> technology, there is considerable room for immediate market expansion among the vast majority of establishments using chlorinated solvents that are increasingly subject to regulation. Furthermore, market assessments for this technology have uncovered several other markets in which this technology might be adapted, including cleaning gyroscopes and filling hardware; optical components; instrument bearings; computer disk drive components; medical devices; and fabrics, clothes, and rags.<sup>16</sup>

Those designing the carbon dioxide-based cleaning processes recognize the potential hazards of handling liquid carbon dioxide: it can cause suffocation in large quantities in enclosed areas, and as a solid or cold liquid it can cause burns to skin when contacted directly or by cold equipment. The process is engineered as a closed system where the used carbon dioxide is filtered, distilled, and recycled. Sensors linked to alarms monitor the site and warn users if any leakage should occur.<sup>17</sup>

<sup>14</sup>J. M. DeSimone, Z. Guan, and C. S. Elsbernd, "Synthesis of Fluoropolymers in Supercritical Carbon Dioxide," *Science*, No. 257, 1992, pp. 945-947.

<sup>15</sup>Adapted from the Pacific Northwest National Lab's supercritical fluid technology group website, available at [http://www.pnl.gov/supercriticalfluid/matrix\\_parts.stm](http://www.pnl.gov/supercriticalfluid/matrix_parts.stm).

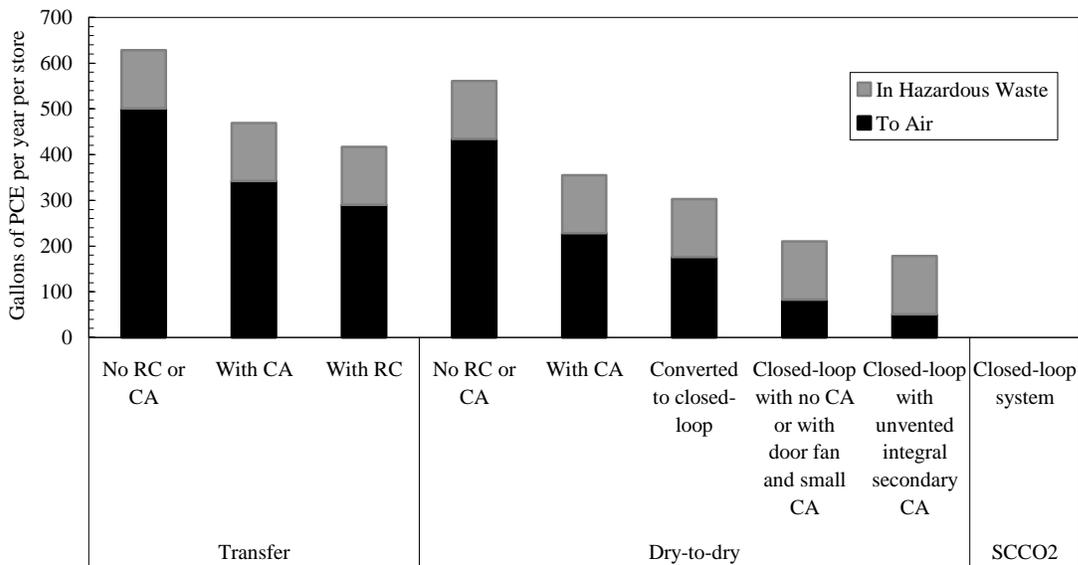
<sup>16</sup>L. J. Snowden-Swan, *Supercritical Carbon Dioxide Cleaning Market Assessment and Commercialization/Deployment Plan*, Office of Industrial Technologies (Industrial Waste Program), Pacific Northwest Lab, PNL-10044, August 1994.

<sup>17</sup>See [www.washpoint.com](http://www.washpoint.com) for a full discussion of the process and benefits.

## Long-Term Environmental Significance

Replacing cleaning technologies using halogenated and other organic solvents can have several long-term environmental benefits. PCE is one of the most heavily released chemicals in the TRI. Nearly 30 billion pounds per year of halogenated and other organic solvents are used in cleaning operations in the United States. These VOCs produce smog and ozone-depleting chemicals; replacing them could alleviate emissions problems associated with garment and parts cleaning industries. In addition to the nearly 96,000 tons of emissions currently resulting from use of dry cleaning solvents such as PCE, petroleum solvents, chlorofluorocarbons, and trichloroethane,<sup>18</sup> filtration residue in the cleaning industry leads to 47,500 tons per year of hazardous air pollutants (HAPs) disposed off site.

Other potential long-term environmental benefits abound. Using the most recent petroleum solvent emission data available for the dry-cleaning industry and a release factor of 23 pounds of solvent per 100 pounds of clothes cleaned yields an estimate of approximately 51,000 tons per year in total petroleum solvent releases currently emanating from dry-cleaning establishments. These releases are roughly split between commercial and industrial plants (there are no coin-operated dry-cleaning plants using petroleum-based solvents). More than 75 percent of the releases are from dryers; the remainder are from a combination of evaporation from filters, still releases, and fugitive emissions. All could be eliminated by universal adoption of CO<sub>2</sub> cleaning technology (although these estimates of current releases will be



**Figure A1. Comparison of a Model Facility's Emissions of PCE.** (SCCO<sub>2</sub> = supercritical carbon dioxide;

CA = carbon absorber; RC = refrigerated condenser)<sup>19</sup>

<sup>18</sup>EPA Office of Compliance, *Sector Notebook Profile of the Dry Cleaning Industry*, 1995.

<sup>19</sup>Adapted from EPA Office of Pollution Prevention and Toxics, 1998.

slightly overstated if vapor control technologies such as carbon absorbers or condensers have been added to existing machines). A reasonable comparison of the environmental benefits of supercritical carbon dioxide as a replacement for PCE as a solvent in garment cleaning is the difference in emissions of the two technologies over different expectations of future advances (Figure A1).<sup>20</sup>

In addition to its hazardous emissions, PCE often contaminates surface-water sites throughout the United States. One survey found PCE in 38 percent of 9,232 U.S. surface-water sites; releases into the soil and other sediments have also been found.<sup>21</sup> PCE has also been found in at least 771 National Priorities List (NPL) hazardous waste sites identified by EPA as the most serious in the nation<sup>22</sup> and targeted for cleanup.<sup>23</sup> As EPA looks at more sites, the number of sites known to have PCE contamination may increase.

In sum, air, land, and water releases of the chemicals associated with dry cleaning could all be reduced if a suitable substitute for current technology is found. Replacing organic compounds such as PCE with liquid carbon dioxide in dry cleaning could yield many environmental benefits, particularly if used in a closed loop system that does not increase CO<sub>2</sub> emissions to the atmosphere, as CO<sub>2</sub> is stable, nontoxic, unreactive, and can be produced from renewable resources.

### ***Commercializing Firms***

Two competing dry-cleaning systems have been developed. Applying CO<sub>2</sub> technology to dry cleaning has been suggested since 1977, but commercial realization of this goal has appeared only within the past seven years. Environmentally friendly weapon-cleaning technology developed by Raytheon has now been applied to dry cleaning.<sup>24</sup> Raytheon developed the technology with help from the U.S. Department of Energy's (DOE's) Los Alamos National Laboratory and funding from EPA's Environmental Technologies Initiative. The firm subsequently in 1995 granted exclusive rights to Global Technologies, LLC (a subsidiary of Raytheon), which sublicensed the Drywash™ Cleaning Process to a group of commercial manufacturers, each of which has developed its own equipment and chemistry.<sup>25</sup> For example, AGA/Linde developed a new carbon dioxide-based fluid called Washpoint, designed to be compatible with the competing Micell system and to help liquid CO<sub>2</sub> challenge the entrenched position of hydrocarbons and PCE in the dry-cleaning solvents market. Washpoint combines liquid CO<sub>2</sub> with an

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<sup>20</sup>Office of Pollution Prevention and Toxics, EPA, *Cleaner Technologies Substitutes Assessment: Professional Fabricare Processes*, EPA 744-B-98-001, June 1998. Available at <http://www.epa.gov/opptintr/dfe/pubs/garment/ctsa/fabricare.pdf>.

<sup>21</sup>Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological Profile for Tetrachloroethylene Draft for Public Comment*, U.S. Department of Health and Human Services, Public Health Service, August 1995.

<sup>22</sup>ATSDR, 1995.

<sup>23</sup>EPA Office of Pollution Prevention and Toxics, *Cleaner Technologies Substitutes Assessment*, EPA 744-B-98-001, June 1998.

<sup>24</sup>See [www.drywash.com](http://www.drywash.com) and [www.washpoint.com](http://www.washpoint.com).

<sup>25</sup>Including Alliance Laundry Systems, largest commercial laundry company in North America; Chart Applied Technologies, division of world's largest cryogenic equipment manufacturer; Electrolux Wascator, world's largest commercial laundry company; Sail Star USA, U.S. subsidiary of one of Asia's largest dry-cleaning equipment manufacturers; Nuevo Comeco, Spa, Europe's leading developer of pressure systems for gas technology; Caled Chemical, leading U.S. maker of detergents, additives, and filters for dry cleaning; Laidlaw Corp., U.S. maker of hangers, detergents, and additives for dry cleaners; Alex Reid, Ltd., the United Kingdom's largest provider of chemistry and consumables for dry cleaners; and AGA/Linde, the recently merged company, now the world's second-largest industrial gas company.

undisclosed “booster,” possibly a fluorine- or silicon-based surfactant. Global Technologies claims that at full productive output this group will be able to produce 4,000 machines annually for small business dry cleaners worldwide.

A second organization, Micell Technologies, has evolved from the work of J. M. DeSimone and his group at the University of North Carolina at Chapel Hill. Following the invention of polymer solutions and molecularly engineered detergents that would dissolve in liquid carbon dioxide, DeSimone, with fellow scientists Timothy Romack and James McClain and with private and corporate investors, founded Micell Technologies in 1995. Micell acquired the DeSimone patents and also know-how and patents of carbon dioxide surfactant technology from Pacific Northwest National Laboratories. Micell then developed the MICARE<sup>®</sup> system, a dry-cleaning process and manufacturing equipment that use liquid CO<sub>2</sub> just below ambient temperature (or 18 to 22 degrees C) and vapor pressure (or approximately 50 millibars). Micell adapted the basic research on CO<sub>2</sub> surfactants for use in its 16-store Hangers dry-cleaning chain. Equipment maker Cool Clean Technologies bought Hangers in 2001 and became the exclusive licensee of the technology, but Micell has since pursued other applications of CO<sub>2</sub> technology ranging from electronics to metal cleaning.

A process using liquid CO<sub>2</sub> is being developed for fabric cleaning. Liquid CO<sub>2</sub> appears to be adequate for dry-cleaning garments; ongoing research is examining all the capabilities of dry cleaning with liquid CO<sub>2</sub>.

Other commercial applications of CO<sub>2</sub> cleaning technologies include a no-clean flux in a “flip-chip” in a ceramic carrier assembly plant for IBM, a process that reportedly resulted in a 10 percent savings in assembly costs.<sup>26</sup> Researchers at Sandia National Laboratory have reported the cost for large-scale manufacturers to convert to a “no-clean” process using CO<sub>2</sub> technology would be about \$25,000 but result in savings of \$100,000 to \$200,000 per year.<sup>27</sup>

Research on a number of other applications continues at the National Science Foundation (NSF) Science and Technology Center for Environmentally Responsible Solvents and Processes and the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing at both the University of North Carolina at Chapel Hill and North Carolina State University.<sup>28</sup>

### ***Incentives to Adopt***

Tightening environmental regulations and fluctuating petroleum costs provide incentives for adopting CO<sub>2</sub> technology. EPA has regulated air emissions of PCE from dry cleaners since 1993. Dry cleaners using carbon dioxide technology report realizing other benefits from converting from technology using PCE, including the elimination of noxious fumes and odors, cleaner and safer facilities, and lower worker attrition rates. Landlords also appreciate the new technology; it can be difficult to sell a property that was used for perc dry cleaning with ground contamination from the solvent.

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<sup>26</sup>James J. Clementi et al., “Converting to No-Clean For Flip Chip Assembly,” *Electronic Packaging and Production*, May 1996, pp. 37–42.

<sup>27</sup>Ronald L. Iman et al, *Evaluation of a No-Clean Soldering Process Designed to Eliminate the Use of Ozone Depleting Chemicals*, Albuquerque, New Mexico: Sandia National Laboratories, 1992.

<sup>28</sup>Ruben G. Carbonell, “CO<sub>2</sub>-Based Technologies,” NRC Workshop on the Environment, 2002, proceedings forthcoming.

## ***Government Role***

Beyond the environmental regulations noted above, governmental bodies affect the use of dry-cleaning technologies and the adoption of CO<sub>2</sub> technology, through a variety of other regulations, recognitions, and tax policies. The EPA Design for the Environment Garment and Textile Care Program encourages professional cleaners to explore more environmentally benign technologies for cleaning garments labeled “dry clean only.” In addition, EPA regulates releases of PCE through laws such as the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, the Resource Conservation and Recovery Act, and the Comprehensive Environmental Response, Compensation and Liability Act (Superfund). Dry cleaners are also required to comply with the EPA PCE dry-cleaning National Emissions Standards for Hazardous Air Pollutants (NESHAP).

The Clean Air Act requires dry cleaners to install certain levels of emissions control equipment and institute mandatory performance testing to ensure that the equipment is functioning properly, although NESHAP standards, in place for all dry cleaners since 1996, depend on the maximum achievable control technology rather than on absolute emissions, so that users of perchlorethylene are not forced to constantly monitor emissions levels. The use of CO<sub>2</sub> as a solvent in dry cleaning received the EPA Presidential Green Chemistry Challenge Award in 1997 in recognition of its contribution toward reducing the use of harmful chemicals. The use of CO<sub>2</sub> in chip manufacturing cleaners received the R&D [Research and Development] 100 Awards Programs in 2001.<sup>29</sup>

The 1999 Dry Cleaning Environmental Tax Credit Act offered a tax credit for small business dry cleaners for 20 percent of the cost of environmentally friendly technologies such as liquid CO<sub>2</sub> and wet-cleaning (water-based) systems. Other tax policies regarding use of dry-cleaning solvents include taxes in 15 states on the use and handling of PCE (including, in one state, a \$25 per gallon tax for a solvent that usually costs \$5 per gallon), with taxes going into a remediation fund for contaminated dry-cleaning plants.<sup>30</sup> Two states also have incentives for dry cleaners to purchase equipment using liquid CO<sub>2</sub> technology.<sup>31</sup> Government funding has supported the NSF Center at North Carolina and North Carolina State and the work at Raytheon, which evolved into the two dry-cleaning processes.

## ***Barriers***

The development of liquid CO<sub>2</sub> as a dry-cleaning agent has faced several obstacles. First, the unavailability of an appropriate process and high-pressure equipment has now been overcome. Working with supercritical carbon dioxide necessitates in parts of the process both lower and higher temperatures and higher pressures beyond those used by normal dry-cleaning machines. Special care must be taken to ensure that the CO<sub>2</sub> does not escape during cleaning. Although CO<sub>2</sub> is relatively nontoxic and unreactive, large quantities of the gas can inhibit the ability of an operator to breathe. Second, typical detergents used

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<sup>29</sup>Presented by *R&D Magazine* ([www.rdmag.com](http://www.rdmag.com)).

<sup>30</sup>“Helping Small Dry Cleaners Adopt Safer Technologies: Without Losing Your Shirt!” Prepared Testimony of Joseph DeSimone to the House Committee on Small Business, July 20, 2000.

<sup>31</sup>“Helping Small Dry Cleaners Adopt Safer Technologies: Without Losing Your Shirt!” Prepared Testimony of Gordon Shaw to the House Committee on Small Business, July 20, 2000.

in conventional dry cleaning do not work in a liquid CO<sub>2</sub> system; competing systems have now been developed and are continually being improved. Professor Eric Beckman of the University of Pittsburgh has developed a number of nonfluorinated surfactants that do not have the environmental persistence of some of the fluorinated materials: functional silicones, poly(ether-carbonates) and acetate functional polyethers. He received the 2002 EPA Presidential Green Chemistry Challenge Award (Academic).<sup>32,33</sup>

A major barrier is the up-front investment required to replace perc machines with carbon dioxide machines. The perc machines cost about \$60,000, while the carbon dioxide equipment costs \$120,000, although the payback periods are quite similar.

## **Carbon Dioxide for the Extraction of Caffeine**

Carbon dioxide is used as a solvent for the extraction of caffeine from coffee and teas and represents the first application of the use of supercritical carbon dioxide as a solvent. Because tea and coffee are the two most popular beverages in the world, there is considerable market for CO<sub>2</sub> technology in providing decaffeinated coffee or tea. The extent to which such technology has and is replacing solvent methods for extracting caffeine brings environmental benefits.

### ***Chemistry***

The first process for extracting caffeine from coffee developed in 1905 by Ludwig Roselius used benzene in an extractor. Today, there are three well-known (and less hazardous) means for removing caffeine from teas and coffees, including water processes, direct solvent methods, and use of SCCO<sub>2</sub>.

Using water for decaffeinating involves washing green coffee beans or tea leaves then passing them over activated charcoal to remove caffeine. The direct solvent method uses solvents such as methylene chloride (MeCl<sub>2</sub>), previously used in Europe, or ethyl acetate to extract the caffeine. Using ethyl acetate is known as the natural method because this solvent is found naturally in fruits and vegetables such as bananas and apples. The solvent is mixed with the green coffee beans or tea leaves until the caffeine has dissolved into the solution and can be removed from the solids. The decaffeinated remains retain some of the solvent, which can prove to be hazardous if methylene chloride is used. Using supercritical carbon dioxide is a similar process to the solvent method, but with CO<sub>2</sub> rather than a volatile organic compound such as MeCl<sub>2</sub> used to extract the caffeine.

### ***Immediate Impacts and Long-Term Environmental and Economic Significance***

Replacing any methods using volatile organic compounds such as MeCl<sub>2</sub> with those using SCCO<sub>2</sub> would have an immediate beneficial environmental impact.

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<sup>32</sup>According to Laidlaw Corp., they have stopped producing these detergents. Additional information available at [www.laidlawcorp.com](http://www.laidlawcorp.com). Other participants in the Global Technologies group such as Caled, however, are producing the surfactants.

<sup>33</sup>J. B. McClain et al., "Design of Nonionic Surfactants for Supercritical Carbon Dioxide," 1996.

## ***Commercializing Firm***

A large number of commercial supercritical carbon dioxide extraction plants were built in the early 1980s, starting with coffee bean decaffeination (HAG AG [Bremen, Germany] and the Maxwell House Division of General Foods Corporation) as well as several hops extraction plants in Germany, England, Australia, and the United States. More than 1,800 patents have been filed worldwide related to supercritical fluid technologies.<sup>34</sup>

## ***Incentives to Adopt***

A significant marketing or economic incentive for using SCCO<sub>2</sub> is the fact that CO<sub>2</sub> decaffeination produces more flavorful coffee products. Carbon dioxide, unlike organic compounds, does not lead to residual aftertastes and bitterness when used for decaffeination. Using SCCO<sub>2</sub> can also enhance flavor and aroma when extracting herbs and spices. Furthermore, there are no harmful chemicals or by-products of the process. Traditionally, the major motivation for developing these supercritical fluid (SCF) processes was the elimination of residual solvents in the products, especially methylene chloride. Solvent residues in pharmaceutical and food products have been subject to increasing regulation since the 1970s.

## ***Government Role***

An example of the role governmental bodies can play in encouraging the use of SCCO<sub>2</sub> for decaffeination are European Union regulations that first limited MeCl<sub>2</sub> residue to 2 parts per million in decaffeinated coffee and now ban the solvent in decaffeination altogether. There are no such restrictions for CO<sub>2</sub> (or ethyl acetate) in most countries. Further government regulation may be warranted in the United States. Although residual methylene chloride levels in U.S. coffee are limited to “legally safe” (and the U.S. Food and Drug Administration [FDA]) levels of 10 parts per million, some health-conscious consumers contend such levels are unacceptably high.

## ***Barriers***

Perhaps the greatest barrier to using carbon dioxide for decaffeination is its cost. Methylene chloride is the cheapest way to decaffeinate coffee; ethyl acetate and water are also cheaper than using carbon dioxide for decaffeination. Greater investment is also required to build a CO<sub>2</sub> decaffeination plant. Because of this, the process has been primarily used to decaffeinate large volumes of commercial-grade coffee, but a growing market for safer and more flavorful decaffeinated products is leading to greater availability of specialty coffees decaffeinated by carbon dioxide.

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<sup>34</sup>Supercritical Technology Consultants, [www.rljdev.com/sc/about\\_sf\\_tech.htm](http://www.rljdev.com/sc/about_sf_tech.htm), accessed November 2002.

## Other Applications

### *Chemistry*

The Kenan Center for the Utilization of Carbon Dioxide in Manufacturing conducts research on technological, scientific, and educational advances in processing systems. The center is comprised of chemists, chemical engineers, and materials scientists from the University of North Carolina and North Carolina State University. Currently more than 20 faculty and 40 students and postdoctoral associates participate in Kenan Center research. National Laboratory partners at Oak Ridge, Los Alamos, and Pacific Northwest allow use of their facilities for Kenan Center studies and industrial members. The center serves as the industrial outreach component for a newly established Science and Technology Center for Environmentally Responsible Carbon Dioxide Processes, a project funded by NSF that involves scientists from campuses in North Carolina and Texas. Sixteen industrial partners support the work at the center, and a number are commercializing NGETs based on such chemistries as:<sup>35</sup>

- Materials synthesis and catalysis: work on homogeneous dispersion and polymerization explores reaction kinetics and routes to new materials.
- Materials processing: carbon dioxide is being used to develop new materials by plasticization of polymers, micro- and nano-crystalline materials from dispersed organic and inorganic particulates, and polymer and colloidal coatings.
- Cleaning and extractions: polymeric surfactants are designed to increase the utility of liquid and supercritical carbon dioxide in cleaning and extraction, including cleaning and surface treatments, bio-extractions, and soil decontaminations.

DuPont licensed the technology developed at the center to use liquid carbon dioxide rather than chlorofluorocarbons (CFCs) or water as the polymerization solvent for producing a number of Teflon<sup>®</sup> fluoropolymer products not for cost but for performance and quality reasons. Products with significantly improved properties were produced. Molecular weights and molecular weight distributions and end-group chemistry could be more effectively controlled. This translates to an improved competitive market position. The \$40 million plant is now in operation at Fayetteville, N.C.<sup>36</sup>

IBM is working with the center to develop improved photolithography processes for chips with ever-decreasing dimensions (138 nm).

Commercialization efforts continue elsewhere. In partnership with Los Alamos National Laboratory, SC Fluids developed a new process—Supercritical Carbon Dioxide Resist Remover (2002 Small Business Award EPA Presidential Green Chemistry Challenge Award). The process removes photoresist and post-ash, etch, and particulate residue from semiconductor wafers.

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<sup>35</sup>See <http://www2.ncsu.edu:8010/champagne/>; Michael C. Cann and Marc E. Connelly, *Real World Cases in Green Chemistry*, Washington, D.C.: American Chemical Society, 2000, pp. 13–18, and references therein; and *The Presidential Green Chemistry Challenge Awards Program: Summary of 1997 Award Entries and Recipients* ([www.epa.gov/greenchemistry](http://www.epa.gov/greenchemistry)), p. 6.

<sup>36</sup>Carbonell, “CO<sub>2</sub>-Based Technologies.”

Fahlman<sup>37</sup> has described other applications:

- SCF extraction has been used to remove PCBs and other organics from water and soil; to extract metal contaminants, a chelating agent is often added to the fluid.
- Nanometer metal powders can act as burn rate modifiers in propellants and in fuel air explosives, energetic structural materials, and high-energy explosives. Powders of some transition metals and their alloys are used in thick-film technology for the production of conductive pastes for hybrid integrated circuitry and metallization of multilayer ceramic capacitors. Only in the past two years have researchers begun to use SCFs as a medium for nanoparticle growth. One approach uses an aqueous metal salt solution, a reducing agent, and surfactants that are added to the liquid carbon dioxide.
- Recently chemical vapor deposition has used SCF technology, allowing relatively nonvolatile precursors to be introduced into the deposition chamber.
- To address the safety issues of handling SCFs at high pressures and in large autoclaves, some applications use flow reactors. To scale up a reactor, the reactor is simply run for a longer period of time with in-situ process monitors when needed.

Elsewhere we report the use of liquid carbon dioxide in a new synthesis for hydrogen peroxide (Case 6) and use in oil exploration (Case 7).

Related work on supercritical water continues. When water reaches the critical temperature of 374 degrees C and pressure of 221 bar, it goes into a supercritical state and becomes an excellent solvent for nonpolar organics. Barriers to applying this technology focus on the design of a practical reactor that can withstand the extremely corrosive conditions and may prevent application on any large scale.<sup>38</sup>

### ***Long-Term Environmental Significance***

Using CO<sub>2</sub> rather than solvents can eliminate toxic releases emanating from many of the processes being commercialized. As an additional example, although the toxic solvents used in spinning acrylonitrile/maleic anhydride copolymers must be recovered, some amounts inevitably escape into groundwater and rivers. By contrast, CO<sub>2</sub> used in this process can be extracted from and released back into the air with no net addition of it to the atmosphere.

### ***Commercializing Firm***

The firms mentioned above are commercializing the processes for reasons of cost and performance with the additional benefits to the environment.

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<sup>37</sup>Bradley D. Fahlman, "Supercritical Fluid Technology: Expanded Applications Are Making SCFs the Green Solvent of the 21st Century," *Today's Chemist at Work*, February 2002, pp. 81-83.

<sup>38</sup>"Green Chemistry: The Beginning of a New Trend for Process Industries," *Technical Insights Alert*, October 4, 2002.

## ***Government Role***

As noted, the government has funded research at technology centers involving Los Alamos, Pacific Northwest National Laboratory, Sandia, The University of North Carolina, North Carolina State University, Texas, and others. The NSF Center in North Carolina could result in \$35–40 million of NSF funding over the ten years beginning in 1999.

## 2. Ibuprofen Synthesis

### Introduction<sup>39</sup>

The well-known case of reducing the number of steps in synthesizing ibuprofen helped eliminate 35 million pounds of waste each year and reduce plant investment and operating costs. Originally, in the 1960s, ibuprofen<sup>40</sup> synthesis was a six-step process that used AlCl<sub>3</sub> in stoichiometric amounts, resulting in large amounts of aluminum trichloride hydrate waste going to landfills. For the 30 million pounds of ibuprofen made yearly, nearly 45 million pounds of waste was generated.

### Chemistry

Nearly all of the economically competitive processes to produce ibuprofen begin with iso-butyl benzene (IBB) and produce varying levels of different impurities controlled by the FDA. Seven routes have been described.

The routes A–G are shown in Figure A2:<sup>41</sup>

A. The commercial manufacturing process developed by the Boots Pure Drug Company in England (U.S. Patent 3,385,886): six steps involving a cyanide functionality that must be completely hydrolyzed to avoid contamination. It has been reported that this process in the United Kingdom has now been shut down.<sup>42</sup>

B. Developed by the Council of Scientific & Industrial Research in India (European Patent 336031). Following acylation of IBB with propionyl chloride, the resulting 4-isobutylpropiophenone is chlorinated to yield the key intermediate 2-chloro-4-isobutylpropiophenone. Rearrangement of this compound yields the methyl ester of ibuprofen, which is then hydrolyzed and purified for sale. This may be the process operated by Shasun Chemicals & Drugs Ltd. since 1986. Shasun has about 22 percent of the worldwide market ([www.shasun.com](http://www.shasun.com)).

C. Developed and implemented by the BHC Company (U.S. Patents 4,981,995 and 5,068,448). IBB is reacted with toxic and corrosive HF to produce 4-isobutylacetophenone, reduced to 1-(4-isobutylphenyl)ethanol, which is reacted with CO to produce crude ibuprofen. This is the process run by Celanese for BASF at the Bishop, Texas plant, supplying about 25 percent of the market.

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<sup>39</sup>See Cann and Connelly, *Real World Cases in Green Chemistry*, 2000, and references therein; *The Presidential Green Chemistry Challenge Awards Program: Summary of 1997 Award Entries and Recipients*, p. 2.

<sup>40</sup>U.S. Patent 3,385,886.

<sup>41</sup>John B. Dubeck and Frederick Searns (Keller and Heckman LLP), letter to Dockets Management Branch FDA, October 3, 2001, accessed at [www.fda.gov/chrms/dockets/dailys/01/Oct01/100401/c000239.pdf](http://www.fda.gov/chrms/dockets/dailys/01/Oct01/100401/c000239.pdf), November 2002.

<sup>42</sup>John Cooper, BASF personal communication.

D. Developed by the Nippon Company (European Patent Specification 0170147). IBB is reacted with acetaldehyde to form 1,1-di(4-isobutylphenyl)ethane, which is then thermally cracked to 4-isobutylstyrene, which is then reacted with CO to produce the ibuprofen ester, which is hydrolyzed to crude ibuprofen.

E. Developed by Dow (U.S. Patent 4,186,270). IBB is reacted with formaldehyde and hydrogen chloride to form 4-isobutylbenzylchloride that is converted to the cyanide-containing derivative 4-isobutylphenylacetonitrile with sodium cyanide. Alkylation with methyl chloride followed by hydrolysis of the cyanide functionality gives the methyl ester of ibuprofen that is then hydrolyzed with acid to ibuprofen.

F. Developed in China by the Wuhan Institute of Chemical Technology.<sup>43</sup> Acylation of IBB with propionyl chloride gives isobutylpropionophenone. Halogenation with copper bromide gives 2-bromo-4-isobutylpropionophenone. Ketalization with ethylene glycol gives the intermediate 2-(1-bromoethyl)-2-(4-isobutylphenyl)-1,3-dioxolane, which is rearranged to give the methyl ester of ibuprofen, which is then hydrolyzed to ibuprofen. This might be the process operated by Rochem in China (www.rochemintl.com). Their process was rebuilt in 1999 to provide product to the Juhua Group.

G. Developed by Upjohn (U.S. Patent 3,975,431). Acylation of isobutylbenzene yields 4-isobutylacetophenone, which is then converted to 3-methyl-3-(p-isobutylphenyl)glycidonitrile by reaction with chloroacetonitrile. Hydrolysis followed by acetylation and dehydrochlorination yields 2-acetoxy-3-(4-isobutylphenyl)acrylonitrile. Hydrolysis of the nitrile in the presence of an alcohol yields the ester, which is further hydrolyzed to ibuprofen.

Albemarle announced in April 2001 that it was expanding its plant in Orangeburg, S.C., by 30 percent. According to Albemarle, the plant was already “the largest bulk active ibuprofen facility in the world”<sup>44</sup> and utilized the most “cost effective manufacturing process” for ibuprofen<sup>45</sup>. It is not known which of these processes is used in its operation, but the firm holds improvement patents related to route D<sup>46</sup> and the Wu patent states that route C is at an economic disadvantage when starting with 1-(4-isobutylphenyl)ethanol, “a compound which is not economical to make by known processes.”

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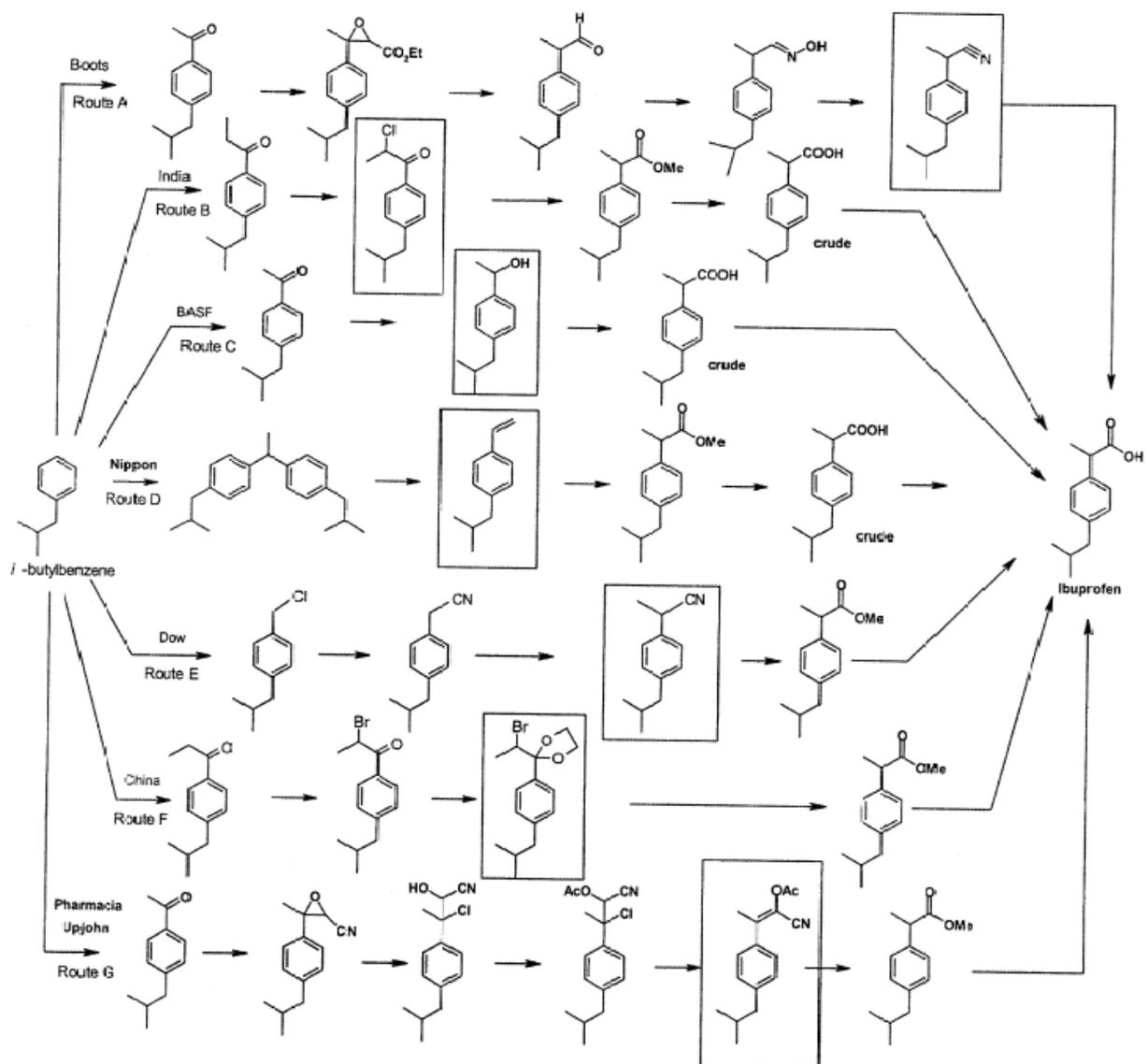
<sup>43</sup> *Huaxi Yaoxue Zazhi* (West China Journal of Pharmaceutical Sciences), 1995, Vol. 10, No. 3, pp. 129–131.

<sup>44</sup> [www.albemarle.com/prelease/ibuprofcappr.htm](http://www.albemarle.com/prelease/ibuprofcappr.htm).

<sup>45</sup> Marc S. Reisch, “Albemarle Is on a Roll,” *Chemical & Engineering News*, Vol. 79, No. 4, 2002, p. 40.

<sup>46</sup> Tse-Chong Wu, “Mixed Ligand Catalyst for Preparing Aryl-Substituted Aliphatic Carboxylic Esters,” U.S. Patent 5,482,596, January 9, 1996, and Robert H. Allen et al., “Preparation of Carboxylic Compounds and Their Derivatives,” U.S. Patent 6,096,920, August 1, 2000.

### Selected Ibuprofen Manufacturing Processes



**Figure A2. Routes to Ibuprofen. (Dubeck and Seams, letter, 2002)**

The BHC (Boots, Hoechst-Celanese) process adopted in the Celanese ibuprofen plant in Bishop, Texas, now uses a three-step catalytic process (Route C) that increases the atom efficiency from 40 percent in the

original process to nearly 77 percent.<sup>47</sup> This process uses hydrogen fluoride rather than  $\text{AlCl}_3$ , with the hydrogen fluoride being regenerated rather than resulting in landfill waste. As a result, the Bishop plant, in producing 7 million pounds of ibuprofen per year—or nearly one-fourth of the world's supply—has managed to avoid producing nearly 10.5 million pounds of waste that would have resulted from using the old six-step process. The Bishop plant also has less investment costs and fewer operating costs than would a plant using the  $\text{AlCl}_3$  process. Celanese now operates the plant for BASF.

## **Immediate Environmental and Economic Impacts**

As noted, the traditional six-step process for manufacturing ibuprofen resulted in considerable aluminum chloride waste: up to 45 million pounds of landfill waste for the 30 million pounds of ibuprofen produced annually worldwide. Because the Celanese plant now produces up to 7 million pounds of ibuprofen, more than 10 million pounds of waste that would have been produced has already been eliminated. Nevertheless, there is considerable room for further reduction; assuming that the remaining ibuprofen production worldwide were converted to the BHC process, and all production had been by Route A, an immediate landfill waste reduction of up to 35 million pounds would occur.

## **Commercializing Firm**

The largest commercial application of this process is the Celanese plant, which has operated since October 1992 and has remained competitive to this day in the face of ever-growing competition.

## **Incentives to Adopt**

As noted, the BHC process has fewer operational and investment costs than the traditional process using  $\text{AlCl}_3$ , giving firms an incentive to adopt it.

## **Government Role**

The federal government has provided official recognition and encouragement of the BHC process, which received the Presidential Green Chemistry Challenge Award in 1997.

## **Barriers**

The manufacturing of any pharmaceutical product introduces trace impurities. When a new process is used to manufacture a pharmaceutical product, different trace impurities result in the final product. There is a considerable cost to ensuring these impurities are not harmful to the consumer. This cost represents the greatest barrier to changing the manufacturing process of ibuprofen. At the same time, this

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<sup>47</sup>The atom efficiency is even greater (99 percent) if the generation of the acetic acid is not considered.

cost could be offset by the advantages firms will realize when replacing the more expensive equipment needed for the old process using  $\text{AlCl}_3$  with that needed for the BHC process.

## 3. Recycling for PET and Nylon: Converting Polymers to Monomers

### Introduction

Americans use large amounts of plastics each year. The plastic food and drink containers Americans use annually, for example, include about 750 million pounds of polyethylene terephthalate, or PET. PET is also used in automobile body panels, fenders, bumpers, and grilles, as well as for lawn mower housings. Carpeting comprises another ubiquitous use of plastics, with nylon being used in about two-thirds of the carpeting in the United States. Producing this material uses significant amounts of energy and pollutes the air and water. Recycling this material can reduce energy use and pollution, as well as, of course, the amount of waste eventually going to landfills.

### Chemistry<sup>48</sup>

The processes for recycling plastics can be challenging. Polyesters must be very dry during processing (e.g., with moisture of less than 50 ppm) to prevent any hydrolysis. PET is not this dry. This means recycled PET, unless undergoing expensive cleaning to be returned to use as high-quality material, can be used only for low-grade uses. New processing technology, however, is allowing scrap terephthalate polyester products like PET to be converted into high-quality material without costly cleaning. DuPont has invested more than \$12 million in the Petretec process, converting an existing dimethyl terephthalate production unit at the Wilmington, N.C., plant.

Recycling carpet also poses technological challenges, particularly in handling multiple carpet layers, distinguishing between plastics and other fibers, and dealing with other waste products from carpet collection. Nevertheless, several commercial firms, including DuPont, BASF, Toyo Rayon, and Monsanto (now Solutia), have developed processes for depolymerizing pure nylon, such as that used in carpeting, into its constituent monomers. Most of these are based on hydrolyzing the polymer in acid, a process developed by Hosino in 1940.

### Immediate Environmental and Economic Impacts

A carpet recycling plant, if economically profitable, could have immediate and substantial environmental effects. One such plant, Evergreen Nylon Recycling, LLC, in Augusta, Ga., a joint venture of DSM

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<sup>48</sup>*The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, EPA744-R-00-001 ([www.epa.gov/greenchemistry](http://www.epa.gov/greenchemistry)), p. 44; Cann and Connelly, *Real World Cases in Green Chemistry*, 2000, and references therein.

Chemicals and Honeywell International, was designed to produce 100 million pounds of caprolactam from 200 million pounds of recycled carpet each year, before shutting down in August 2001. In addition to reducing landfill waste, such recycling would also eliminate annual use of 700,000 barrels of crude oil, 83 million pounds of benzene, 120 million pounds of cumene, and 86 million pounds of phenol. Such production of caprolactam would also result in 89 percent fewer air emissions than traditional manufacturing of the material. Such recycling might also reduce the costs of addressing recycled content goals and have the potential to reduce costs of producing new products, although such potential does not appear to have been realized.

## **Long-Term Environmental Significance**

Depolymerization technology has several important environmental benefits. It would reduce the amount of material going to landfills, raw materials consumed, and environmental emissions required to make new products.

The most easily measurable benefit of recycling would be the amount of nylon averted from landfills because of recycling or other post-consumer conversion process. Currently, about 4.5 billion pounds of nylon are discarded in the United States each year, nearly all of which goes to landfills. By the year 2012, more than 7 billion pounds of nylon will be discarded each year. Clearly an aggressive approach, including recycling, is needed to ensure that the amount of nylon waste going to landfills each year does not increase.

## **Commercializing Firm**

The most notable commercial example of nylon carpet recycling is the Evergreen plant. This plant opened in 1999 but shut down two years later, with owners blaming mechanical problems and more intractable weak market conditions. The recycled nylon was not able to consistently compete with that of virgin materials.<sup>49</sup> The price of virgin materials fluctuates widely depending on the price of oil as well as on the demand for plastics at any given time. Investment in depolymerization facilities may also be affected by the fact that the supply of recycled material cannot be expanded as quickly as manufacturing capacity for virgin materials. More generally, nylon recyclers have pursued several different business models. Evergreen paid for the carpet it received from recyclers, while DuPont charged associated retail outlets for accepting carpet for recycling. DuPont also emphasized the commercial market, in which recycling is more prominent, than Evergreen did. DuPont's focus included architects and developers, making them more aware of the details of acquiring and disposing of carpet. Some other processes undertake recycling that does not involve complete depolymerization. BASF, for example, operates plants that repolymerize carpets with Nylon 6 into Nylon 6 yarns. DuPont has a carpet processing center, supported by 80 collection facilities, for recycling nylon 6,6 (from hexamethylenediamine and adipic acid).

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<sup>49</sup>Jacques G. H. Joosten of DSM at the First International Conference on Green & Sustainable Chemistry, Tokyo, March 2003, explained that the operation became a significant "cash drain," with carpet collection a significant contributor.

## **Incentives to Adopt**

The incentives for carpet recycling vary with economic conditions. Under favorable market conditions, where virgin caprolactam prices and supply of recycled nylon are high, a “back-to-monomer” carpet recycling plant could be economically attractive. The market for carpets with post-consumer recycled nylon has been weak, however, because of consumers’ lack of interest in this feature or because of unsuccessful marketing.

The nylon industry has been considering the automotive resin market as another outlet for its recycled products. Since color specifications are not stringent for automotive plastics, nylon of mixed color can be used. The problem is that these products tend to cost more than polypropylene. Nevertheless, there are high-heat applications for which recycled nylon could compete with polypropylene on the basis of quality.

## **Government Role**

Governments at all levels have played an important role in creating the technology and markets for depolymerization of nylon and PET. Regulations on dumping facilities and tipping fees help create a potential supply of materials for recycling, augmented by recycling programs run by local governments. The federal government has also invested directly in the development of nylon reprocessing technology. The DOE Office of Industrial Technologies, for example, provided funding for experimental phases of technology development of the Evergreen plant. “Take-back” legislation and voluntary agreements in the United States and elsewhere may also provide impetus for the further development of depolymerization technology.

Voluntary agreements—such as the January 2002 Memorandum of Understanding for Carpet Stewardship signed by representatives of the carpet industry; federal, state, and local governments; and several nongovernmental organizations—may also help encourage nylon recycling. The voluntary agreement set a ten-year schedule to increase the amount of reuse and recycling of post-consumer carpet by encouraging manufacturers to assume product stewardship of carpet from sale to disposal. A third-party organization, known as the Carpet America Recovery Effort, was established to improve collection of used carpeting as well as economics of production and markets for recovered carpet.

## **Barriers**

The market for PET and nylon recycling and depolymerization may face some of the barriers of markets with relatively low rates of return for new investments. Depolymerized material must compete in price-sensitive commodity markets with established suppliers, which can be difficult. One of the largest barriers to the adoption of PET depolymerization technology appears to be reliability of the supply of material returned by customers. At present, current reprocessing facilities are also well over capacity or able to process far more waste material than is available.

The case of the Evergreen Nylon Recycling Plant is particularly instructive. Given economic conditions in 1999, the Evergreen plant was able to produce caprolactam at a significantly lower price than that

available on the merchant market. An economic downturn in 2001, however, led to a drop in carpet demand, causing carpet mills to cut their purchases of nylon and also to substitute cheaper polypropylene for nylon. As a result, prices for caprolactam, which had fluctuated between 65 and 90 cents per pound, dipped to as low as 35 to 40 cents per pound. Faced with throttling down production of virgin caprolactam, which would have increased unit costs, or shutting down the recycling plant, the operators of Evergreen chose the latter.

One fundamental technical barrier is the lack of a viable technology that can economically depolymerize both nylon 6 and nylon 6,6 carpet into their constituent monomers. Separate technologies exist for both, with nylon 6,6 depolymerization being more costly and less effective with current technologies. Nylon 6,6 recyclers seek high-volume applications, such as that for automotive resins, that do not require repolymerization with virgin-level monomers. A stronger market for nylon 6,6 recycling would also benefit nylon 6 recyclers by allowing the industries to share transportation and handling costs.

BASF has an agreement with Shred Tech, a Canadian company, to separate carpet backing from the face fiber, under which BASF then uses the face fiber for depolymerization. Although this preprocessing step makes the depolymerization process more simple and less costly, it costs almost as much as the caprolactam is worth.

DuPont spelled out the incentives for investing in the Petretec process and the barriers:<sup>50</sup>

**Project drivers:** providing opportunity for PET film consumers to realize the additional value that their products make with recycle content may bring in the marketplace; providing an opportunity to increase the growth rate of PET film globally by reducing the overall cost to use/dispose of it and by positioning it as the environmentally friendly choice of film substrates.

**Project benefits:** municipal landfills will see 100 million pounds less of solid waste in the United States; affords our customers, most of whom landfill their PET waste, with an economically and environmentally acceptable alternative; everyone in the film supply chain can benefit by increased growth in consumption vs. alternative products that do not have similar post-use solutions; and such regeneration technology can produce raw materials at competitive costs for production of PET film.

**Project barriers:** demonstrating the ability to handle a wide range of impurities in the waste stream and establishing an effective and efficient reverse distribution system to return waste from all participants along the PET film supply chain.

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<sup>50</sup>See Len Jannaman, Jr., DuPont Films, [www.p2pays.prg/ref/02/01578.pdf](http://www.p2pays.prg/ref/02/01578.pdf).

## 4. Bio-Based Processes

### Introduction

Biocatalysis, biocatalyst systems, and other bio-based manufacturing processes are important applications of green chemistry. Recently there have been significant advances toward removing the technical and economic barriers to the commercialization of bio-based processes, particularly those in the pharmaceutical, fine chemicals, and pulp and paper industries, with significant environmental, security, and economic benefits resulting. Greater benefits could be realized by commercializing bio-based processes for energy, metals, mining, and other chemical industries.

This case reviews 47 separate processes. We chose to include many examples, recognizing that they all would not be examined in depth. Treating them as one case gives a picture of the landscape of bio-based manufacturing processes and its breadth and extent. Several of the more detailed examples point out the promise of bio-based NGETs as well as some barriers to implementation. Table A6 summarizes the processes, the development stage, the benefits, and the industries for each. Many of the commercialized processes use biotechnology to manufacture products not available by conventional chemistry. Others provide means for producing currently available products more economically and efficiently while using less energy. Still others reduce or eliminate the use of environmentally toxic chemicals.

### Chemistry

Bio-based processes may involve:

1. Use of renewable feedstocks (biomass) in conventional chemical processes.
2. Fermentation using immobilized or free cells (microorganisms or microbes) with renewable feedstocks such as sugars in a number of stepwise reactions.
3. Use of enzymes as biocatalysts conducting a single reaction. Other reaction steps may involve traditional chemistry. Feedstocks may be petrochemical based. Enzymes are proteins classified according to the chemical reaction they catalyze and may include oxidoreductases (for oxidation/reduction), transferases (for transfer of functional groups), hydrolases (for hydrolysis), lyases (for addition or elimination of small molecules on sp<sup>2</sup>-hybridized carbon), isomerases (for

isomerization), and ligases (for forming carbon-oxygen, carbon-sulfur, carbon-nitrogen, carbon-carbon, and phosphoric ester bonds).<sup>51</sup>

4. Use of multicellular organisms (animals or plants) to process renewable feedstocks.

Often the enzymes, microorganisms, and multicellular organisms are genetically modified.

Significant advances have been made in biocatalysis and with additional advances expected soon from research in progress. Such advances include:<sup>52</sup>

1. Development of biocatalysts that are better, faster, and cheaper than currently used chemical catalysts.
2. Development of a “toolbox” of biocatalysts, or those that can catalyze a broader range of reactions with greater versatility.
3. Development of enzymes with increased temperature stability, activity, and solvent compatibility.
4. Design of new enzymes with molecular modeling.
5. Advances in metabolic engineering for high-volume, high-productivity fermentation reactions.
6. Improved biochemical engineering techniques for developing optimized unit operations downstream of the bioreactor.

## Immediate Environmental and Economic Impacts

Many commercialized processes are currently providing a range of benefits as seen in Table A6. Some examples are the following:

1. Environmental—removal of:
  - a. Toxics
    - Biochemie, a member of the Novartis group, is one of the leading producers of antibiotics. 7-aminocephalosporanic acid (7-ACA) (Example 4b) is the key intermediate for the semi-synthetic cephalosporin antibiotics. A chemical process uses toxic and hazardous reagents such as N, N-dimethylaniline, trimethylchlorosilane, and

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<sup>51</sup>See <http://us.expasy.org/enzyme>.

<sup>52</sup>See Council for Chemical Research, “New Biocatalysts: Essential Tools for a Sustainable 21st Century Chemical Industry,” 1999, <http://www.ccrhq/vision/index.html>.

phosphorous pentachloride and methylene chloride solvent. Wastes cannot be biotreated and must be incinerated, and some processes use zinc salts (problems of heavy-metal disposal) and low temperature chemistry and high energy use. The bio-based process uses no toxic ingredients; it is an aqueous room temperature process; and biological waste treatment is possible. Annual production of 7-ACA is about 2,000 tons.

- The bioleaching and minerals biooxidation processes are commercially used worldwide<sup>53</sup> by the mining industry for the extraction of base and precious metals. Bioleaching uses several different bacteria, including those that act at high temperatures to leach such metals as copper, zinc, and cobalt from sulfide minerals. Biooxidation refers to a pretreatment process that uses the same bacteria as bioleaching to catalyze the degradation of mineral sulfides, usually pyrite or arsenopyrite that hosts or occludes gold and/or silver. In the process the metals remain in the solid phase, and the solution is discarded. The solids are washed and treated with dilute NaCN to solubilize the precious metals. Benefits of a copper bioleaching/biooxidation process in Chile are reported: no noxious gases are produced vs. the arsenic oxide and sulfur dioxide from roasters; no toxic liquid effluents are released; environmentally stable iron arsenate residue is produced; and increased safety as processing is at ambient temperature and pressure. Also, environmental permits are acquired faster, reporting is less onerous, and smaller projects can be developed economically. Metals bioremediation and recovery (Example 4n) involve micro-organisms that immobilize, mobilize, or transform metals by extracellular precipitation reactions. In extracellular precipitation, sulfate-reducing bacteria produce H<sub>2</sub>S to precipitate heavy metals as sulfides that can be recycled from the waste streams back to the process. Budel Zink in the Netherlands adopted such a process, replacing one that precipitated metals as the hydroxides and sulfate as gypsum with limestone when the Dutch government indicated it would prohibit further storage of contaminated gypsum.

b. Carcinogens

A Life Cycle Analysis<sup>54</sup> comparing enzyme pulp bleaching with elemental chlorine free (ECF) bleaching found a 16 percent reduction in carcinogens as well as 12 percent

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<sup>53</sup>A. T. Bull, B. L. Marrs, and R. Kirane, "Biotechnology for Clean Industrial Products and Processes," in *Towards Industrial Sustainability*, Paris: OECD, 1998, pp. 52, 151.

<sup>54</sup>To understand the complete benefits and impact of any NGET requires a Life Cycle Analysis. An excellent introduction is found in the Royal Society of Chemistry Environmental, Health, and Safety Committee's note on Life Cycle Analysis at [www.rsc.org](http://www.rsc.org).

reduction in heavy metals in conjunction with the kraft process. The study<sup>55</sup> looked at the bleach plant—the production of all the inputs such as the chemicals, energy, and fuels and all the emissions generated by the plant (including transportation of the enzyme and cofactor from Germany to Canada). The enzyme system (laccase plus a chemical redox-cofactor) does not completely replace chlorine dioxide in the whole bleaching process but only replaces it in the first stage of the five-stage ECF bleaching sequence.

c. Endocrine disrupters/persistent materials

- Elimination of chlorinated hydrocarbons from the pulp and paper industry will help eliminate several possible endocrine disrupters (Case 4m).
- An enzyme pulp bleaching process in Japan reduced absorbable organic halides (AOX) by 40 percent.<sup>56</sup> The xylanase enzymes were isolated from Japanese soil and were found to have high activity over a wide pH range. Quantities of chlorine and chlorine dioxide were reduced by 35 percent and 65 percent, respectively, giving important cost savings.

d. Greenhouse gases

- Polylactic acid (PLA) (Example 4i) life cycle reduces fossil fuel consumption by up to 50 percent vs. competing materials (such as polystyrene). The manufacture of PLA generates 15 to 60 percent less volume of greenhouse gases than the material it replaces. The recently opened 300 million pound (140,000 metric ton) plant represents investment of nearly \$750 million to develop the technology—a bet by Cargill Dow that the economic advantages of this new plastic will yield significant returns.
- A unique bioprocess has been developed to convert waste power carbon dioxide into algae that subsequently are fermented into a variety of organic feedstocks—methane and acetic acid. A marine alga is used in a photo-bioreactor using light emitting diodes with a wavelength of 68nm and gas residence time of three seconds at ambient temperatures and pressures. More than 98 percent removal efficiency was achieved for carbon dioxide from a typical coal-fired power plant stack gas effluent.<sup>57</sup>

e. Total waste

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<sup>55</sup>OECD, *The Application of Biotechnology to Industrial Sustainability*, 2001, pp. 115–118.

<sup>56</sup>OECD, 2001, pp. 119–121.

<sup>57</sup>EPA, *The Green Chemistry Challenge Awards Program, Summary of 1996, 1997, 1998, 1999, 2000 Award Entries and Recipients*, 1999, <http://www.epa.gov/greenchemistry/past.htm>, p. 9.

- Since bio-based processes in general produce considerably higher yields than their traditional chemical counterparts, waste is significantly reduced in going to a biocatalyzed process as seen in Table A6 and implied by Sheldon's E-factor for fine chemicals and pharmaceuticals.
- The bio-based process for riboflavin (Example 4a) reduced air emissions by 50 percent and water emissions by 66 percent (while cutting operating costs in half).
- The process for Cephalexin (Example 4c) reduced both air and water emissions by 80 percent with "considerable reduction" in operating costs.
- 5-cyanovaleramide (Example 4x) is a starting material for the synthesis of a new DuPont herbicide. The chemical hydration of adiponitrile (ADN) with manganese dioxide was replaced by an immobilized bacterium containing a nitrile hydratase. The bioprocess gave 93 percent yield and 96 percent selectivity with high catalyst productivity. The manganese dioxide process gives low yields (20 percent by-products at only 25 percent conversion) with production of 1.25 kg of catalyst waste per kg of product. The 100 metric tons of product that had been produced by late 2001 eliminated 126 metric tons of heavy-metal catalyst waste.

## 2. Security

### a. Critical materials

- Biocatalysts (especially hydrolases)<sup>58</sup> have the potential to replace precious metal (platinum, palladium) catalysts and obviate the need for metal vessels operating at high pressures or in highly corrosive conditions.

### b. Quantities of stored hazardous materials

- The bio-based processes in pulp and paper are helping to eliminate the storage of chlorine and chlorine dioxide; in mining, H<sub>2</sub>S is generated on-site by the bacteria rather than being transported and stored.

### c. Reduced energy use

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<sup>58</sup>Michael Freemantle, "Can We Exploit Hydrogenases? Insights into Nature's Substitute for Platinum May Lead to the Design of Inexpensive Catalysts," *Chemical & Engineering News*, Vol. 80, No. 29, July 22, 2002, pp. 35-39.

- Energy use was reduced by 80 percent with the bio-based process for acrylamide from acrylonitrile (Example 4-f), while air and water emissions, as well as operating costs, were also reduced.
- A number of projects sponsored by DOE's Office of Industrial Technologies target significant energy savings:<sup>59</sup> (1) Production of succinic acid from wood wastes and plants—energy savings of 9.8 trillion Btus/year along with 252,000 tons of waste saved per year. (2) Manufacture of industrial chemicals from levulinic acid—energy savings of 76 trillion Btus/year by 2020 with cost savings of \$3.5 billion/year and reduced waste by 26 million tons/year. (3) Biocatalysis under extreme conditions for the chemical industry (direct polymerization of phenols and epoxidation of propylene)—energy savings of 70 trillion Btus by 2020 with elimination of epichlorohydrin for the epoxidation and formaldehyde in the polymerization of phenols.

d. Worker safety

- The bio-based process for 1,3-propanediol (Example 4-cc) avoids the use of either ethylene oxide or acrolein and potential worker exposure.
- The development of genetically modified plants (Case 4jj) has proven to greatly reduce the exposure of fieldworkers to harm from pesticides.
- Also, because most bio-based processes are conducted at ambient temperatures and pressures, they are inherently safer in the workplace.

3. Performance/economics

a. Quality, performance

Many of the processes produce materials that cannot be produced by traditional chemistry; this is especially true where stereochemistry is involved in the production of pharmaceuticals and fine chemicals listed in Table A6.

b. "Green" markets

International amino acid markets were completely dominated by the Japanese in the early 1980s (Example 4-d). However, starting in the 1990s, U.S. companies using inexpensive corn-

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<sup>59</sup>See [www.oit.doe.gov/chemical.PDF](http://www.oit.doe.gov/chemical.PDF).

based sugars and immobilized cell technology began to penetrate these markets. Today they are major players in the industry with Archer Daniels Midland the major player.<sup>60</sup>

c. Reduced manufacturing costs or reduced investment

- Significant cost reductions are found in most of the examples. Example 4a—the new process for riboflavin—gave an overall cost reduction of 50 percent with a similar capital investment for an equivalent chemical plant.<sup>61</sup>
- Of the three processes for refining gold—roasting, pressure oxidation, and bacterial oxidation<sup>62</sup>—the bio-based process has substantially lower investment with essentially the same operating costs (15–40 percent lower investment).

d. Reduced regulatory costs

- In some of the cases reviewed here, the regulatory burden was reduced through the use of a bio-based process. This was noted for Case 4o. In Europe, however, firms have had to deal with regulations or rules related to the handling of genetically modified organisms (GMOs) (Case 4-jj).

## Long-Term Environmental Significance

Additional benefits will accrue as more bio-based processes are commercialized and as advances are made in biotechnology. In fact, the NRC Committee on Bio-based Industrial Products<sup>63</sup> sees the development of efficient “biorefineries” (Example 4vv)<sup>64</sup> that could replace petrochemical refineries throughout the 21st century and produce current petrochemicals plus many other products that oil refineries cannot—foods, feed, and biochemicals. In 2002, DuPont and several research partners were awarded an \$18.3 million grant from DOE to develop a biorefinery for ethanol production—the Integrated Corn-Based Bioproducts Refinery project. DuPont will match the grant with \$18.9 million in company funds.<sup>65</sup>

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<sup>60</sup>National Research Council, Commission on Life Sciences, *Bio-Based Industrial Products: Priorities for Research and Commercialization*, Washington, D.C.: National Academy Press, 2000, pp. 21, 91.

<sup>61</sup>OECD, *The Application of Biotechnology to Industrial Sustainability*, 2001, p. 53.

<sup>62</sup>A. T. Bull, B. L. Marrs, and R. Kirane, “Biotechnology for Clean Industrial Products and Processes,” 1998, p. 154.

<sup>63</sup>National Research Council, *Bio-Based Industrial Products*, 2000.

<sup>64</sup>This 48th example is not included in the count of examples because a biorefinery represents many of the 47 examples.

<sup>65</sup>Rick Mullin, “Biotechnology—Corn Chemistry: DuPont Lands Big Government Grant, Comes Close to New Route to Fiber,” *Chemical & Engineering News*, October 21, 2002, p. 14.

## Commercializing Firms

Processes have been commercialized by pharmaceutical, pulp and paper, mining, fine chemical, and large chemical companies. Table A6 lists the firms that have commercialized or are commercializing bio-based processes.

## Incentives to Adopt

To a great extent, the bio-based processes provided less-expensive routes to the desired product; in a number of cases for pharmaceuticals, the bio-based route was the only practical one for chiral molecules, and in pulp and paper the ability to eliminate the use of chlorine to meet regulations was the primary driving force.

## Barriers

The significant barriers are economic, the technical inability to develop a process that has lower manufacturing costs that can displace the traditional chemical routes.<sup>66</sup> The savings would need to be especially great when there is significant investment in place, and the bio-based process is not a “drop-in” or “add-on” for installed investment. In many cases a single product may be part of a manufacturing complex or system where by-products and energy generation are highly integrated. A new route to one chemical in this system may not be compatible with the existing complex. This barrier can be overcome when there is an opportunity for increased capacity and manufacture at a new site.

A growing number of bioprocesses are being commercialized to manufacture specialty chemicals and pharmaceuticals, and in processing pulp and paper, food, textiles, metals, and minerals. Significant advances have been made to knock down the technical and cost barriers in these applications where manufacturing scale is relatively small or where multipurpose equipment is employed. Significant cost technical and investment barriers, however, still exist in the development and commercialization of bio-based processes for larger-scale commodity chemicals. Product isolation from dilute solutions and creation of reaction conditions to allow higher concentrations (titers) continue to be great challenges. The overall economic advantages of biotechnology-based processes are not yet sufficient to displace traditional chemical processes nor have the environmental benefits been sufficient for their adoption. Capital, development, and commercialization costs have been estimated for nine large-volume potential bio-based organic chemicals to be produced from corn.<sup>67</sup> Significant barriers are evident.

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<sup>66</sup>DuPont and Genencor announced in October 2002 that their work on biocatalysis for 1,3-propanediol had resulted in a 500x increase in processing productivity—a significant improvement in process economics (Mullin, “Biotechnology,” 2002).

<sup>67</sup>National Research Council, Commission on Life Sciences, 2000, pp. 71–72.

**Table A5. Needed Investments in Bio-Based Processes.**

<b>Organic Chemical</b>	<b>Rank on TRI- Emissions/ Waste Streams</b>	<b>Volume (million pounds)</b>	<b>Capital, Development, Commercialization (\$ million)</b>
Acetic acid		3,658	1,350
Acetone	7	2,462	1,221
Butanol		1,328	1,157
Maleic anhydride		424	230
Methyl ethyl ketone	11	556	484
Isopropanol		1,236	1,084
Butanediol		200	196
Adipic acid		760	230
Lactic acid		10,063	2,208

The capital required to commercialize the eight chemicals besides lactic acid exceeds \$6 billion. Such investments would not be made without significant cost savings. In smaller batch processes for fine chemicals and pharmaceutical intermediates, equipment expense is much less, and certainly the ratio of plant investment to product revenue is lower. Rules of thumb on R&D expense and scale-up indicate that before this \$6 billion is spent, \$60 million would be required for research aimed at solving the technical issues with the greatest impact on process economics and \$600 million on pilot plant studies to demonstrate the technical feasibility and develop design data for plant construction.

## **Government Role**

During 1999 and 2000, the federal government developed the “Bioenergy Initiative” to accelerate the development of technologies for using renewable carbon as a feedstock for the production of power, fuel, and products, with the intent to create a carbohydrate economy to replace some fossil fuels. In 1999 President Clinton signed an executive order regarding or creating the initiative, and in 2000 the Sustainable Fuels and Chemicals Act was signed into law. The act authorized spending of \$250 million over five years on R&D and established a technical advisory committee to provide leadership, advice for

federal agencies and Congress on priorities for R&D spending, and to foster cooperation between the Departments of Agriculture and Energy.<sup>68</sup>

EPA's Presidential Green Chemistry Challenge Awards have featured nearly a dozen bio-based processes. In October 2002, DOE announced the grant to DuPont for a biorefinery, noted previously.

Abroad, for example in the United Kingdom, the newly formed Pro-Bio Faraday Partnership is seeking to maximize commercial benefits from biotechnology—discovering and developing new biocatalysts, developing integrated production processes, and designing and modeling new and improved processes.<sup>69</sup>

It appears that this area is attracting more R&D dollars than the other areas of green chemistry; much work in biotechnology is related to the life sciences, which has had broad funding increases, rather than to environmental sciences, which has not.

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<sup>68</sup>OECD, *The Application of Biotechnology to Industrial Sustainability*, 2001, p. 14.

<sup>69</sup>OECD, *The Application of Biotechnology to Industrial Sustainability*, 2001, p. 14.

**Table A6. Examples of Bio-Based Processes.**

Example 4-	Product/Description	Development Stage	Benefits— Primary and Secondary	Details	Industry- Reference
a	Riboflavin (Vitamin B2) Fermentation of glucose	Commercial—Hoffmann La Roche	1. economic 2. environmental	Reduced air emissions by 50 percent and water emissions by 66 percent (while cutting operating costs in half) with a similar capital investment for an equivalent chemical plant.	Food 1
b	7-Amino-cephalosporanic acid (antibiotic intermediate); involves reactions using two enzymes	Commercial—Biochemie (Novartis)	1. environmental 2. economic 3. health/safety	A chemical process uses toxic and hazardous reagents such as N,N-dimethylaniline, trimethylchlorosilane, and phosphorous pentachloride and methylene chloride solvent. Wastes cannot be biotreated and must be incinerated and some processes use zinc salts (problems of heavy metal disposal) and low temperature chemistry and high energy use. The bio-based process uses no toxic ingredients, is an aqueous room temperature process, and biological waste treatment is possible. Annual production of 7-ACA is about 2,000 tons. Taxes on incinerated wastes led to commercialization of bio-based process.	Medicine 1
c	Cephalexin (antibiotic) four-step process; fermentation followed enzymatic reactions; further reduction in steps anticipated	Commercial—DSM	1. economic 2. environmental	Cost pressures from Asia called for more economic process if company wanted to stay in antibiotic business; 70 percent reduction in waste and its toxicity (replaced use of methylene chloride and silylating agents).	Medicine 1
d	Amino acids—use immobilized enzymes,	Commercial —Tanabe	1. economic	International amino acid markets were completely	Medicine,

	continuous process replaced batch enzymatic process	(Japan)  (see comment in column 5)	2. environmental	dominated by the Japanese in the early 1980s. However, starting in the 1990s, U.S. companies using inexpensive corn-based sugars and immobilized cell technology began to penetrate these markets and are today major players in the industry, with Archer Daniels Midland the major player.	food, animal feed  1
e	S-Chloropropionic acid (CPA) (agricultural intermediate); racemic CPA enzymatically dechlorinated R-enantiomer only; S-CPA isolated by solvent extraction; development of enzyme was critical	Commercial—Avecia	1. economic  2. environmental	Need to produce single enantiomeric material replaces process: glucose fermented to R-lactic acid that is extracted and recovered, esterified, and chlorinated with thionyl chloride.	Agrochem  1
f	Acrylamide; reaction of acrylonitrile with nitrile hydratase enzyme (immobilized whole cell catalyst)	Commercial—20,000 metric tons Mitsubishi Rayon	1. economic  2. environmental	Replaces copper catalyzed reaction that produces range of by-products, both processes produce only minor amounts of waste; energy savings for new process.	Chemicals (water treatment)  1,8
g	Ammonium acrylate; acrylonitrile hydrolyzed by nitrilase to ammonium acrylate	Demonstration—Ciba (not to be commercialized)		Replaced sulfuric acid hydrolysis, reducing hazards and wastes; but neutralization of purchased acrylic acid became favored route.	Chemicals (water treatment)  1
h	Polyesters; diols and diacids polycondensation with lipase enzyme	Demonstration—Baxenden	1. economic (potential)	Driving force was improved product quality with energy savings; unique higher molecular weight products developed; environmental and health benefits seen in use of particular products developed.	Potential: Adhesives  1
i	Polylactic acid; fermentation of dextrose gives two chiral isomers of lactic acid; chemically cracked to form three lactide	Commercial—Cargill Dow	1.economic  2. environmental	From the corn planter to retail counter polylactic acid life cycle reduces fossil fuel consumption by up to 50 percent vs. competing materials (such as	Chemicals, plastics, fibers

	isomers; various combinations of lactides give a range of different polymers (compostable and recyclable)			polystyrene). The manufacture of PLA generates 15–60 percent less volume of greenhouse gases than the material it replaces. The recently opened 300-million-pound (140,000-metric-ton) plant represents investment of nearly \$750 million to develop the technology—a bet by Cargill Dow that the economic advantages of this new plastic will yield significant returns.	fibers 1,2(1999)
j	Vegetable oil degumming: EnzyMax process; in processing oilseeds to produce vegetable oils, meals, concentrated proteins and lecithins, low phosphatide content is needed for downstream processing; enzymatic hydrolysis enables removal of phosphatides	Commercial— Cereol/Lurgi	1. economic 2. environmental	Replaces the conventional process eliminating use of phosphoric and sulfuric acids, reducing caustic and energy, lower investment and operating costs.	Food 1
k	Wastewater recovery in a vegetable processing plant; groundwater supply was limited, drinking water relatively expensive; biotreatment and membrane ultrafiltration allowed reuse of effluent water	Commercial—Pasfrost	1. economic 2. environmental	Reduces use of groundwater and process effluent; water quality in contact with food must be guaranteed.	Food 1
l	Removal of peroxide bleach residues-textiles; to ensure quality dyeing, peroxide residues from bleaching must be removed; use of the enzyme catalase	Commercial—Windel	1. economic 2. environmental	Replaces repeated rinsing with hot water; reduces costs by 6–8 percent; reduced environmental pollution with reduced resources used and reduced discharge of industrial wastewater.	Textiles 1
m	Pulp bleaching, brightening, biopulping, deinking	Commercial—Leykam, Domtar, others	1. environmental 2. economics 3. health/safety	Life Cycle Analysis: enzyme pulp bleaching vs. elemental-chlorine-free bleaching—a 16 percent reduction in carcinogens as well as 12 percent reduction in heavy metals with the kraft process.	Pulp and paper 1

			4. security	The enzyme system (laccase plus a chemical redox-cofactor) does not completely replace chlorine dioxide in the whole bleaching process but only replaces it in the first stage of the five stage ECF bleaching sequence.	
n	Zinc, refining, roasting, oxidation	Commercial—Budel Zink (Netherlands),	1. environmental	Replaces zinc precipitation of metals as the hydroxides giving sulfate contaminated gypsum (storage now prohibited).	Metals, 1
o	Copper, gold bioleaching. Metals bioremediation and recovery involve micro-organisms that immobilize, mobilize, or transform metals by extracellular precipitation reactions. In extracellular precipitation, sulfate-reducing bacteria produce H <sub>2</sub> S to precipitate heavy metals as sulfides that can be recycled from the waste streams to the process	Commercial—Billiton, others	1. environmental 2. safety 3. economics	In gold refining, the bio-based process has 15–40 percent lower investment with essentially the same operating costs. Copper recovery bioleaching/biooxidation gives no noxious gases (As <sub>2</sub> O <sub>3</sub> and SO <sub>2</sub> ); shorter construction time; faster environmental permits; no toxic effluents; simple and safe operation, as processing is at ambient temperature and pressure; smaller projects can be developed economically and have higher net present value.	Metals, mining 1,7
p	Ethanol from biomass; fermentation of biomass rather than corn	Demonstration—Iogen; research, Purdue	1. environmental (potential)	Large-scale production of bio-based ethanol is a long-term possibility; assuming advanced technologies are in place for processing lignocellulosics rather than corn; longer term an intermediate to ethylene and commodity chemicals.	Fuels 1,2(1998)
q	Oil-well completion; enzymes to remove filter cake	Commercial demonstration—BP Exploration	1. economics 2. environmental	Little benefit in using nondamaging drilling muds if the chemicals used to remove their residue (“break” the polymers in the filter cake) damage lifetime productivity of the well. Enzymes replace acids and oxidizing agents; may need	Fuels 1

				thermophilic enzymes for broader use.	
r	Using enzymes in large-scale organic reactions: oligosaccharides (and complex carbohydrates for clinical evaluation); enantiomerically pure hydroxy compounds, and novel monosaccharides	Research—Scripps Research Institute	1. economics (potential)	Enables syntheses of materials not available by other routes.	Food 2(1999)
s	Bioconversion of CO <sub>2</sub> to chemicals; converts waste power carbon dioxide into algae then fermented into a variety of organic feedstocks—methane and acetic acid. A marine algae is used in a photobioreactor using light-emitting diodes with a wavelength of 68 nm and gas residence time of 3 seconds at ambient temperatures and pressures	Research; University of Cincinnati	1. environmental (potential)	More than 98 percent removal efficiency was achieved for carbon dioxide from a typical coal fired power plant stack gas effluent.	Fuels 2(1999)
t	Cross-linked enzyme crystals, formulation of enzymes in cross-linked crystalline form	Pilot plant—Altus Biologics	1. economic 2. environmental	Twenty enzymes demonstrated on pilot plant scale; used for aspartame and cephalosporin with further reduction in waste and increased efficiency; gives greater chemical and physical stability to the biocatalysts; may lead to applications in commodity chemicals.	Chemicals 2(1997)
u	p-hydroxybenzoate contacting an active cell mass with toluene that is transformed through a series of intracellular enzymatic reactions	Research—North Carolina State	1. environmental (potential)	Replaces two-step carboxylation of phenol, reduces generation of waste by-products; mild reaction conditions for safety to human health and the environment.	Chemicals 2(1999)
v	Polyhydroxyalkanoates in green plants; studying the transformation of plants with four separate transgenes and a novel	Research—Monsanto	1. environmental (potential)	Potential biodegradable plastics; poly(beta-hydroxybutyrate-co-beta-hydroxyvalerate (PHBV) is currently produced by fermentation of the	Chemicals 2(1999), 3

	application of one endogenous plant enzyme			bacterium <i>Ralstonia eutropha</i> but is not economically competitive with the petrochemical routes.	
w	adipic acid; glucose to cis,cis-mutaconic acid with a single genetically engineered microbe; hydrogenation gives adipic acid; catechol also synthesized	Research—Michigan State	1. environmental (potential)	Replaces the benzene-based process that also produced nitrous oxide, which must be captured, used, or eliminated; process cannot be justified economically at this time.	Chemicals 2(1998), 8
x	5-Cyanovaleramide, starting material for the synthesis of a new DuPont herbicide. The chemical hydration of ADN with manganese dioxide was replaced by an immobilized bacterium containing a nitrile hydratase	Commercial—DuPont	1. economics 2.environmental	The bioprocess gave 93 percent yield and 96 percent selectivity with high catalyst productivity; with the manganese dioxide process low yields (20 percent by-products at only 25 percent conversion of the ADN with production of 1.25 kg of catalyst waste per kg of product. The 100 metric tons of product that had been produced by late 2001 eliminated 126 metric tons of heavy metal catalyst waste.	Chemicals 2(2000), 8
y	Lead mine water treatment; sulfate reducing bacteria produce hydrogen sulfide and precipitate metals from the mine water, also removes nitrates	Commercial—Asarco	1. environmental	No chemicals used; no sludge produced; water quality standards met.	Mining 2(1997)
z	Acetic acid	Commercial	1. economics 2. environmental	May be produced by fermenting corn starch or cheese whey or as by-product of the sulfite wood pulping process; combined with dolomite lime to produce calcium magnesium acetate for deicing roads without corrosion; biodegradable; research for more than 50 years has focused on homoacetogenic bacterium, which can convert glucose, xylose, and some other pentoses.	Food Chemicals 3

aa	Enzyme optimization; biodiversity search technology scans natural sources for useful enzymes.	Research— RecominantBioCatalysis		Develops robust catalysts for the chemical process industry.	Chemicals 2(1996)
bb	Ascorbic acid (vitamin C)	Pilot plant— Eastman/Genencor	1. economics 2. environmental	Eastman and Genencor have developed a one-step fermentation process for the ascorbic acid intermediate, 2-ketogluconic acid from glucose; replaces four-step conventional process and cuts investment in half.	Chemicals 1
cc	1,3-propanediol	Pilot plant—DuPont	1. economics 2. safety 3. environmental	Avoids the use of either ethylene oxide or acrolein and potential worker exposure. Since most bio-based processes are conducted at ambient temperatures and pressures, they are inherently safer.	Chemicals, Fibers 1
dd	Nicotinamide (Vitamin B3)	Commercial—Lonza Guangzhou Fine Chemicals (China)	1. economics 2. environmental	Chemoenzymatic process: 2-methyl-1,5-diamino pentane is converted to 3-methyl pyridine, then ammoxidized and resulting 3-cyanopyridine is hydrolyzed to nicotinamide using immobilized <i>Rhodoccus rhodochrous</i> J1 cells (acrylonitrile catalyst).	Food 7,8
ee	Terephthalic acid and isophthalic acid	Research—DuPont	Not economically viable at present	Process described in U.S. Patent 6187569.	Chemicals 8
ff	Aspartame	Commercial—600 metric tons	1. economics 2. environmental	Included in table of reference.	Food 7
gg	6-aminopenicillanic acid	Commercial—6,000 metric tons	1. economics 2. environmental	Included in table of reference.	Medicine 7

hh	L-lysine	280,000 metric tons; \$700 million, 7 percent/year growth; improvements by Degussa	1. economics 2. environmental	Included in table of reference; has been produced many years by fermentation; new process by Degussa reduces wastes and by-products almost to zero; dextrose as raw material and product is 60 percent lysine.	Food 7
ii	L-threonine/L-methionine	10,000/200 metric tons	1. economics 2. environmental	Included in table of reference.	Food 7
jj	Roundup Ready® Soybeans, Corn, Cotton	Major business for Monsanto	1. economics 2. environmental	Genetically modified plants affecting output traits allow ready use of glyphosate (Case 25) Benefits in use of less pesticides, greater land productivity, less harm to nontarget and beneficial organisms, less contamination of drinking water; improved U.S. farm competitiveness.	Food 12
kk	Vitamin B-12	12 metric tons	1. economics 2. environmental	Included in table of reference; three major production routes to vitamins: chemical synthesis, fermentation, extraction from plants; with the exception of B-12, all are produced chemically; some are produced both by chemically and by a bio-based route.	Food 7
ll	Vitamin C (see bb for improvements)	70,000 metric tons	1. economics 2. environmental	Included in table of reference.	Food 7
mm	Vitamin F	1,000 metric tons	1. economics 2. environmental	Included in table of reference.	Food 7
nn	D-p-hydroxyphenyl glycine	3,000 metric tons	1. economics 2. environmental	Included in table of reference.	Food 7

oo	Feed enzymes	20,000 metric tons	1. economics 2. environmental	Included in table of reference.	Food 7
pp	Levulinic acid from biomass; high temperature, dilute acid hydrolysis	Demonstration plant—Biofine Inc.	1. environmental 2. economics	One ton per day paper mill sludge converted to levulinic acid; potential for larger-scale units with a number of chemicals as products from waste paper, municipal waste, waste wood, and agricultural wastes.	Chemicals 2(1999)
qq	Citric acid	Commercial—\$900 million	1. economics 2. environmental	Nonrecombinant <i>Aspergillus niger</i> .	Food 3
rr	High-fructose syrups	Commercial—\$3.1 billion—A. E. Staley, ADM, Cargill.	1. economics 2. environmental	Volatility in world sugar (sucrose) market created incentive to seek domestic replacements. In the 1950s, scientists discovered enzyme to convert glucose to fructose—led to high-fructose corn syrup industry; development of immobilized glucose isomerase enzymes enabled the production; thermostable alpha-amylases contributed to increased yields, and in the 1990s recombinant thermostable amylases contributed to reduced costs.	Food 3
ss	Monosodium glutamate	Commercial—\$800 million	1. economics 2. environmental	The environmental benefits of producing food additives by fermentation or enzymatic routes instead of organic synthesis are similar to those for other specialty chemicals—reducing processing steps and the use of organic solvents.	Food 3
tt	Succinic acid	Pilot plant—Applied CarboChemicals	1. economics 2. environmental (energy)	\$7 million agreement between 4 DOE labs and Applied CarboChemicals to manufacture chemical feedstocks from renewables; succinic acid is	Chemicals 3

				produced by fermentation of glucose from corn to then produce 1,4-butanediol, tetrahydrofuran, N-methyl pyrrolidone.	
uu	Biodiesel (methyl ester of plant oils—soy beans, rapeseed)	Not economically viable in near term	1. environmental 2. economic	Made by transesterifying plant oils with methanol in presence of catalyst; usually mixed with petroleum diesel at 20 percent (B20); some environmental benefits—absence of sulfur and aromatics; price of soy beans an economic barrier; in Europe rapeseed is used, subsidized, and has progressed further than in the United States.	Fuels 3
vv	Biorefinery concept—relevant to many of the cases above	Long-term goal being piloted	1. environmental 2. economics	Development of biorefineries comparable to petroleum refineries will be essential to make many bio-based products competitive with fossil-based equivalents; fermentation feedstocks: starch, dextrose, sucrose, cellulose, hemicellulose, molasses; food: oil, starch, sweeteners; chemical intermediates: lactic, acetic, citric, succinic acids; fuels: ethanol, acetone, butanol; solvents; industrial enzymes; biodegradable plastic resins; prototypes for such refineries exist.	Chemicals, Food 3 (p. 75)

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## 5. Dimethyl Carbonate

### Introduction

Dimethyl carbonate (DMC) can be used to manufacture many products, primarily polycarbonates, and polyurethanes but also pesticides and herbicides, pharmaceutical products, polyimide films, and electrolytic fluids for lithium batteries. It also may be used as a fuel additive, and as a solvent it is more environmental benign than other carbonating and methylating agents such as phosgene, dimethylsulfate, and methyl halides.<sup>70</sup> DMC is biodegradable and nontoxic, it does not have irritating or mutagenic effects, and its use does not generate inorganic salts.

### Chemistry

The most common method for producing DMC is to use methanol and phosgene, a highly toxic and corrosive chemical. A by-product of this process is hydrogen chloride, which is also corrosive. An alternative production process could eliminate the use of phosgene in the manufacture of many products, especially polyurethane and polycarbonates. Alternative means of producing DMC could increase its use considerably, with the market demand reaching 100 kilotons, or even several megatons, per year from the minimal amounts used commercially today.

There are several alternative approaches to producing DMC, including:

**Oxidative carbonylation of an alcohol over a copper chloride catalyst.** There are two weaknesses to this process, including a low per-pass conversion and difficult separation. EniChem of Italy produces DMC using an oxidative carbonylation process with a copper chloride catalyst.

**Oxidative carbonylation using methyl nitrite.** Ube Industries of Japan commercially produces DMC in this way. Bayer has also studied this process. Because methyl nitrite is toxic, there are some risks in handling the reactants.

**An ester exchange reaction between methanol and an alkylene carbonate** is used by Catalytic Distillation Technologies (CDTech).

Some other possible alternative methods for producing DMC have not been used because their catalysts were not sufficiently active, their by-product formation was too high, or product recovery was difficult and expensive.<sup>71</sup> Producing DMC from methanol, carbon monoxide, molecular oxygen, and cuprous

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<sup>70</sup>Pietro Tundo "Dimethyl Carbonate as a Green Reagent," collection of lectures of the Summer Schools on Green Chemistry, Venice 1998, 1999, 2000, INCA 2001, <http://helios.unive.it/inca>.

<sup>71</sup>EPA, *The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, August 2001.

chloride via oxidative carbonylation in a two-step slurry process has a low production rate, high cost for the separation of products and reactants, formation of by-products, high recycle requirements, and a need for corrosion-resistant reactors and process lines. Producing DMC from methyl nitrite, itself a hazardous material, instead of cupric methoxychloride involves separating materials and balancing materials in various flow sections of the process, requiring complicated process control. Producing DMC from methanol and carbon dioxide in a two-step process requires high pressure and has a slow reaction rate and difficult product separation.<sup>72</sup>

## **Immediate Environmental and Economic Impacts**

Alternative means of DMC production could reduce or eliminate the use of phosgene and the generation of chloride-containing waste streams in the production of polycarbonates, polyurethanes, pharmaceuticals, and other chemicals. Phosgene is an acute hazardous substance that can cause short-term irritation to the eyes, skin, and breathing passages, and, with repeated exposure, it can cause permanent lung damage. TRI data indicate 16,067 pounds of phosgene from various processes were released into the air, and 543 pounds were transferred for treatment off site in 1999. At production facilities, more than 10 million pounds of phosgene were recycled, and nearly 11.5 million pounds were treated. Reduction of both workplace and environmental exposures to phosgene, as well as the chlorinated by-products of the polycarbonate manufacturing processes such as hydrogen chloride and carbon tetrachloride, therefore constitute immediate benefits resulting from alternative means of DMC production not requiring phosgene. Alternative DMC production methods may also reduce the costs to comply with health, safety, and environmental regulations and workman's compensation resulting from accidental exposures. Worker productivity may be increased with the elimination of much equipment and many procedures necessary for handling toxic materials.

## **Long-Term Environmental Significance**

If DMC can be produced economically and with reduced pollution, it could replace other hazardous substances. DMC is a nontoxic, biodegradable compound, the use of which can help eliminate the formation of undesirable inorganic salts and replace toxic products used in some reactions.<sup>73</sup>

The CDTech patent application for producing DMC notes that it could replace halogenated solvents such as chlorobenzene,<sup>74</sup> claiming DMC is "a viable alternative to acetate esters and ketones in most applications, from paints to adhesives, taking advantage of its good solvency power." DMC could also be used in lithium rechargeable batteries and as a blowing agent in polyurethane foam after the CFC ban. Such DMC might also take the place of halogenated solvents used in dry-cleaning fluids, degreasing solvents, electrical cleaning solvents, inks, paint strippers, and extractants for removing caffeine from

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<sup>72</sup>J. Yong Ryu, U.S. Patent: "Process for Making Dialkyl Carbonates," Patent Number RE37,337, issued August 21, 2001. Reissue of U.S. Patent 5,902,894 (May 11, 1999).

<sup>73</sup>Tundo, 2001.

<sup>74</sup>Yong Ryu, 2001.

coffee. It could also be used in place of chlorine compounds for dyes, pharmaceuticals, insecticides, synthetic rubber and resins, as well as for bulk storage food and soil fumigants.

The largest potential market for DMC may be as a fuel additive. DMC has about three times the oxygen content as methyl tert-butyl ether (MTBE).<sup>75</sup> DMC is, however, more expensive to produce than MTBE. Union Oil has patented the use of DMC as a fuel additive for reducing particulate emissions from diesel engines. A Japanese firm has found the use of DMC reduces CO, NO, and NO<sub>2</sub> emissions more than ethanol.<sup>76</sup> DMC could also be used to convert natural gas to a liquid transportation fuel.<sup>77</sup>

## Commercializing Firms

Patent activity on DMC has increased in recent years. Most address copper chloride catalysts.<sup>78</sup> The first patent citation suggesting the use of DMC as a fuel additive dates to 1943. DMC was first patented specifically as a fuel additive in the early 1980s.<sup>79</sup>

In 1983, EniChem established the first industrial plant to produce DMC with an alternative method to the phosgene process; by 2001, it was able to produce 70 kilotons per year.<sup>80</sup>

Ube Industries first began using an alternative process to produce DMC in the mid-1990s. Development of this alternative process was a business decision to take advantage of the corporate expertise in nitrite chemistry and the availability of ammonium, a raw material for DMC synthesis.<sup>81</sup> Ube developed a catalyst that increases the production efficiency of DMC.<sup>82</sup> This process maintains a high level of catalyst activity for a long period of time under mild reaction conditions.<sup>83</sup> The avoidance of phosgene in the process has brought Ube recognition as a leader in environmental, worker health, and safety issues. The Ube City plant currently synthesizes 5,300 tons of DMC annually and has the capacity to synthesize 40,000 tons each year.<sup>84</sup> The plant was built largely to provide Ube Industries with an intermediate product for use in its own production of electrolytic fluids used in lithium batteries and polycarbonate diols as well as in pharmaceuticals and polyimide films.<sup>85</sup> These are niche-markets linked to Ube's own product mix, processes, and the availability of raw materials required for DMC synthesis. Should a market for DMC as a fuel additive develop, production would dramatically increase and unit costs would

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<sup>75</sup>Michael A. Pacheco and Christopher L. Marshall, "Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive," *Energy & Fuels*, No. 11, 1997, pp. 2-29.

<sup>76</sup>Pacheco and Marshall, 1997.

<sup>77</sup>Pacheco and Marshall, 1997.

<sup>78</sup>Pacheco and Marshall, 1997, pp. 6-7.

<sup>79</sup>Pacheco and Marshall, 1997.

<sup>80</sup>Tundo, "Dimethyl Carbonate as a Green Reagent," 2001.

<sup>81</sup>Personal interview with Akazu Takahashi, Ube Industries, June 2002.

<sup>82</sup>"Ube Bares Low-Cost Catalyst for DMC," *Japan Chemical Week*, March 28, 1996, p. 3.

<sup>83</sup>Keigo Nishihira, Shuji Tanaka, Kunioki Kodama, Takayoshi Kaneko, Tetsuro Kawashita, Yuki Nishida, Tokuo Matsuzaki, and Koji Abe, "Process for Preparing Carbonic Diester," Ube Industries, U.S. Patent Application 5,380,906, January 10, 1995.

<sup>84</sup>"Ube to Debottleneck Dimethyl Carbonate," *Chemical Week*, Vol. 162, No. 8, February 23, 2000, and *Chemical Week Asia*, Vol. 5, No. 5, March 8, 2000.

<sup>85</sup>"Ube to Debottleneck Dimethyl Carbonate," 2000.

decrease. Because production cost is a function of scale, relatively little DMC using alkyl nitrite and carbon monoxide is made, and the cost of the product Ube synthesizes cannot at present compete with the costs of products made with phosgene-based processes.

CDTech has patented a process for producing dimethyl carbonate from methanol, carbon monoxide, and oxygen with a copper chloride catalyst. DMC and ammonia are produced from methanol and urea using dibutyltin dimethoxide in triethylene glycol dimethyl ether as a catalyst. The ammonia can be recycled into urea production. This process has been demonstrated only on a laboratory scale.<sup>86</sup>

Nippon GE Plastics Company has developed polycarbonate-manufacturing technology using the DMC process. It currently manufactures 25,000 tons of polycarbonates per year using this process. Several Chinese firms are also developing DMC production capability.

Direct synthesis of DMC from carbon dioxide and alcohols is in the early stages of investigation, with substantial additional work probably needed to find more efficient catalytic systems.

## **Incentives to Adopt**

The primary incentive to implement alternative methods of DMC production is, as noted, elimination of phosgene from the process, as well as the costs associated with handling a toxic material. The use of DMC as a fuel additive will depend on environmental regulations and reduced manufacturing costs. Ube Industries adopted new DMC manufacturing processes to take advantage of other materials it procured and manufactured as well as for potential use and marketing of DMC as a fuel additive.

## **Barriers**

Barriers to adopting new means of DMC production include investment and operating costs. The costs of the CDTech technology are not competitive with those of existing processes. In addition, its “available catalysts were not sufficiently active, by-product formation was too high, and product recovery was complicated and expensive.”<sup>87</sup>

To date, the catalysts for alternative methods of producing DMC have had relative inactivity, a lack of specificity, and have been difficult to recover.<sup>88</sup>

## **Government Role**

NSF funding helped in developing a preliminary design for alternative methods of production for DMC. The International Center for Environmental Technology Transfer and the New Energy and Industrial

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<sup>86</sup>EPA, *The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, 2001.

<sup>87</sup>EPA, *The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, 2001.

<sup>88</sup>EPA, *The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, 2001.

Technology Development Organization have helped to publicize the benefits and applications of the Nippon GE and Ube Industries work.

## 6. Production of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) Directly from Hydrogen and Oxygen

### Introduction

Hydrogen peroxide is an environmentally benign oxidant whose widespread adoption in the chemical processing industry is hindered by its high cost relative to chlorinated alternatives. Coincidentally, the aspects of conventional hydrogen peroxide production that make it expensive also make it less environmentally attractive. As a result, while there have been many attempts over the past several decades to produce hydrogen peroxide directly from hydrogen and oxygen, none have proven to be commercially viable. Most hydrogen peroxide produced in the United States is used by the pulp and paper industry for the bleaching of pulp from wood, the production of chlorine dioxide at kraft pulp mills, and the production of recycled paper. A direct synthesis route might fundamentally change the economics and environmental impact of hydrogen peroxide production and might also develop a significant market for it as a “green” oxidant in a number of industries.

### Chemistry

#### *The Traditional Anthraquinone (AQ) Process*

Hydrogen peroxide can be produced from the direct reaction of oxygen and hydrogen, but such a process would be an explosion hazard.<sup>89</sup> As a result, a hydrogen “carrier,” an alkyl anthraquinone, has been adopted for use in 95 percent of hydrogen peroxide production in the United States.<sup>90</sup>

In the most common industrial process, the anthraquinone is mixed with a proprietary organic solvent, termed the “working solution,” and then hydrogenated over a palladium catalyst in a three-phase reactor. After filtration of catalyst particles, the solution is oxidized, regenerating the anthraquinone. Hydrogen peroxide is stripped from this organic mixture into water in a counter-current column and then further purified and concentrated via vacuum distillation. In principle, the working solution is contained within a closed-loop process. In reality, the lack of precise control over the hydrogenation results in the over-hydrogenation of a fraction of the organic species, which must be periodically replaced.

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<sup>89</sup>Hydrogen has a lower explosion limit (LEL) of 4 percent and an upper explosion limit (UEL) of 75 percent. The implication is that any gas phase concentration of hydrogen between 4 percent and 75 percent can result in an explosion if exposed to an ignition source, such as a hot surface, flame, or spark, of sufficient energy, <http://www.afcintl.com/applica2.htm>.

<sup>90</sup>This process mimics the biological process used by the bombardier beetle to produce a hot stream of hydrogen peroxide.

Researchers at Argonne National Laboratory and UOP have had promising results in using a membrane technology for replacing the vacuum distillation sequence of the traditional anthraquinone auto-oxidation process, which requires considerable capital and energy. A comparison of the unit operations involved in various hydrogen peroxide synthesis routes is shown in Table A7.

### ***Direct Synthesis from H<sub>2</sub> and O<sub>2</sub>***

Academic and industrial researchers in recent decades have explored various means of synthesizing hydrogen peroxide directly from hydrogen and oxygen. One such effort, research by Eric J. Beckman of the University of Pittsburgh on catalysts for facilitating the direct synthesis of hydrogen peroxide and use of CO<sub>2</sub> as a solvent, received a Presidential Green Chemistry Challenge Award in 2000. DuPont has pursued a direct synthesis from hydrogen and oxygen gases, and Hydrocarbon Technologies, Inc. (HTI), has investigated direct catalysis in aqueous solvents.

There is a fundamental trade-off in direct synthesis between catalyst reactivity and mass transfer concerns. Formulations involving gas phase contact of H<sub>2</sub> and O<sub>2</sub> must address safety concerns, particularly in an industrial environment. An aqueous solvent offers the opportunity for low-cost, low-pressure, and safe operation but suffers from the fact that gases do not dissolve well in water. A synthesis route using CO<sub>2</sub> as a solvent is relatively safe and impervious to unwanted oxidation reactions, but researchers have had difficulty finding a robust catalyst for this approach.

### ***In-Situ Hydrogen Peroxide Synthesis for Polypropylene Oxide Production***

Currently, 55 percent of global propylene oxide (PO) production is based on the chlorohydrin process, which produces significant amounts of aqueous waste. PO is used to make polyurethanes (65 percent), propylene glycol (20 percent), and other products (15 percent). Recently, HTI received a DOE Small Business Innovation Research grant for \$100,000 for research in propylene oxide synthesis via in-situ direct H<sub>2</sub>O<sub>2</sub> formation.<sup>91</sup> HTI is developing a one-step process for producing propylene oxide directly from hydrogen, oxygen, and propylene by using a dual-function nanoparticle catalyst that creates hydrogen peroxide in situ, which subsequently reacts with propylene to create propylene oxide.

A team at the Chinese Academy of Sciences used a tungsten oxide cluster and combined it with a process for synthesizing hydrogen peroxide in-situ. The tungsten cluster is soluble when used with hydrogen peroxide and can be easily recovered. It is claimed that no undesirable by-products are produced.<sup>92</sup>

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<sup>91</sup>[http://sbir.er.doe.gov/sbir/Awards\\_Abstracts/sbirsttr/cycle19/phase1/172.htm](http://sbir.er.doe.gov/sbir/Awards_Abstracts/sbirsttr/cycle19/phase1/172.htm).

<sup>92</sup>*Technical Insights Alert* (newsletter), "Green Chemistry: The Beginning of a New Trend for Process Industries," October 4, 2002, Frost and Sullivan.

**Table A7. A Comparison of Unit Operations Involved in Various Hydrogen Peroxide Production Routes.**

Unit	Traditional AQ Process		Novel Processes			
	Description	Issues	Direct			Membrane
			CO <sub>2</sub> Solvent	Gas Phase	Aqueous Solvent	Argonne/UOP
<b>Hydrogenation</b> (AQ + H <sub>2</sub> → AQH <sub>2</sub> )	Working solution hydrogenated over palladium catalyst in three-phase reactor (solid catalyst, liquid solution, gaseous hydrogen)	Transport limitations lead to difficulty in controlling reaction stoichiometry and residence time; by-products and wasted AQ and solvent	No AQ used.  Issue is catalyst robustness.	No AQ used  Issue is avoiding explosive regime (operating below LEL or adding nitrogen). Balance productivity with safety.	No AQ used.  Issue is mass transfer and catalyst robustness.	Traditional AQ process
<b>Oxidation</b> (AQH <sub>2</sub> + O <sub>2</sub> → AQ + H <sub>2</sub> O <sub>2</sub> )	Anthrahydroqui-none oxidized in two-phase reactor without catalyst					Traditional AQ process
<b>Extraction</b>	H <sub>2</sub> O <sub>2</sub> stripped from organics into water in countercurrent column	Cross-contamination of aqueous and organic phases; H <sub>2</sub> O <sub>2</sub> must be further purified	Countercurrent extraction with water			Membrane

<p><b>Drying</b></p>	<p>Vacuum distillation (several in series, depending on concentration desired)</p>	<p>Large capital cost, energy cost, safety issues; most industrial processes do not require such high concentration.</p>	<p>Distillation not needed  (Distributed applications do not require high concentration)</p>	<p>Distillation not needed  (Distributed applications do not require high concentration)</p>	<p>Distillation not needed  (Distributed applications do not require high concentration)</p>	<p>Distillation not needed  (Distributed applications do not require high concentration)</p>
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## Commercializing Firm

Most procedures for direct synthesis of  $H_2O_2$  are still in the research and development phase. The in-situ direct production of hydrogen peroxide for producing other chemicals will likely be the first commercial application of direct catalytic synthesis.<sup>93</sup> BASF and Solvay recently announced a joint venture for a PO plant that will use in-situ direct synthesis of  $H_2O_2$ .<sup>94</sup> Direct synthesis of  $H_2O_2$  for a commercial end product could then follow within the decade.

## Immediate Environmental and Economic Impacts

### *Hydrogen Peroxide Production*

New means of synthesizing hydrogen peroxide can have immediate economic benefits if both the capital and energy requirements are less than the AQ process. Environmental benefits would also result from eliminating the need to use organic solvents in the process and the subsequent need to dispose of organic wastes. Both the Argonne/UOP membrane and the various direct catalytic means of synthesizing  $H_2O_2$ , for example, eliminate the need for vacuum distillation. An Office of Industrial Technologies assessment indicates the Argonne membrane technology could realize an energy savings of 6.6 million Btus per ton of hydrogen peroxide.<sup>95</sup>

By enabling industrial production of hydrogen peroxide at the site it is used, alternative methods may reduce manufacturing and distribution costs.<sup>96</sup> Currently, hydrogen peroxide is concentrated to 70 percent purity and then transported to industrial users who dilute it before use. On-site generation would eliminate the need for concentration before transport and dilution after it, as well as the costs of transporting corrosive products. An additional environmental advantage of direct synthesis of  $H_2O_2$  lies in eliminating the use—and the associated storage, separation, and disposal—of nearly 5 million pounds of organic solvents.

### *Use of Hydrogen Peroxide in the Pulp and Paper Industry*

We note here the use of hydrogen peroxide detailed later in Case 15. Hydrogen peroxide could be substituted for chlorine dioxide in bleaching pulp and paper, which has been used since EPA banned elemental chlorine for this purpose. Advocates of using hydrogen peroxide to bleach pulp and paper maintain that only “Totally Chlorine Free” (TCF) processes can completely

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<sup>93</sup>Personal communication with Prof. Eric Beckman, University of Pittsburgh, July 18, 2002; Jeff Gendler, Hydrocarbon Technologies, Inc., July 19, 2002; and Ray Ballee, Hydrocarbon Technologies, Inc.

<sup>94</sup>Solvay, “Agreement with BASF Points to New Growth Potential for Solvay’s Hydrogen Peroxide Business,” Press Release, May 23, 2002, <http://www.solvay.com/news/press/pr2002/pr020523.htm>.

<sup>95</sup>[http://www.oit.doe.gov/chemicals/portfolio\\_corrosiveoxidations.shtml](http://www.oit.doe.gov/chemicals/portfolio_corrosiveoxidations.shtml).

<sup>96</sup>Personal communication with James Frank, Argonne National Laboratory, July 11, 2002, and Niel Rorskar, UOP, July 11, 2002.

eliminate dioxin and furan formation in pulp and paper effluent. This environmental benefit, however, is currently offset by the fact that H<sub>2</sub>O<sub>2</sub> processes require 3 to 4 percent more pulp (and hence trees) for making paper. The Alliance for Environmental Technology, an international association of chemical manufacturers who support ECF, also maintains that the transition from ECF to TCF would have three to five times the capital costs than the transition to ECF did and that bleaching costs would increase 60 percent. In the short term, TCF is expected to be a marginal/niche market, representing about 5 percent of pulp and paper bleaching worldwide.

## **Incentives to Adopt**

Alternative means could eventually result in lower capital and energy costs for hydrogen peroxide production. Pulp and paper firms, however, likely may not see an incentive to adopt unless legislation is passed requiring TCF production.

## **Government Role**

The most likely government intervention affecting H<sub>2</sub>O<sub>2</sub> production would be legislation affecting pulp and paper production, such as legislation requiring TCF production. Such legislation, however, is not probable in the short term because of costs to industry that would result from shifting to TCF from ECF production.<sup>97</sup>

## **Barriers**

There are both technical and economic barriers to the adoption of alternative methods for producing hydrogen peroxide. Among the technical barriers are the facts that, as noted, direct synthesis catalysts have not yet proven sufficient for commercial use and that other methods (e.g., ECF) can bleach paper and pulp more efficiently than hydrogen peroxide. The cost of hydrogen peroxide processes for bleaching paper products would need to drop 50 percent before they would be competitive with chlorinated alternatives.<sup>98</sup> An economic barrier to adoption of alternative methods of hydrogen peroxide production is the domination of the market by a small number of firms that have little incentive to modify their existing capital stock before its lifecycle ends or it deteriorates significantly.

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<sup>97</sup><http://www.aet.org/reports/articles/1997/chemtech-rebuttal.html>.

<sup>98</sup> Assuming that the hydrogen peroxide is a reactant rather than an efficient catalyst.

# 7. Advanced Oil and Gas Exploration and Production Technology

## Introduction

In recent decades, new technologies have been key to the finding and extracting recoverable oil and gas resources—located in deeper, more remote, and challenging locations. Technology innovation has enabled the domestic industry to remain viable in a highly competitive global marketplace. Many technologies developed by the industry have not only economic but also environmental benefits. This case studied two dozen technologies described in a recent report by DOE's Office of Fossil Energy<sup>99</sup> to see if any qualified as NGETs. No mention was made of the concept of green chemistry. Three technologies were selected.<sup>100</sup> All were in the drilling and completion processes, and all involved chemistry.

## Chemistry

**Improved drill bits.**<sup>101</sup> Advances in materials technology and bit hydraulics, spurred by competition between roller cone and polycrystalline diamond compact bits, have yielded tremendous improvement in drilling performance, cutting the drilling time in half from the 1970s. By reducing the time for the rig to be on site, advanced drill bits reduce potential impacts on soils, groundwater, wildlife, and air quality. Polycrystalline diamond compact (PDC) drill bits have become increasingly effective. Between 1988 and 1994, technology increased the average footage drilled per PDC bit by more than 260 percent, from 1,600 feet to 4,200 feet per bit; total footage drilled worldwide by diamond bits has climbed steadily from 1 percent in 1978 to 10 percent in 1985 to 25 percent in 1997; and latest generation PDC bits are even more improved.

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<sup>99</sup>DOE, Office of Fossil Energy *Environmental Benefits of Advanced Oil and Gas Exploration and Production Technology*, [http://www.fe.doe.gov/oil\\_gas/envIRON\\_rpt/index.html](http://www.fe.doe.gov/oil_gas/envIRON_rpt/index.html), accessed June 2002.

<sup>100</sup>The complete list of technologies: *Drilling and completion*: (a) CO<sub>2</sub> sand fracturing, (b) coiled tubing, (c) horizontal drilling, (d) hydraulic fracturing, (e) measurement—while drilling, (f) modern drilling bits, (g) multilateral drilling, (h) offshore drilling, (i) pneumatic drilling, (j) slimhole drilling, and (k) synthetic drilling muds; *Production*: (a) acid gas removal and recovery, (b) artificial lift optimization, (c) coalbed methane recovery, (d) freeze-thaw/evaporation, (e) gas-to-liquids conversion, (f) glycol dehydration, (g) advanced data management, (h) improved recovery processes, (i) leak detection and measurement systems, (j) low-bleed pneumatic devices, (k) offshore platforms, (l) downhole oil/water separation, (m) safety and environment management programs, and (n) vapor recovery units.

<sup>101</sup>DOE, Office of Fossil Energy, *Benefits of Advanced Oil and Gas Exploration and Production Technology*, p. 39.

**Advanced synthetic drilling fluids.**<sup>102</sup> Drilling an oil or gas well may require investments of hundreds of millions of dollars or more after all the analyses have pinpointed the reservoir. Drilling fluids are essential to carry bore cuttings to the surface, maintain pressure, and lubricate and clear the drilling system. Drilling fluids (muds) must perform effectively in extreme temperatures and pressures and must be environmentally compatible. In deepwater formations, synthetic drilling muds combine the higher drilling performance of oil-based fluids with the lower toxicity and environmental impacts of water-based fluids. The synthetics can be recycled and produce wastes believed to be environmentally benign. By eliminating the use of diesel as a mud base, synthetics have low toxicity and low-irritant properties that significantly enhance worker health and safety. The synthetics are manufactured by chemical synthesis from basic building blocks forming highly uniform products such as polyalphaolefins, linear alphaolefins, internal olefins, and fatty acid esters.

**Carbon dioxide—sand fracturing.**<sup>103</sup> Fracturing has been widely used since the 1970s to increase production from formations with low permeability or wellbore damage. Unlike the previously used hydraulic and acid fracturing techniques, CO<sub>2</sub>-sand fracturing stimulates the flow of hydrocarbons without the risk of formation damage with no wastes. The carbon dioxide vaporizes leaving only the sand with clean fractures to increase well deliverability while avoiding the waste management and well maintenance costs associated with more-traditional fracturing operations.

## **Immediate Environmental and Economic Impacts**

**Improved drill bits:** lower waste volumes, reduced maintenance and workovers, reduced fuel use and emissions, enhanced well control, and less time on site.

**Advanced drilling muds:** lower waste volumes, enhanced well control, lower toxicity of discharges, less time on site, and protection of sensitive environments.

**Carbon dioxide-sand fracturing:** increased recovery, lower waste volumes, fewer wells drilled, and protection of groundwater resources.

## **Long-Term Environmental Significance**

The benefits will increase as the use of these technologies and approaches expands.

## **Commercializing Firms**

The technologies are being used broadly throughout the oil and gas exploration industry.

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<sup>102</sup>DOE, Office of Fossil Energy, p. 40; note also Case 4, Example 4-q.

<sup>103</sup>DOE, Office of Fossil Energy, p. 41.

## **Incentives to Adopt**

The primary driving forces for the three technologies are reduced costs reflected in speed of drilling and greater yields; environmental benefits were secondary but important.

## **Barriers**

There are no unusual barriers in getting the technology into the field.

## **Government Role**

DOE provided support for all three technologies, especially in sponsoring field tests.

## 8. Approaches to Water Purification

### Introduction

New techniques of water purification and disinfection have far-reaching implications for ensuring adequate water supplies worldwide. Current techniques in the United States are based on chlorine or chlorine compounds as oxidants. The 1995 Community Water Systems Survey by EPA found that 98 percent of the 339 billion gallons of drinking water used in the United States were treated with chlorine compounds.

Chlorine is widely used for water treatment because it has many attributes of a good oxidant; its chemistry is well known; it is reliable and effective against a wide range of pathogens; and often it is cheaper than other forms of disinfection. Nevertheless, there are several reasons for developing an alternative to chlorine for water purification. Chlorine residual may harm aquatic life. All forms of chlorine are toxic to some extent, and therefore there are risks in shipping and storing chlorine. Chlorine reacts with certain types of organic matter in wastewater to create more hazardous compounds such as trihalomethanes. Several commercial firms and government agencies are therefore exploring means other than chlorine for water disinfection and purification.

### Chemistry

There are a number of significant efforts to develop means other than chlorine for water disinfection and purification. Five of these include:

1. Albright and Wilson's development of Bricorr<sup>®</sup> 288, a phosphonocarboxylate mixture that readily biodegrades, does not bioaccumulate and is an effective corrosion inhibitor with applicability to industrial cooling systems.
2. Nalco development of STABREX, a microorganism control based on a stabilized hypobromite compound is designed to mimic bromine antimicrobials in the human immune response system. The system is based on N-bromoaminoethane sulfonic acids (produced by enzyme-catalyzed reaction of bromine with hydrogen peroxide and 2-aminioethanesulfonic acid, or taurine).
3. Eka Chemicals has developed a new process to generate ClO<sub>2</sub> from sodium chlorate and hydrogen peroxide. This method has been registered with EPA as a disinfectant for drinking water and wastewater.

4. DOE development of a number of technologies and capabilities for addressing water quantity and quality issues. The Lawrence Berkeley National Laboratory developed an ultraviolet waterworks unit for disinfecting drinking water in communities of the developing world.<sup>104</sup>
5. Lawrence Livermore National Laboratory has development of a Capacitive Deionization (CDI) process which purifies brackish water (or water with salt content between 800 ppm and 3,200 ppm) between two carbon aerogel electrodes.<sup>105</sup> This method uses 10 to 20 times less energy than conventional electrolysis. For purifying seawater, the method uses about as much energy as reverse osmosis but without the need for costly membranes.

## Immediate Environmental and Economic Impacts

The immediate effects of these processes may be far reaching and include elimination of the use of chlorine for many processes, lowered costs, and increased availability of water supplies.

1. The Bricorr 288 is a unique corrosion inhibitor that is free of halogen, metals, and volatile organic compounds and does not contribute to dioxin or AOX formation.
2. The use of STABREX in almost 100 billion gallons of industrial wastewater since 1997 replaced 20 million pounds of chlorine that would have otherwise been used.<sup>106</sup>
3. The Eka Chemicals process to produce  $\text{ClO}_2$  from  $\text{NaClO}_3$  and  $\text{H}_2\text{O}_2$  obviates the need for gaseous or liquid chlorine feeds and chloride ion addition. It also reduces by-product chlorine production, thereby reducing the formation of trihalomethanes and chloroform disinfection by-products.<sup>107, 108</sup>
4. Using ultraviolet radiation to disinfect drinking water requires substantially less energy than boiling. Worldwide, nearly 1 billion persons boil water, often over wood fires, for drinking. Eliminating the need for such fires would reduce greenhouse gas emissions.

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<sup>104</sup> [eetd.llnl.gov/iep/archive/uv\[0\]/](http://eetd.llnl.gov/iep/archive/uv[0]/).

<sup>105</sup> <http://www.llnl.gov/IPandC/tech/aerogels/capacitive.html>.

<sup>106</sup> *The Presidential Green Chemistry Challenge Awards Program: Summary of 1999 Award Entries*.

<sup>107</sup> The first three examples were discussed by Dennis L. Hjeresen, "Green Chemistry and the Global Water Crisis," *Pure Appl. Chem.*, Vol. 73, No. 8, August 2001, pp. 1237–1241.

<sup>108</sup> Additional references: *The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, p. 52; EPA, *Community Water System Survey, Volumes I and II, Overview*; 815-R-97-001a, January 1997. Various industry sites: [http://www.consolidatedtreatment.com/manuals/Fact\\_sheet\\_chlorine\\_disinfection.pdf](http://www.consolidatedtreatment.com/manuals/Fact_sheet_chlorine_disinfection.pdf); <http://www.aiche.org/government/pdfdocs/chlorine.pdf>; <http://www.eurochlor.org/chlorine/industry/97xbr2.htm>.

5. Using CDI for desalinization requires less energy and does not produce electrostatic generation, acids, bases, or salt solutions such as those resulting from ion-exchange systems.

## **Long-Term Environmental Significance**

Methods of water purification that obviate the need for chlorine or chlorine-containing materials will reduce the effects that those compounds have on the environment. Chlorine has been implicated in the creation of dioxins and other contaminants when used in waste streams and water purification.

## **Commercializing Firms**

As noted above, several firms are working on differing techniques for water purification and disinfection. The efforts of chemical suppliers have recently been summarized.<sup>109</sup>

## **Incentives to Adopt**

Increasing government regulations on the use of chlorine provide several incentives to adopt alternative methods for disinfecting and purifying water. Security concerns regarding the use of chlorine may also lead to the adoption of alternative methods for treating drinking water. Washington, D.C., authorities, as discussed in this report, recently substituted a safer chemical for the chlorine gas stored in 90-ton railcars and used at the Blue Plains Wastewater Treatment Plant.

## **Government Role**

As noted above, regulations regarding the use of chlorine may lead to the adoption of alternative methods of water treatment. DOE also sponsors research programs at national laboratories on water purification and disinfection techniques.

## **Barriers**

The low cost and wide availability of chlorine has slowed the adoption of many alternatives.

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<sup>109</sup>Alexander H. Tullo, "Turning on the Tap: The World's Growing Concern About Water Supply Is Making the Water Treatment Market More Attractive for Chemical Suppliers," *Chemistry & Engineering News*, Vol. 80, No. 46, November 18, 2002, pp. 37-42.

## 9. Wood Preservation

### Introduction

The pressure-treated wood industry is a \$4 billion industry, producing approximately 7 billion board feet of preserved wood each year, protected from insects and rot. More than 95 percent of pressure-treated wood in the United States uses chromated copper arsenate (CCA). Replacing CCA with alkaline copper quaternary (ACQ) represents a significant route to pollution prevention.

### Chemistry

More than 95 percent of pressure-treated wood in the United States has been preserved using CCA. CCA contains two known human carcinogens—hexavalent chromium and arsenic. ACQ wood preservative provides the same level of performance as CCA in controlling decay fungi and termites in preserved wood. The active ingredients in ACQ are copper and a quaternary ammonium compound—dodecyl dimethyl ammonium chloride (DDAC) or alkyl dimethyl benzyl ammonium chloride (BAC). Neither copper, DDAC, nor BAC has been designated as a human or mammalian carcinogen.

Other approaches to wood preservation are under development—boron-based systems and several bio-based approaches.

### Immediate and Long-Term Environmental Significance

Replacing CCA with ACQ represents an important pollution prevention advancement. Complete replacement will

- Virtually eliminate the use of arsenic in the United States. More than 90 percent of the 44 million pounds of arsenic used in the United States each year is used to make CCA.
- Eliminate the importation of 40 million pounds of arsenic from China each year.
- Eliminate the use of 64 million pounds of hexavalent chromium.
- Eliminate potential risks associated with the production, transportation, use, and disposal of the CCA wood preservatives and CCA-treated wood.

- Eliminate Resource Conservation and Recovery Act hazardous waste generation from production and treating facilities.
- Eliminate serious disposal issues associated with CCA-treated wood and ash residues associated with the burning of treated wood.

## **Commercializing Firm**

In 1996, Chemical Specialties, Inc. (CSI) introduced Preserve (ACQ) wood preservative in the United States. In 2001, CSI produced more than 1 million pounds of ACQ to produce more than 100 million board feet of preserved wood. In 2002, 60 percent of CSI's product will have moved from CCA to ACQ.

## **Incentives to Adopt**

The impending phase-out of CCA has given CSI the competitive advantage and has allowed it to expand its market.<sup>110</sup> Presumably this approach is somewhat more expensive than the previously dominant CCA, but the impending regulation and possible consumer concern may make the cost of ACQ quite acceptable.

## **Government Role**

EPA has moved to phase out the use of CCA for residential construction, while more regulatory pressure is being placed on pentachlorophenol and creosote.

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<sup>110</sup>See *The Presidential Green Chemistry Challenge Awards Program: Summary of 2002 Award Entries and Recipients* ([www.epa.gov/greenchemistry](http://www.epa.gov/greenchemistry)), forthcoming; [www.epa.gov/pesticides/citizens/cca\\_transition.htm](http://www.epa.gov/pesticides/citizens/cca_transition.htm); and [www.preservedwood.com](http://www.preservedwood.com).

## 10. Sentricon<sup>®</sup> Termite Colony Elimination System

### Introduction

Over the past half century, the most common method of subterranean termite control has involved injecting large volumes of insecticides, diluted in the soil surrounding a structure to act as a chemical barrier through which termites would not penetrate. This method poses environmental risks because of the requirements for significant amounts of insecticide and poses safety hazards because of the need for workers to handle these hazardous substances. Research on both termite physiology and the behavior patterns of termite colonies has allowed the development of a new approach. A chemical compound that causes delayed insect mortality by interfering with their growth regulators is combined with appropriate monitoring/baiting procedures. Tiny amounts (less than 1 gram) of this new material could be carried by termites back to the nest, thereby destroying the entire colony. If proven effective, this approach could significantly reduce the environmental and health hazards from subterranean termite control.

### Chemistry

Sentricon, developed by Dow AgroSciences in collaboration with Nan-Yao Su of the University of Florida, employs an integrated pest management approach using monitoring and targeted delivery of a highly specific bait. The properties of hexaflumuron as a termite control agent are attractive from an environmental and human risk perspective, but more importantly, the potential for adverse effects is dramatically reduced because it is present in only very small quantities in stations with termite activity.<sup>111</sup>

### Immediate Environmental and Economic Impacts

The annual cost of termite treatments to the U.S. consumer is about \$1.5 billion. Each year, as many as 1.5 million homeowners will experience a termite problem and seek a control option. From 1940 to 1995 the nearly universal treatment involved insecticides in the soil surrounding the structure to create a chemical barrier for the termites. Hazards arose in handling, misapplication, spills, and worker exposure to the insecticides. More than 300,000 structures are now being safeguarded.

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<sup>111</sup>See *The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients*, p. 7; Su Nan-Yao, and Rudolf H. Scheffrahn, "Comparative Effects of Two Chitin Synthesis Inhibitors, Hexaflumuron and Lufenuron, in a Bait Matrix Against Subterranean Termites (Isoptera:Rhinotermitidae)," *Journal of Economic Entomology*, October 1996, Vol. 89, No. 5, pp. 1156-1160; U.S. Patent 5,811,461 for the Sentricon system; and U.S. Patent 6,178,834 (discusses various termite control systems and claims improvements over Sentricon).

## **Commercializing Firm/Incentives to Adopt**

The Sentricon system provided Dow AgroSciences with a new business opportunity providing homeowners with a cost-effective solution to a problem; the incentive was not in solving an environmental problem.

## **Government Role**

The system is regulated by EPA, but there was no direct federal support in the research and development of the system.

## **Barriers**

The barriers were those common in the development of a new product. As competitive products appear, Dow AgroSciences will face cost and performance barriers in maintaining their market position.

# 11. Inert Anodes in Aluminum Smelting

## Introduction

Energy is one of the principal costs for producing aluminum. The aluminum smelting industry therefore is continually interested in finding new ways to reduce its energy costs. A new smelting technology developed by Alcoa for aluminum smelting, using inert anodes instead of carbon anodes, could, if feasible on a commercial scale, increase smelter capacity, lower production costs, and reduce the emission of carbon dioxide and sulfur derivatives. Test cells are currently operating in Europe and North America, with full-scale testing expected by the end of 2002.

## Chemistry<sup>112</sup>

In the 1980s the electrometallurgy of aluminum involved the electrolysis of a cryolite-alumina ( $\text{Na}_3\text{AlF}_6 + \text{Al}_2\text{O}_3$ ) melt using a carbon anode and an aluminum cathode to yield aluminum:  $2 \text{Al}_2\text{O}_3 + 3\text{C}$  gives  $4\text{Al} + 3 \text{CO}_2$  and by-products from the cryolite.<sup>113</sup> The aluminum cathode was subsequently replaced by a carbon-lined cathode in the Hall-Heroult process. The improved process involves the replacement of the anode with  $\text{NiO-NiFe}_2\text{O}_4\text{-Cu}$  and the cathode with  $\text{TiB}_2\text{-Al}_2\text{O}_3$ .

This change enables a reduction in the anode-cathode distance from 1.75 inches to 1 inch, reducing the energy required for aluminum smelting by more than 25 percent. Work is proceeding on schedule to test and improve Alcoa's revolutionary smelting technology using inert anodes instead of carbon anodes. If it proves to be feasible on a commercial scale, the new process promises to increase smelter capacity and lower production costs. It also would benefit

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<sup>112</sup>References:

*Alcoa 2001 Annual Report* (www.alcoa.com).

Siba Ray et al., Alcoa, "Electrolysis with an Inert Electrode Containing a Ferrite, Copper, and Silver," U.S. Patent 5,865,980 February 2, 1999.

Siba Ray et al., Alcoa, "Inert Electrode Containing Metal Oxides, Copper, and Noble Metal," U.S. Patent 6,126,799, October 3, 2000.

Siba Ray et al., Alcoa, "Inert Electrode Containing Metal Oxides, Copper and Noble Metal," U.S. Patent 6,332,969, December 25, 2001.

Jainagesh A. Sekhar et al., University of Cincinnati, "Composite Electrode for Electrochemical Processing and Method for Using the Same in Electrolytic Process for Producing Metallic Aluminum," U.S. Patent 5,217,583, June 8, 1993.

M. B. Bevern, (ed.), *Encyclopedia of Material Science*, Vol. 2, Pergamon Press, 1986, pp. 1410-1414.

Aluminum Project Fact Sheet, "Advanced Anodes and Cathodes Utilized in Energy-Efficient: Aluminum Production Cells," Office of Industrial Technologies, Energy Efficiency and Renewable Energy, DOE, www.oit.doe.gov/aluminum.

The Aluminum Association Inc. in conjunction with DOE, "Inert Anode Roadmap" February 1998, prepared by Nancy Margolis and Jack Eisenhauer, Energetics Inc., Columbia, Md.

F. C. Walsh, "Electrochemical Technology for Environmental Treatment and Clean Energy Conversion," *Pure Appl. Chem.*, Vol. 73, No. 12, 2001, pp. 1819-1837.

<sup>113</sup>Bevern, 1986.

the environment because the principal emission is oxygen rather than carbon dioxide and sulfur derivatives.

## **Immediate and Long-Term Environmental Significance**

This includes: possible energy savings of 6 trillion Btus annually in the United States by 2010 (\$90 million); elimination of carbon and fluorocarbon emissions ( $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ ); reduction of cyanide formation and dust emissions; nonenergy savings of \$20 million; elimination of polycyclic organic matter (POM) generated during anode manufacture and consumption.

## **Commercializing Firm**

Alcoa is commercializing the process.

## **Incentives to Adopt**

Alcoa has the primary incentive to lower costs in aluminum smelting.

## **Government Role**

DOE has supported the development of this program. The Alcoa patents for it note the government support and grant the government certain rights to the invention.

## **Barriers**

The only apparent barrier is the time needed to demonstrate and scale up the process.

# 12. Process for Production of Cytovene<sup>®</sup> Potent Antiviral Agent

## Introduction

Cytovene (ganciclovir) is a potent antiviral agent used to treat infections in patients with compromised immune systems, including those with AIDS. Roche Colorado Corporation (formerly Syntex Chemicals) developed the first commercially viable production process for the drug in the early 1990s. In the mid-1990s, the firm redesigned the production process using the principles of green chemistry to make it significantly more efficient. The new process uses half the number of reagents and intermediate chemicals that its predecessor used, eliminates a significant fraction of hazardous waste streams, recycles and reuses most ingredients not incorporated into the final product, and eliminates the need for operating and monitoring three different and potentially hazardous chemical reactions.

## Chemistry<sup>114</sup>

The second-generation Guanine Triester process reduced chemical reagents from 28 to 11, eliminated the only two hazardous solid waste streams, and efficiently recycled and reused four of the five ingredients not incorporated in the final product for an overall yield increase of more than 25 percent and a 100 percent increase in production throughput. The process eliminated the use of dichloromethane, dimethylformamide, palladium hydroxide, and hydrogen. In addition, large-scale processing conditions employing active palladium catalysts in a hydrogen and methanol charged atmosphere, the mixture of which is a potential hazard for ignition, were completely eliminated. In this new process, silylation of guanine and subsequent coupling with the triester reagent gave a highly regioselective alkylation product. The in-situ acylation of the N-9/N-7 product mixture followed by selective crystallization of the N-9 product provided a facile method for isolating the desired N-9 product in high yield. Final deprotection to remove the esters and amide protecting groups could be accomplished in a single step with aqueous ammonium hydroxide. Overall yield was 65 percent.

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<sup>114</sup>Garry B. Semones, Sam L. Nguyen, J. D. Yuen-Kwei Han, Eric Lodewijk, and George Schloemer, "The Development of an Environmentally Friendly, Cost Effective Process for the Production of Cytovene<sup>®</sup> Antiviral Agent," prepared for presentation at the 2000 Spring AIChE Meeting, Atlanta, Ga., March 5-10; available at [www.aspentech.com/publication\\_files/AICHE2000.pdf](http://www.aspentech.com/publication_files/AICHE2000.pdf); also described in U.S. Patent 5,565,565.

## **Immediate Environmental and Economic Impacts**

The second-generation Guanine Triester process reduced air emissions by 66 percent and liquid/solid waste generation by 89 percent, eliminating 1.1 million kg/year of liquid waste and 25,000 kg/year of solid waste. The increases in raw material costs were more than offset by improvements in equipment utilization as reflected in the overall process throughput.

## **Long-Term Environmental Significance**

The process has been adapted for manufacture of other antiviral agents, Acyclovir (Zovirax<sup>®</sup>) and ganciclovir monovalinate (Cymeval<sup>®</sup>).<sup>115</sup>

## **Commercializing Firm**

Roche Colorado Corp.

## **Incentives to Adopt**

Presumably cost as well as capacity increase for facilities.

## **Government Role**

Winner of Green Chemistry Challenge Award in category "Alternative Synthetic Pathways Award" 2000.<sup>116</sup>

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<sup>115</sup>Described in U.S. Patent 5,567,816 and Application No. 09/127,380, now allowed.

<sup>116</sup>The *Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients* (www.epa.gov/greenchemistry), p. 5.

## 13. High-Yield Melting of Aluminum

In alliance with Praxair, Alcoa is testing High-Yield Melting.<sup>117</sup> This R&D project involved constructing and operating a commercial scale aluminum-melting furnace in Alcoa's Warrick, Ind., Operations' ingot plant. Benefits are improved environmental performance, safer work environment, reduction in natural gas usage, and significant waste elimination. The project received the Indiana Governor's Award for Excellence in Pollution Prevention.

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<sup>117</sup> *Alcoa Annual Reports*, [www.alcoa.com](http://www.alcoa.com).

## **14. Elimination of Ozone-Depleting Chemicals in the Printed Wire Board and Electronic Card Assembly and Test Processes**

### **Chemistry<sup>118</sup>**

IBM Austin is a manufacturing and development facility. Operations include the manufacture of printed wire board (PWB) in the Panel Plant facility and electronic circuit cards in the Electronic Card Assembly and Test Process (ECAT) facility. In 1992, IBM Austin completely eliminated the use of CFCs and other ozone-depleting substances from its PWB and ECAT processes. This elimination program resulted in 100 percent reduction of CFC-113 (1988 peak usage of approximately 432,000 pounds) and 100 percent reduction of methyl chloroform (1988 peak usage of approximately 308,000 pounds) from IBM Austin's PWB and ECAT processes. These accomplishments were achieved by converting to an aqueous-based photolithographic process in the PWB facility in 1989, an interim aqueous cleaning process in the ECAT facility in 1991 and 1992, and a final no-clean process (eliminating the aqueous cleaning process) in the ECAT facility. Changing from a solvent-based photolithographic process to an aqueous-based process eliminated methyl chloroform (MCF) from PWB panel manufacturing (1988 usage of 181,000 pounds). The interim process changes to aqueous cleaning eliminated MCF from manufacturing processes in ECAT (1989 peak usage of 196,000 pounds) and were largely responsible for eliminating CFC-113 from all manufacturing processes at the IBM site. Although CFC-113 was eliminated from the site in 1991.

### **Incentives to Adopt/Government Role**

IBM was meeting EPA requirements in phasing out the use of chlorofluorocarbons.

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<sup>118</sup>*The Presidential Green Chemistry Challenge Awards Program: Summary of 1996 Award Entries and Recipients*, [www.epa.gov/greenchemistry](http://www.epa.gov/greenchemistry), p. 25.

# 15. Producing Pulp for Paper Manufacture

## Introduction

The pulp and paper industry annually produces approximately \$50 billion in bleached pulp worldwide for use in paper products. Wood comprises two biopolymers: cellulose, which imparts strength to trees and paper, and lignin, which imparts color, texture, and mechanical properties to wood. The goal in the manufacture of high-quality paper is to remove the lignin with as little damage to the cellulose fibers as possible (high-quality paper is composed of lignin-free cellulose fibers). Traditionally, the industry has used chlorine compounds to produce the lignin-free cellulose. Decades of optimization have led to highly selective delignification (or minimally damaged cellulose), but these man-made technologies produce waste streams that contain environmentally deleterious phenolic compounds as well as nonbiodegradable chloroaromatics. As a result, there is regulation in all developed countries requiring pulp manufacturers to phase out the use of chlorine.

Nature pursues entirely different pathways for the selective delignification of wood or wood pulp, using only the readily available and nontoxic agents air and water. Nature carries out this chemically and technically challenging multistep process by using a complex ensemble of selective metalloenzymes (glyoxal oxidase, ligninase, and Mn peroxidase). Industry has yet to reproduce such processes economically. The most attractive alternative oxidants, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ozone ( $\text{O}_3$ ), are encumbered by inherent limitations. Hydrogen peroxide acting alone is simply not effective. Ozone processes, while potentially effective, fall far short of the selectivity required for general commercial use or of the selectivity seen in nature.

A variety of green chemistry approaches are being developed to remove the chlorine from the manufacture of wood pulp.

# 15a. Delignification and Bleaching of Pulp in Paper Manufacture Without the Use of Chlorine or Chlorine Dioxide

## Chemistry<sup>119</sup>

Hydrogen peroxide, oxygen, or ozone is used in only 6 percent of the world's paper pulp bleaching. Use of chelated iron compounds can make the use of hydrogen peroxide more efficient and more competitive with the ClO<sub>2</sub>-based process. (EPA banned the use of Cl<sub>2</sub> effective April 2001.)

## Immediate Environmental and Economic Impacts

Eliminates formation of dioxin and other organo-chlorine waste products.

## Long-Term Environmental Significance

Increases the elimination as above.

## Commercializing Firms

Innumerable paper companies.

## Incentives to Adopt/Government Role

EPA's action on use of chlorine in bleaching.

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<sup>119</sup>References:

1. Cann and Connelly, *Real World Cases in Green Chemistry*, 2000, pp. 55-59, and references therein.
2. *The Presidential Green Chemistry Challenge Awards Program: Summary of 1999 Award Entries and Recipients*, [www.epa.gov/greenchemistry](http://www.epa.gov/greenchemistry), p. 3.

For discussion of elimination of chlorine in certain applications of green chemistry in relation to water scarcity, see Dennis L. Hjeresen, "Green Chemistry and the Global Water Crisis," *Pure Appl. Chem.* Vol. 73, No. 8, August 2001, pp. 1237-1241.

A survey of U.S. patents, 1996-2002 for "biopulping" yielded 26 patents.

## 15b. Trees to Paper Using Air in Place of Sulfur and Chlorine

### Introduction

A new catalytic biomimetic approach using versatile, nontoxic, and inexpensive inorganic clusters known as polyoxometalates has achieved the selective removal of lignin from wood, using only air and water. Its proponents call it an ideal process that only nature has achieved to date. This biomimetic and catalytic technology eliminates the environmental problems associated with conventional chlorine-based processes while overcoming the limitations inherent in other chlorine-free pulp bleaching strategies. It is green in at least six ways, including the complete elimination of waste streams (a “closed process” is achieved). The high selectivity entails less consumption of the natural renewable resource, wood. It is energy-efficient and, its proponents claim, cost-effective.

### Chemistry<sup>120</sup>

The new catalytic biomimetic approach uses versatile, nontoxic, and inexpensive inorganic clusters known as polyoxometalates in two steps: (1) Wood or pulp is reacted with the oxidized polyoxometalate leaving high-quality cellulose fibers. As the polyoxometalate is reversibly reduced, the lignin is oxidized and solubilized; (2) O<sub>2</sub> is added, and the same polyoxometalate catalyzes the complete conversion (mineralization) of the dissolved lignin fragments to CO<sub>2</sub> and water.

### Immediate Environmental and Economic Impacts

Eliminates the environmental problems associated with conventional chlorine-based processes while overcoming the limitations inherent in other chlorine-free pulp bleaching strategies; complete elimination of waste streams.

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<sup>120</sup>The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients, p. 16.

## 15c. TAML™ Oxidant Activators for Hydrogen Peroxide

### Introduction

Two decades of research have led to the development of a series of environmentally friendly oxidant activators based on iron. These tetraamido-macrocyclic ligand (TAML™) activators catalyze the reactions of oxidants in general. In particular, TAML can make hydrogen peroxide effective as a selective delignifying agent.

### Chemistry

A series of environmentally friendly oxidant activators based on iron—TAML activators catalyze the reactions of oxidants such as hydrogen peroxide. These activators act much as oxidizing enzymes. These activators can provide the pulp and paper industry with the first low-temperature hydrogen peroxide-based delignification technology for treating pulp. This process proceeds rapidly and efficiently at 50 degrees C, indicating that minimal capital will be required to retrofit existing mills for its use. This approach is more selective than any other TCF process and, except at low lignin content, is as selective as the current dominating delignification technology based on chlorine dioxide.<sup>121</sup>

### Immediate Environmental and Economic Impacts

As discussed in 15a and 15b above.

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<sup>121</sup>The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients, p. 16.

# 16. Aqueous Biphasic Systems for Liquid-Liquid Extractions

## Introduction

Liquid-liquid extraction is a process for separating components that are in solution by their distribution between two immiscible liquid phases. The extraction occurs because of the relative affinity of the solute for the hydrophobicity or electric potential of the two phases and can be facilitated by the addition of salting or complexing agents or by chemical reaction. Liquid-liquid extraction is used chiefly when distillation is impractical or too expensive.<sup>122</sup> It is particularly useful when the relative volatility between two components is close to unity, or when the components are heat sensitive, as in the case of antibiotics or nonvolatile minerals.

Although this method can be highly selective, efficient, rapid, adaptable, and scalable, it suffers from the emission of VOCs, which are precursors to ozone formation in the atmosphere. In some cases, VOCs can be toxic or flammable, posing safety concerns requiring costly designs to mitigate.

The promise of aqueous biphasic systems (ABS) lies in the substitution of the organic phase of a liquid-liquid extraction process with an aqueous system composed of water, water-soluble polymers, and inorganic salts. Such a system would retain the essential characteristics of traditional liquid-liquid extractions without the toxicity, flammability, VOC emissions, and denaturing environment inherent in some organic solvents. Furthermore, a polyethylene glycol (PEG)-based system would be inexpensive and “tunable.”

## Chemistry

The liquid-liquid extraction procedure is based on the selective partitioning of a desired solute into a particular phase in order to recover it. The two liquids are immiscible on account of their large difference in hydrophobicity—in effect, a water-based and oil-based system. Typically, the organic phase contains volatile organic chemicals that are precursors to ozone formation when exposed to sunlight. Industrial designs of such extraction procedures must include safety precautions because certain vapor phase concentrations of hydrocarbons can produce flammable or explosive conditions.

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<sup>122</sup>Robert H. Perry and Don W. Green, *Perry's Chemical Engineers' Handbook*, 7th edition, Section 15-4, 1997.

Aqueous biphasic systems were first discovered in 1896 by Beijerinck, who noticed the formation of two phases upon mixing agar with gelatin.<sup>123</sup> Since then, many biphasic aqueous systems have been discovered by the addition of hydrophilic polymers to aqueous solutions. Depending on the pH, ionic strength, and temperature of the solution, addition of certain polymers past a critical concentration results in the formation of two immiscible phases, both of which are rich in water.

Most modern applications of aqueous biphasic systems are in biotechnology, where labile biomolecules can be rapidly separated in a nondenaturing environment with low interfacial tension. However, this type of separations process has only recently been considered for other industrial applications.

## **Immediate Environmental and Economic Impacts**

The most promising applications in the near term, outside of the field of bio-separations, are in the remediation of radioactive nuclear and medical waste.<sup>124</sup> For example, millions of gallons of radioactive waste are stored at sites managed by DOE, such as Hanford, West Valley, Idaho Falls, Oak Ridge National Laboratory, and Savannah River.<sup>125</sup> These sludges and supernatants could be treated as low-level waste if the radioactive material, such as cesium, strontium, and technetium radionuclides, could be selectively and efficiently removed. High concentrations of sodium, potassium, chloride, and nitrates have limited the effectiveness of many traditional separations methods. Research by Robin Rogers has shown that aqueous biphasic systems could be very effective at recovering TCO<sub>4</sub> from simulated Hanford waste tanks.<sup>126</sup> In these cases, aqueous biphasic separations would be used simply for their technical utility, rather than their absence of VOCs.

## **Long-Term Environmental Significance**

In the long-term, proponents of ABS envision the substitution of some industrial separations processes with ABS technologies. Although ABS formulations are still in the laboratory phase, initial findings indicate that certain classes of liquid-liquid extractions could be redesigned, producing virtually no VOCs and eliminating toxic and flammable solvents. Researchers have demonstrated that PEG-ABS systems are tunable, so that the phase characteristics of the PEG-rich phase can match the hydrophobicity and water content of analogous organic solvents. PEG-ABS systems would be commercially available and usable in traditional solvent extraction equipment. According to Rogers, one of the first research goals could be comprehensive partition studies for predicting distribution coefficients in a wide variety of ABS systems.

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<sup>123</sup><http://www.sbu.ac.uk/water/biphasic.html>.

<sup>124</sup>Private communication with Robin Rogers, October 25, 2002.

<sup>125</sup>ORNL website, <http://www.ornl.gov/divisions/ctd/ESP/97tasks/task10.html>.

<sup>126</sup><http://bama.ua.edu/~rdrogers/webdocs/cleansx.html>.

## **Commercialization Firm**

Most of the current applications of ABS are in biotechnology.

## **Incentives to Adopt**

In some cases, such as radioactive waste remediation, ABS could offer superior separations performance. In others, the advantages would primarily lie in the reduction of the toxicity, flammability, and environmental effects of VOC emissions. The advantage of PEG-based ABS is that the FDA has already approved many applications with PEG in the chemical industry, and it is not likely to be regulated more stringently.

## **Barriers**

Liquid-liquid extraction is very well established in the chemical processing industry. The prospects for market penetration in this sector depend on environmental regulations limiting industrial VOC emissions of common liquid-liquid extractions solvents or development of a “drop-in” ABS system. Niche applications could be found for high-value products on a case-by-case basis.

## **Government Role**

The adoption of ABS by industry will depend on environmental regulations regarding VOCs and toxic chemicals.

# 17. Room Temperature Ionic Liquids

## Introduction

Room Temperature Ionic Liquids (RTILs) are liquids that are composed entirely of ions and that have melting points below or near room temperature. First discovered in the early 20th century, RTILs have attracted renewed interest by the chemical industry for their favorable environmental properties and promise of improved reaction kinetics and solution properties for some classes of organic synthesis.

The fine chemical and pharmaceutical industry is less waste-conscious than industries that are traditionally considered “dirty,” such as oil refining and bulk chemicals (see Table A8). Volatile organic solvents, many of which have toxic or hazardous properties and contribute to atmospheric emissions and contamination of aqueous effluents, serve as the primary media for organic synthesis.

**Table A8. The Sheldon E-Factor.**<sup>127</sup>

Industry	Production (tons/year)	E-factor
Oil Refining	$10^6$ – $10^8$	0.1
Bulk Chemicals	$10^4$ – $10^6$	1–5
Fine Chemicals	$10^2$ – $10^4$	5–50
Pharmaceuticals	$10^1$ – $10^3$	25–100

As a result, the chemical industry has shown increasing interest in RTILs, which have very low vapor pressures and thus pose no flammability or atmospheric emissions concerns. Although it is premature to predict the widespread replacement of organic solvents with RTILs, RTILs have shifted the focus in the chemical industry to designer solvents.

<sup>127</sup>The E-factor, defined by Roger Sheldon, is the ratio (by weight) of the by-products to the end product(s). From J. D. Holdbrey and K. R. Seddon, “Ionic Liquids,” *Clean Products and Processes*, 1999, pp. 223–236, and R. A. Sheldon, “Atom Economy and Catalysis,” *Chemistry Reviews*, May 2000, pp. 10–13. The E-factor for semiconductor manufacture may exceed 100, according to Sheldon at the First International Conference on Green and Sustainable Chemistry.

## Chemistry

In contrast to molten salts, RTILs are typically salts of bulky, asymmetric organic cations and are fluid at ambient temperatures, are colorless, and have low viscosity. The first modern RTIL work began in the early 1970s, when John S. Wilkes, a chemist at the U.S. Air Force Academy in Colorado Springs, Colo., was conducting battery research, attempting to find salts that remained liquid at low temperatures so as not to damage component materials. In the late 1990s, Kenneth R. Seddon,<sup>128</sup> a chemist at the Queen's University of Belfast, Northern Ireland, and Robin D. Rogers, professor of chemistry at the University of Alabama, began making a wide variety of ionic liquids and testing them out as solvent in old reactions.

RTILs can offer some unique properties as media for homogeneous catalysis. They are easy to contain, have reasonable thermal stability, can dissolve a wide range of compounds, and are “tunable” with the choice of appropriate anion and function groups on the cation. Anions can be chosen so that they are weakly coordinating, allowing the solvent to be highly polar but not coordinating, thus having a strong rate-enhancing effect on reactions that involve cationic intermediates. Also, because RTILs are immiscible with some organic solvents, they can be used in two-phase systems. For example, in some reactions, the products are not soluble in the ionic liquid, forming a layer that can easily be separated, while the catalyst remains dissolved in the ionic liquid phase, allowing for efficient recycling.

## Immediate Environmental and Economic Impacts

It is difficult to quantify the benefits of room temperature ionic liquids as a singular class of technologies because the innovations are entirely application specific. Because ionic liquids have very low vapor pressure, the replacement of any organic solution with an ionic liquid would benefit directly from reduced VOC emissions. Research in a number of laboratories has shown their advantage as designer solvents in a number of reactions, exhibiting desirable properties such as solvent thermal stability, enhanced separations capabilities, and faster reactions kinetics.<sup>129</sup>

According to Rogers,<sup>130</sup> ionic liquids will likely make inroads in the near future in the dissolution of the natural polymer cellulose, obviating the need for chemical derivitization or the use of a very limited class of existing solvents.<sup>131</sup>

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<sup>128</sup><http://www.ch.qub.ac.uk/resources/ionic/ionic.html>.

<sup>129</sup>For a review of catalytic reactions in ionic liquids: Roger Sheldon, *Catalytic Reactions in Ionic Liquids*, The Royal Society of Chemistry, October 18, 2001, pp. 2399–2407; also Professor Seddon's introduction to the special issue on ionic liquids, *Green Chemistry*, April 2002, pp. G25–26.

<sup>130</sup><http://bama.ua.edu/~rdrogers/webdocs/ionicliquids.html>.

<sup>131</sup>Private communication with Robin Rogers, October 2, 2002.

## Long-Term Environmental Significance

Many argue that, as environmental regulations become stricter, and the associated cost of nonremunerative capital investments larger, the chemical process industry will gradually move outside the United States.<sup>132</sup> Efforts to find low cost methods of redesigning traditional industrial processes could make the industry more competitive and less vulnerable to regulatory shocks, ensuring its long-term health. Some researchers argue that the promise of RTILs has spurred a paradigm shift in how chemists look at solvents and waste.

## Commercializing Firm

The French Petroleum Institute (IFP)<sup>133</sup> has commercialized an ionic liquid process (DIFASOL) for the conversion of butene into isooctane. Solvent Innovation<sup>134</sup> and SACHEM<sup>135</sup> have also reported commercialization efforts for RTILs.

*Chemical Week*<sup>136</sup> reported:

Solvent Innovation (Cologne, Germany), a leading developer of ionic liquids, says it is close to introducing commercial materials in ton quantities. Ionic liquids—salts that exist in liquid form at relatively low temperatures—are being targeted to replace conventional solvents in a range of reactions, including enzyme catalyzed processes, lubricants production, and desulfurization of diesel fuel.

Solvent Innovation says it is developing a series of ionic liquids to replace solvents with a high environmental impact. Its Ecoeng family of halogen-free ionic liquids is being sold in quantities up to 1 m.t., it says. That range includes 1-alkyl-3-methyl-imidazolium octylsulfate, which is being targeted at replacing halogenated solvents. “Ecoeng will lead to improved and greener products and processes,” says chief technology officer Thomas Schubert. “Only two or three ionic liquids will make it to multi-ton industrial production within the next few years. It is hard to predict which will make it, but most likely these ionic liquids will be the ones that don’t contain halogen atoms,” says Schubert. Solvent Innovation, “is also focused on the design of special solution and task-specific ionic liquids,” including chiral forms, Schubert says. “These are for a range of different applications where ionic liquids are not used in large quantities, but add a significant advantage to a device, product, or process,” he says. Solvent Innovation was among a group of ionic liquids developers that discussed their commercial plans at a recent meeting of the American Chemical Society in Boston. The group also included Cytec Industries, Merck KGaA, Ozark Fluorene (Tulsa), and SACHEM (Austin, TX).

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<sup>132</sup>Brendan Horton, “Green Chemistry Puts Down Roots,” *Nature*, August 19, 1999, pp. 797–799.

<sup>133</sup><http://quill.qub.ac.uk/pdf/ti.pdf>.

<sup>134</sup><http://www.solvent-innovation.com/Englisch/index2.htm>.

<sup>135</sup><http://www.sacheminc.com/>.

<sup>136</sup>Alex Scott, news item, *Chemical Week*, September 11, 2002.

## **Incentives to Adopt**

RTILs are of particular interest because they have the potential to increase the performance of certain organic syntheses without emitting VOCs or creating flammable conditions. The incentives for adoption of RTILs will be on a case-by-case basis.

## **Government Role**

Regulations on industrial emissions are the primary driver for the development of RTILs.

## **Barriers**

In the short term, the high price of RTILs will be a barrier for their market penetration beyond the laboratory scale. Even if prices decrease substantially, it is unclear how easily well-established industrial processes could be retrofit with RTILs. Also, it is difficult to translate improved laboratory-scale properties, such as faster reaction kinetics, to direct benefits on the industrial scale. Furthermore, RTILs cannot be purified by distillation because of their inherent low volatility and must therefore be made of very high purity. Other barriers include the dearth of toxicological data on RTILs and uncertain intellectual property issues.

# 18. Environmentally Friendly Refrigerants: New Refrigeration Processes

## Introduction

Modern refrigeration systems are primarily based on the vapor-compression (Rankine) cycle, whereby a working fluid absorbs heat from an insulated unit and expels it to the ambient environment, through continuous cycles of compression and expansion.<sup>137</sup> Working fluids vary by the size and purpose of the refrigerators but have typically been halogenated hydrocarbons or mixtures of them. Spurred by the Montreal Protocol and the Clean Air Act of 1990, the United States has already phased out the production of the most powerful ozone-depleting chemicals, known as “Class I Substances,” such as CFCs, halons, carbon tetrachloride, and methyl chloroform.<sup>138</sup> Of particular interest to the refrigeration community today is the phase-out schedule of the relatively more benign<sup>139</sup> Class II Substances, which are mostly comprised of hydrofluorocarbons (HFCs). The production of these substances will be gradually eliminated between 2003 and 2030.

The refrigeration industry has made a considerable effort to find new refrigerants that (1) offer improved performance, (2) can be retrofitted into existing refrigerators, (3) can be mass-produced economically, and (4) have a desirable environmental, health, and safety profile (see Table A9). Although these, often conflicting, criteria severely limit the potential replacement candidates, researchers have found several promising candidates.

From a long-term standpoint, refrigeration that is based on the Rankine cycle is inherently limited by its thermodynamic efficiency, which poses an unattainable upper limit on the amount of cooling potential for every unit of energy input. Innovations in the physical processes themselves, rather than the chemistry of the working fluid, could offer substantial gains in efficiency and allow the use of benign, common working fluids, such as water or helium. However, the role of these refrigeration systems in the future product mix is highly uncertain.

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<sup>137</sup>Some industrial refrigerators utilize absorption or steam jet cycles. *Perry's Chemical Engineers' Handbook*, 1997, p. 11-76.

<sup>138</sup>A Class I Substance has an ozone depletion potential of 0.2 or higher.

<sup>139</sup>Although they are more benign from the standpoint of ozone depletion, HFCs typically have a higher global warming potential.

# Chemistry

## ***Refrigerant Replacement***

One example of a refrigerant replacement is Ikon<sup>®</sup>B, which is a near-azeotropic blend of zero ozone depleting refrigerants, for use as an alternative to R-12, R-134a, and R-500 medium and low temperature refrigeration systems. Ikon<sup>®</sup> A, B, and C were developed by the Environmental Technology and Education Center and are now being sold by the Ikon Corporation.

## ***Stirling Cycle***

The Stirling cycle was discovered in 1816 by the Scottish engineer and theologian Robert Stirling. This thermodynamic cycle is based on the expansion and compression of a gas, allowing for heat to be absorbed and emitted. Although this cycle is highly efficient, it was supplanted by steam engines and the internal combustion engine in the 19th and 20th centuries. Early Stirling engines were plagued by problems with gas leakage and maintenance.

The modern application of a sterling cycle to refrigeration was revived by researchers at Global Cooling, who used a free-piston design.<sup>140</sup> The advantage of such a design over a Rankine vapor-compression cycle analog is its inherently higher thermodynamic efficiency; the ability to operate efficiently at all levels of demand; simpler, lighter-weight design; and the use of benign working fluids. This technology is ideally suited for autonomous applications because it works efficiently with direct current power sources, such as photovoltaic modules. Also, very efficient, small, lightweight refrigerators can be manufactured.

## ***Magnetocaloric Effect***

The magnetocaloric effect, discovered by E. Warburg in 1881, is a phenomenon where a material heats up upon exposure to a magnetic field of sufficient strength and cools down upon the removal of the magnetic field. The thermal effect occurs because a magnetic field aligns the electron spins of certain materials, resulting in a decrease in the material's spin entropy. If this process is done adiabatically, the total entropy change of the process must be zero. Therefore, the lattice entropy must increase by a corresponding amount, causing an increase in temperature. This is a virtually reversible process.

A refrigerator based on the magnetocaloric effect would utilize a benign working fluid, such as water, alcohol, or antifreeze, to accomplish the heat transfer between the magnetic material, refrigerated space, and ambient environment. The conventional compressor unit would be

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<sup>140</sup> *Mechanical Engineering Magazine Online*, "Stirling Renewal: Refrigerators and Generators That Use an Alternative Thermodynamic Cycle Are a Green Engineering Method," May 1999, <http://www.memagazine.org/backissues/may99/features/stirling/stirling.htm>.

eliminated but would still require heat exchangers and fans to function, thereby decreasing the energy efficiency from a theoretically 99 percent efficient process to approximately 70 percent.

Today, research in the field is devoted to understanding magnetic materials properties in order to improve cooling with less powerful magnetic fields, minimize eddy current dissipation, and lower cost. Researchers have used alloys of gadolinium, germanium, and silicon as the magnetic material. More recently, nanocomposites have allowed researchers to shrink the size of the material.

**Table A9. Refrigeration Technologies**

<b>Process Innovation</b>	<b>Physical Principle or Thermodynamic Cycle</b>	<b>Working Fluid</b>	<b>Main Advantage</b>	<b>Ancillary Advantages</b>	<b>Commercialization Time Frame</b>	<b>Initial Market Niche</b>
<b>Chemistry-based</b>	Traditional Rankine Cycle	Ikon A and Ikon B	Near zero ODP and GWP. Greater energy efficiency.	Can be retrofit into existing refrigerators.	Present	R-12 and R-134a systems
<b>Physics-based</b>	Stirling Cycle	Helium	Higher efficiency than Rankine, better control of temperature.	Light weight, works well with low- voltage DC currents, such as photovoltaic cell.  Very simple machine.	2004	Small refrigerators, portable coolers, and autonomous, PV-powered refrigerators
	Magneto-caloric effect	Water	Theoretical efficiency near 100 percent. Practical efficiency also extremely high.	Less vibration, works well with low voltage DC currents, such as photovoltaic cell.  Wider temperature range possible.	2005–2010	High-end applications, autonomous refrigerators
	Thermoacoustic	Gaseous fluid	Theoretical high efficiency.  Practical efficiency very low currently.	No moving parts.	?	High-end applications with need for a small cold spot, and no movement or vibration

	Optical	Gaseous fluid	Theoretical high efficiency.	No moving parts.	?	High-end applications with need for a small cold spot, and no movement or vibration
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## **Immediate Environmental and Economic Impacts**

### ***Refrigerant Replacement***

Ikon B<sup>®</sup> is blend of zero ozone-depleting refrigerants for use as an alternative for retrofitting R-12, R-134a, and R-500 medium and low temperature refrigeration systems. In laboratory tests, Ikon B has been shown to be 10 to 20 percent more energy efficient than R-12 and R-134a.<sup>141</sup> In fact, it is estimated that the extra cost associated with Ikon B retrofit would be repaid from energy savings in two to three years.

### ***Stirling***

Stirling cycle refrigeration is not likely to make a tangible environmental contribution in the near term because it is not designed to replace medium or large scale refrigerators in its current commercialized manifestation. Instead, this technology would offer refrigeration to communities that do not have access to electricity in the form of autonomous refrigerators with photovoltaic modules as the power source. The Stirling refrigerator's inroads in the markets of the developed world would likely occur for small-scale refrigeration units and coolers.

### ***Magnetic***

Magnetic cooling is already a mature technology for cryogenics applications. However, magnetic refrigeration for residential or commercial use is at least several years from realization. The first market niches for this technology will probably be for high-value applications that demand wide cooling ranges, accurate temperature control, and minimal vibration. Tangible environmental benefits would be seen if magnetic refrigerators displace traditional vapor-compression units because they would be inherently more energy-efficient and would use benign working fluids.

## **Long-Term Environmental Significance**

### ***Refrigerant Replacement***

If Ikon B were to have 20 percent market penetration by 2010, CO<sub>2</sub> emissions would be down by 4 million tons per year, particulates down 12 thousand tons, NO<sub>x</sub> down 16,000, and sulfur dioxide down 24,000.<sup>142</sup>

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<sup>141</sup>Environmental Technology and Education Center: <http://www.etc-nm.com/library/ikonbcut.htm>.

<sup>142</sup>The Presidential Green Chemistry Challenge Awards Program, EPA744-R-00-001, August 2001, p. 25.

## ***Stirling Piston***

According to David Berkowitz, founder of Global Cooling, more than 2.5 billion people do not have access to refrigeration, mostly because of the lack of access to electricity.<sup>143</sup> A Stirling piston refrigerator with a photovoltaic power source would be ideally suited for autonomous refrigeration because it could maximize the energy capture from the solar panel. As Stirling technology begins to make inroads into the refrigeration markets of the developed world, environmental benefits will be seen in the form of benign working fluids and significant improvements in energy efficiency.

## ***Magnetic Cooling***

According to Vitaly Pecharsky,<sup>144</sup> researcher at Ames Laboratory, this technology has progressed from requiring a 5 Tesla magnet to a 1 Tesla permanent magnet, so there is no longer a power requirement to maintain the magnetic field. If sufficient progress is made in materials research, the technology could be more efficient than either the Rankine or Stirling cycle refrigerators because magnetic cooling efficiency is not limited by a mechanical device. The magnetizing/demagnetizing process is almost completely reversible, leading to theoretical efficiencies on the order of 99 percent. Although such a device would not use a compressor, it would still have energy losses from heat exchange devices and inherent eddy current in the magnetic material, reducing the energy efficiency to approximately 70 percent. Thus, efficiencies are expected to be much higher than the theoretical limits of Rankine and Stirling thermodynamic cycles.

## ***Others***

Thermoacoustic and optical refrigerators are in the early research and development phases, and their potential future environmental contribution is thus highly speculative. In theory, both would be highly energy efficient and would use benign working fluids.

## **Commercializing Firms**

### ***Refrigerant Replacement***

First formulation Ikon A can be used in R-12 and R-134a systems and has been demonstrated for over three years in Dole Food Company refrigerated trucks. Ikon B, a less expensive version, has been tested in a refrigerated transport, a five-ton water chiller (National Aeronautics and Space Administration), and a new R-134a domestic refrigerator (EPA).

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<sup>143</sup>Private communication with David Berkowitz, September 27, 2002.

<sup>144</sup>Private communication with Pecharsky, October, 2002.

## ***Magnetic Cooling***

Magnetic cooling is already used for cryogenic applications today. Astronautics Corporation of America, which conducted research for military applications in the 1990s, has worked with Ames National Laboratory on materials research.<sup>145</sup> They will likely be the first to commercialize a refrigerator based on the magnetocaloric effect. According to Vitaly Pecharsky of Ames National Laboratory, the first commercial applications should be seen in three to five years.

## ***Stirling Piston***

Twinbird Corp., based in Niigata, Japan, formed an alliance with Global Cooling BV, to produce and market 40W free-piston Stirling coolers with helium as a refrigerant.<sup>146</sup> Global Cooling has already engaged in a pilot program for PV-powered autonomous refrigeration in the developing world, with some assistance from Greenpeace and the Dutch government.

## **Incentives to Adopt**

The most significant driver of alternative refrigeration technologies is government regulation on ozone-depleting and global warming substances. In particular, the phase-out of HFC production over the next three decades will inevitably increase the price of those refrigerants and a movement toward alternatives.

The incentives for adopting refrigeration technologies that are based on alternative physical processes will emerge primarily for performance and energy efficiency reasons rather than HFC replacement. Stirling, magnetic, thermoacoustic, and optical refrigeration promise to offer revolutionary increases in energy efficiency, with benign working fluids. However, their commercial viability for common refrigeration applications is highly speculative at this time.

## **Government Role**

The phase-out of HFCs from 2003 to 2030 will be the primary driver of alternative refrigerant technologies in the next several decades. However, the role of government for promoting alternative physical processes for refrigeration is not entirely clear.

One example, however, is that Ames National Laboratory has received government funds for their research on magnetic cooling properties. In particular, materials research is a critical element of this technology that would otherwise enjoy little or no sponsorship from private industry.

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<sup>145</sup> Missile Defense Agency website, <http://www.mdatechnology.net/techsearch.asp?articleid=424#listing>.

<sup>146</sup> *Appliance Manufacturer* website, "Industry News: Twinbird Forms Alliance with Global Cooling BV," <http://www.ammagazine.com>, posted August 1, 2002.

According to Berkowitz, the development of the Stirling refrigerator has occurred with little or no assistance from the U.S. government. However, the potentially large market in the developing world for autonomous refrigeration will likely need the assistance of nonindustry entities, especially for rural communities that might not be able to afford the technology.

## **Barriers**

The vapor-compression cycle is fundamentally less efficient than Stirling or magnetic refrigeration. However, with more than 80 years of research, development, and marketing at its advantage, the well-established Rankine cycle will present a formidable barrier to alternative technologies that do not involve a simple retrofitting of working fluids. The refrigeration industry has devoted a great deal of attention to incremental changes in refrigeration technology, such as more-efficient working fluids, better materials, and cabinet placement for improved insulation and more- sophisticated electronics. In particular, compressors have become mass-produced commodities with low margins and little intellectual property protection, whereas Stirling pistons are only used in niche markets today.

# 19. Clean Diesel Breakthrough with Compact Advanced Polymer Membrane

## Introduction

One of the challenges of diesel combustion has been the trade-off between nitrogen oxides (NO<sub>x</sub>) and particulate emissions from compressed ignition engines. Recent innovations in oxygen-enrichment techniques using polymeric membranes to control the amount and timing of oxygen delivered to a diesel engine show promise in breaking this trade-off between nitrogen oxide and particulate emissions with a relatively low-cost, simple design.

## Chemistry

One of the problems with compressed ignition engines is the location of stagnant “hot spots” that produce soot. Some of the soot escapes the engine and is emitted from the tailpipe. Although oxygen-enrichment reduces particulate emissions, it increases NO<sub>x</sub> levels. Conventional strategies for reducing NO<sub>x</sub>, such as exhaust gas recirculation and retarded injection timing, increase particulate emissions. Spark ignition engines have catalytic converters that can handle NO<sub>x</sub> levels, but diesel engines contain high levels of oxygen and particulates that limit the effectiveness of catalytic NO<sub>x</sub> reduction to nitrogen and oxygen.

Researchers at Argonne National Laboratory have developed a process for reducing NO<sub>x</sub> and particulate emissions<sup>147</sup> from a research locomotive engine using a three-way optimization of (1) oxygen content in the engine air supply, (2) retarded timing of fuel injection, and (3) increased fuel flow rate. Oxygen-rich environments help the combustion process go to completion, reducing the production of smoke and soot. The excess oxygen, however, produces NO<sub>x</sub>. The technical barrier has been controlling precisely the oxygen-rich air supply.

The fundamental enabling technology is a membrane unit, or a bundle of hollow tubes made of porous material, developed by Argonne researchers that can separate a pressurized stream of air into oxygen and nitrogen-rich streams. Researchers have been able to reduce the size of the membrane unit, making it 10 times shorter and 60 times more energy-efficient than a prototype unit in 1989.

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<sup>147</sup>The Presidential Green Chemistry Challenge Awards Program: Summary of 2000 Award Entries and Recipients, p. 36.

## **Immediate Environmental and Economic Impacts**

Argonne laboratory combustion conditions have reduced particulate emissions by 60 percent and NO<sub>x</sub> emissions by 15 percent while increasing gross engine power by 18 percent.<sup>148</sup> If such gains can be realized on other diesel engines, these emissions reductions could be achieved for less than \$200 per vehicle. Argonne researchers predict that the membrane technology will cost \$75 to \$160 when in mass production. Approximately 10 percent of all particulate emissions are from locomotives. In theory, a widespread adoption of this technology in the locomotive industry could result in a decrease of 6 percent of total particulate emissions in the United States.

## **Long-Term Environmental Impacts**

The polymeric membrane is a promising, low-cost technology that is likely to spread as diesel emissions standards tighten. Exact long-term impacts, however, may be unclear because the membrane has been tested only under laboratory conditions. Concurrent development of other technologies, such as particulate traps and oxygenated fuels, could obviate the need for this membrane technology.

## **Commercialization Firms**

Diesel manufacturers, such as EMD, are currently considering adopting this technology, but it has not yet been commercialized.<sup>149</sup>

## **Incentives to Adopt**

The Argonne membrane technology offers many incentives for adoption. The technology uses a simple design and is relatively inexpensive. Original engine equipment manufacturers would not need to redesign their engines to adopt it. The membrane system can also be retrofitted into existing vehicles. The membrane system offers flexibility in tuning oxygen intake conditions and can aid in compliance with future EPA standards.

## **Barriers**

One of the issues in using this technology is whether the oxygen should be delivered in molecular form or as an oxygenated hydrocarbon in order to curb particulate emissions in diesel engines. For example, dimethyl ether (DME) has shown promise as a clean replacement (or

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<sup>148</sup>Argonne National Laboratory website, "Technology Tour: Clean Diesel Breakthrough: Simultaneous Decrease in Emissions of Both Particulates and Oxides of Nitrogen During Combustion," <http://www.techtransfer.anl.gov/techtour/clean-diesel.html>.

<sup>149</sup>An engineer at DaimlerChrysler maintains that other approaches may be more cost-effective, and for light truck or automobiles impending 2007 limits cannot be met; Thomas Asmus, personal communication, November 17, 2002.

additive) for diesel. DME's low autoignition temperature, high cetane number (55 to 60, compared with about 45 for diesel), low boiling point (-25 degrees C, which provides for fast fuel and air mixing, reduced engine delay, and excellent cold starting), and high oxygen content (35 percent by weight, providing for smokeless combustion) make it an ideal candidate for a diesel fuel replacement. The Volvo Truck Corporation is an enthusiastic proponent of DME.<sup>150</sup> Tests have shown very low emissions from DME (which behaves as other oxygenates) as well as reductions in combustion noise relative to standard diesel engines. One of the few disadvantages is the lower energy density per volume than conventional diesel because DME does not contain energetic carbon-carbon bonds, only carbon-hydrogen and carbon-oxygen bonds. The low viscosity makes the pumping of DME difficult. Also, DME does not produce soot or smoke because of its lack of carbon-carbon bonds.

Because DME is not produced widely, it can only serve as a long-term solution to diesel emissions problems. Nevertheless, the addition of a small amount of DME to diesel (rather than complete replacement) exhibits very favorable emissions qualities and could obviate the need for modifications of conventional diesel combustion in the long term.

## Government Role

The federal government had supported this new technology through DOE funding for Argonne. Future regulations on diesel emissions will also push this technology and other diesel emissions remediation processes to their limits.

Michael Frenklach, who models combustion phenomena at the mechanical engineering department at the University of California-Berkeley, notes one of the main problems facing combustion research in the United States is the lack of a fundamental understanding of chemical kinetic and transport phenomena that can only be acquired through computer modeling and experimental research.<sup>151</sup> The lack of modeling work has hurt the diesel community by yielding only ad hoc technology developments and not new fundamental understanding. Soot formation in particular is a very complicated phenomenon that is poorly understood. Students are no longer acquiring expertise in combustion modeling because of the paucity of research support in the field. As a result, the most cutting-edge efforts are occurring elsewhere, particularly in Europe.

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<sup>150</sup>Hanna, Tornvall, *Alternative Fuels: A Complication of Facts and the View Volvo Truck Corporation Takes on Some Types of Fuels*, Goteborg, Sweden: Volvo Truck Corporation, September 14, 1998, quote on p. 11:

"Volvo Truck Corporation sees DME as a promising fuel in the long run. The advantages of DME compared with [compressed natural gas] are that DME can be used in the diesel process, it has higher energy content, it does not require such high pressure, and is cheaper to transport. The possibilities of producing DME from biomass are positive. One problem with DME is that no infrastructure has been developed."

<sup>151</sup>Private communication with Professor Michael Frenklach, October 24, 2002.

## 20. Biodegradable Polymers

### Introduction

Although biodegradable polymers have been commercial for more than 20 years, this specialized market faces many barriers, especially high prices, lack of an industry infrastructure to deal with these materials, and lack of a major consumer demand.

Although the term “biodegradable” is well known, there are no universal standards in place as to what constitutes a biodegradable material. Several materials in question include polyolefin-based plastics and polymers containing aromatic groups (see Table A10). Microorganisms have difficulty metabolizing such materials. Most producers, however, consider a material to be biodegradable if it is converted by microorganisms to carbon dioxide, water, and humus or in anaerobic degradation, carbon dioxide methane, and humus.

**Table A10. Major classes of biodegradable polymers**

<b>Polymer</b>	<b>Source</b>	<b>Manufacturing Process</b>
Poly(lactic acid)	Glucose	Chemical
Proteins	Milk, meat, grass ...	Chemical or Isolation
Cellulose	Wood products	Isolation
Starch	Potatoes, wheat, corn	Isolation
Polyhydroxyalkanoate	Glucose—see case 4	Bio-based process
Polycaprolactone	Petrochemicals	Chemical
Polyamide	Petrochemicals	Chemical
Polyesters	Petrochemicals	Chemical
Polyvinylalcohol	Petrochemicals	Chemical

Three representative materials are:

1. polyaspartic acid (PAA)
2. polylactic acid (PLA)

### 3. Biomax<sup>®</sup>.

## Chemistry

The salts of PAA can be obtained by thermal polymerization of maleic anhydride in the presence of nitrogen-containing compounds such as ammonia. The polymer chain contains potentially cleavable critical links in the form of amide bridges.

PLA is a biodegradable polymer derived from corn. Corn is wet milled to dextrose, the fermentation substrate for lactic acid. PLA is made from lactic acid with a solventless polymerization process (see Case 4).

Biomax is a hydro-biodegradable polyester based on polyethylene terephthalate with the incorporation of up to three aliphatic monomers that create the weak links for hydrolysis.

## Immediate Environmental and Economic Impacts<sup>152</sup>

PAA has found uses in a variety of areas, including:

- Corrosion inhibition in drainage pipes (dissolves calcium salts).
- Antiredeposition agent in the detergent industry.
- When used as a fertilizer additive, it forms a thin coating around the roots that keeps the fertilizer and other nutrients closer to the roots.
- Absorption agent in diapers and medical applications.
- Ion scavenger in pharmacological assays.
- Industrial water treatment.
- Other applications where polyacrylic acid might be used.

PLA is discussed in Case 4.

Biomax<sup>153</sup> has been adopted in packaging for its barrier properties and can be used to make injection molded parts, coatings for paper, thermoformed cups and trays, and films.

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<sup>152</sup> Biodegradable Polymer Life Cycle, Supplement D, SRI Process Economics Program Report No. 115D, December 2001. (This report is useful as an analysis of many of the energy and environmental issues associated with biodegradable and conventional polymers. It also provides a detailed description of life-cycle analysis methodologies and of the industry status of biodegradable polymers.)

The environmental benefits of biodegradable products are primarily ones of reduced waste for landfills or litter reduction and, where renewable resources are used as the feedstocks, the added benefit of reduced carbon dioxide emissions and petroleum use.

## **Commercializing Firms**

Although many chemical and diversified companies have been active in PAA R&D, only Donlar and Bayer have emerged as the leaders in PAA technology and market development. Both Donlar and Bayer are targeting the polyacrylate applications for PAA market development. Bayer estimates polyacrylate markets at approximately 2 billion pounds per year. Donlar estimates the market for PAA in preventing scaling and corrosion in offshore oil rigs at \$600 million per year. Both Bayer and Donlar have been planning capacity increases in their existing PAA production capacities of 600,000 pounds per year and 30 million pounds per year, respectively. Other companies active in this area during the 1990s are BASF, Solutia, Rohm & Haas, Mitsubishi Chemical, and Mitsui Chemicals.

According to a recent patent survey, the patenting activity in the area of PAA technology has peaked during the past three years.

Despite all the excitement and growing markets, Donlar lost money in 2001 with net sales of \$2.3 million. Bayer claims that it has a cost advantage over Donlar, while Donlar claims a better product quality. Donlar has now invested \$40 million in PAA technology and filed 50 U.S. and 140 foreign patents.

DuPont, in developing Biomax, found that there is not a ready market for biodegradability in itself and had to ensure that other properties of the resin and cost were initially present.

## **Incentives to Adopt**

Most of the firms are looking for specialty markets where biodegradability is a bonus that comes with superior properties in the polymer as a film, resin, or fiber.

## **Government Role**

The expectation of legislation and overburdened municipal landfills was one reason why companies have sought biodegradable products.

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<sup>153</sup>Richard Leifer, Christopher M. McDermott, Gina Colarelli O'Connor, Lois Peters, Mark P. Rice, and Robert W. Veryzer, *Radical Innovation: How Mature Companies Can Outsmart Upstarts*, Boston: Harvard Business School Press, 2000, pp. 12-18; [www.dupont.com/polyester/resins/products/biomax/biomax.html](http://www.dupont.com/polyester/resins/products/biomax/biomax.html).

## **Barriers**<sup>154</sup>

The major barrier over the past ten years has been the slow market acceptance as the firms seek the right combination of properties to meet specific customer needs.

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<sup>154</sup>Steven Ashley, "It's Not Easy Being Green," *Scientific American*, April 2002, pp. 33–34.

## 21. Capture of Nitrous Oxide in Adipic Acid Manufacture to Use in New Phenol Process

### Introduction

With a 100-year global warming potential (GWP) of 310,<sup>155</sup> nitrous oxide (N<sub>2</sub>O) is potentially a significant contributor to global warming. The main industrial sources of nitrous oxide in the United States are adipic acid and nitric acid production. Adipic acid is a white powder that is used in the manufacture of nylon fiber, plasticizers, lubricants, insecticides, and dyes. More than 90 percent of the adipic acid production capacity in the United States is located in four plants, all of which use a chemical process that produces nitrous oxide as a by-product. Industry efforts in the 1990s dramatically reduced nitrous oxide emissions through the use of post-process catalytic and thermal destruction technologies (Figure A3).

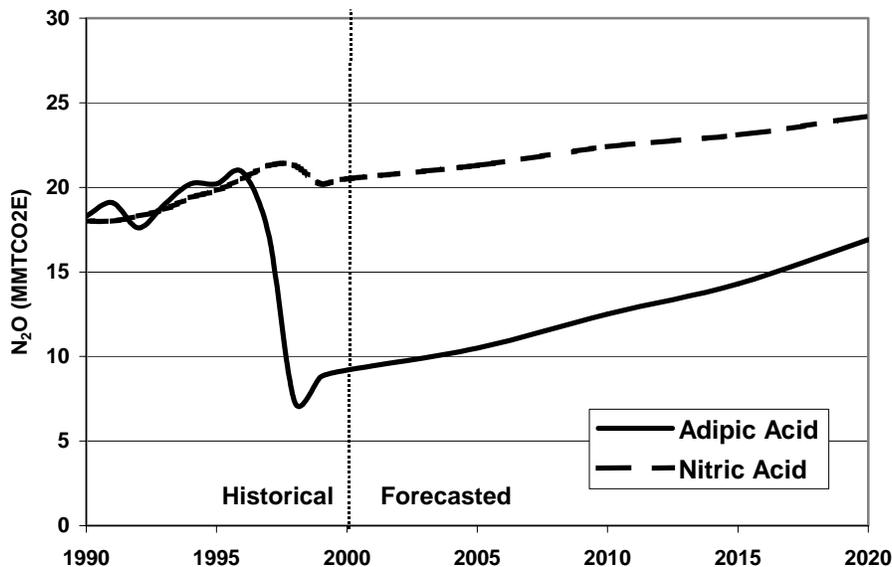


Figure A3. Industrial N<sub>2</sub>O Emissions from the U.S. Industrial Sector.

<sup>155</sup>The 100-year GWP compares the ability of a greenhouse gas to trap heat in the atmosphere to carbon dioxide over a 100-year period.

More recently, researchers have found several potential, economically viable means for producing adipic acid without nitrous oxide emissions, including replacing nitric acid, recycling nitrous oxide, or using a biological pathway. This case study focuses on closing the nitrogen loop at adipic acid plants by recycling and reusing the nitrous oxide off-gas to create phenol, rather than destroying it.

## Chemistry

The innovation in the recycling and reuse of  $N_2O$  we examine is the one-step hydroxylation of benzene to phenol with the nitrous oxide by-product using a zeolite catalyst. This phenol could then be sold on the market, or reduced to cyclohexanol or cyclohexanone for producing adipic acid. Either would close the nitrogen cycle and result in minimal emissions of  $N_2O$  while providing an additional benefit of cheap phenol production. The technical barriers lie in the selective conversion of benzene into phenol through the fine-tuning of the acid sites and iron level of the catalyst.

## Immediate Environmental and Economic Impacts

The AlphOx<sup>®</sup> process developed by Solutia may reduce the cost of producing adipic acid by 20 percent<sup>156</sup> and  $N_2O$  emissions by 90 to 98 percent.<sup>157</sup>

## Long-Term Environmental Benefits

While  $N_2O$  emissions from adipic acid manufacturing have declined sharply in the past decade, EPA forecasts show that they are likely to rebound in coming years if new technologies are not implemented (Figure A3).<sup>158</sup> This increase will likely result from long-term growth in adipic acid demand. Recycling and reuse of nitrous oxide therefore will need to play an important role in adipic acid production because other routes to adipic acid will not be adopted in the foreseeable future.

## Commercialization Firms

Solutia, in collaboration with the Boreskov Institute of Catalysis from Novosibirsk, Russia, developed a one-step benzene to phenol conversion process using recycled nitrous oxide, closing

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<sup>156</sup>“The Winners and Losers of  $N_2O$  Emission Control,” *Chemical Week*, February 18, 1998.

<sup>157</sup>EPA, *U.S. Adipic Acid and Nitric Acid  $N_2O$  Emissions 1990–2020: Inventories, Projections and Opportunities for Reductions*, December 2001, <http://www.epa.gov/ghginfo/pdfs/adipic.pdf>.

<sup>158</sup>These forecasts assume a rate of capacity growth of 3 percent per year and  $N_2O$  abatement destruction factors of 95 percent for catalytic abatement, 98 percent for thermal abatement, and 98 percent for recycling/utilization technologies through 2020.

the nitrogen cycle in adipic acid production. Their AlphOx process reached the pilot plant demonstration stage in mid-1996, but implementation of a full-fledged commercial unit has been delayed.

## **Incentives to Adopt**

The AlphOx process offers a one-step phenol process that reduces both capital investment and operating costs and eliminates acetone as a by-product.<sup>159</sup> The traditional cumene peroxidation process, which accounts for more than 90 percent of phenol production worldwide, yields acetone as a by-product, making the market for phenols dependent on the market for acetone, with an oversupply of acetone negatively affecting the market for phenols.

## **Barriers**

One potential barrier to adoption of this process is that the amount of nitrous oxide recycled in an adipic acid plant would be enough only to supply a relatively small phenol plant. The economics would likely favor an integrated approach, whereby recycled N<sub>2</sub>O is sent to a captive phenol plant producing at low cost, which would produce low-cost feedstock for the adipic acid plant.<sup>160</sup>

## **Government Role**

During the 1990s, manufacturers implemented N<sub>2</sub>O controls because of EPA regulations.

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<sup>159</sup>SRI, "SRI Consulting's Process Economics Program Evaluates the New One-Step Phenol Production Method," SRI Process Economics Program, <http://process-economics.com/survey/wwwroot/PEP/pressrelease15.html>, March 9, 1999.

<sup>160</sup>SRI, 1999.

## 22. Advanced Oxidation Process for the Metal Casting Industry

### Introduction

The metal casting industry is a major segment of the manufacturing industry in the United States, employing approximately 200,000 persons. About 3,000 foundries create 14 million tons of metal castings each year, 60 percent of which are poured in green sand molds, which are a mixture of silica sand, bentonite clay, finely ground coal, and core binders. The high temperatures at the interface of the molten metal surface and mold result in chemical reactions in the coals and adhesives, leading to the emission of VOCs. The surface of the green sand molds is “kilned” upon exposure to high temperatures, meaning much of the mold cannot be recycled.

### Chemistry<sup>161</sup>

A novel advanced oxidation (AO) process, pioneered by Fred S. Cannon at the Pennsylvania State University, presents an opportunity to curb VOC emissions problems in foundries. Traditionally, after a green sand mold is used in a casting process, it is broken up, remoisturized, recycled, and reused for subsequent casting molds. The process of breaking up the mold also emits VOCs and particulates. Many of these particulates are captured with a “baghouse,” but VOCs resulting from this process can be eliminated only through costly incineration.

This AO process uses ozone, hydrogen peroxide, sonification, and underwater plasma to treat the “black water” slurry resulting from mold recycling. The introduction of hydroxyl radicals into the organic slurry results in the production of micro-pores in the green sand mold that resemble activated carbon when exposed to the intense heat of molten metal. The AO process is essentially a technique for the in situ manufacturing of activated carbon, which serves as an adsorbent for the VOCs that would otherwise be released during a metal casting cycle. An ancillary benefit of the AO process is that it reduces the “kiln” effect at the interface, allowing more efficient recycling of the green sand mold.

### Immediate Environmental and Economic Impacts

The advanced oxidation process reduces VOC emissions by 30 to 70 percent and reduces clay and coal consumption by 10 to 30 percent.<sup>162</sup> Cannon says at least one foundry using the process has

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<sup>161</sup>[http://cfpub.epa.gov/ncer\\_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/2177/report/0](http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/2177/report/0);  
<sup>162</sup><http://www.oit.doe.gov/metalcast/environmental.shtml>.

reported annual savings between \$500,000 and \$1 million. For every pound of metal produced in metal casting, approximately seven pounds of green sand are used. The efficient recycling of this product will therefore help reduce landfill costs and liabilities.

## **Long-Term Economic and Environmental Benefits**

Eliminating the need for costly “end of pipeline” incineration can boost the economic health of the metal casting industry. Although the AO process is less effective in limiting VOC emissions than thermal abatement, it does reduce foundry emissions and operating costs. As the foundry industry loses market share to lower-cost foreign producers, it is becoming more sensitive to nonremunerative capital investments. The AO process is one example of a technology that could benefit the industry.

## **Commercialization Firms**

The AO process has already been installed in six full-scale foundries, which produce approximately 3 to 6 percent of all the metal casting in the United States.<sup>163</sup>

## **Incentives to Adopt**

U.S. metal casters have faced increasing competition in an industry that offers little opportunity to add value and low profit margins. The AO process can help not only by providing emissions remediation but also by reducing materials consumption. Approximately 40 percent of environmental compliance costs in the metal casting industry are for the control, treatment, and disposal of air pollutants. Environmental expenditures account for 30 to 60 percent of total annual spending in the industry.<sup>164</sup> Many foundries that failed in the past decade, particularly smaller ones, likely did so because of the costs of complying with environmental regulations. An ideal capital investment in the industry would be one that both offered greater efficiency and reduced environmental effects.

## **Barriers**

Because of its low profit margins, the metal casting industry has difficulty generating the resources for research and development. The net savings from the AO process usually can be realized by medium- and large-scale foundries within six months, but it is not clear how much time small foundries would need to realize savings.

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<sup>162</sup> [es.epa.gov/ncer\\_abstracts/grants/01/sustain/cannon.html](http://es.epa.gov/ncer_abstracts/grants/01/sustain/cannon.html).

<sup>163</sup> Private communication with Professor Fred Cannon, October 24, 2002.

<sup>164</sup> *Metalcasting Industry Technology Roadmap*, January 1998.

## **Government Role**

DOE, along with steel industry trade associations, sponsored the Metalcasting Industry Technology Roadmap Workshop in June 1997. EPA has sponsored part of Cannon's research at Penn State.

## 23. Fluoroaromatics via Copper (II) Fluoride Chemistry

### Introduction

Fluorinated aromatics are used often in synthesizing pharmaceutical products and agricultural chemicals. Fluorobenzene is used as a starting material for many fungicides and drugs. Most fluorobenzene is synthesized by the Balz-Schiemann reaction, which creates large quantities of waste such as  $\text{NaBF}_4$  and  $\text{NaCl}$ . Some efforts have been made to increase the atom economy of fluorobenzene synthesis so as to reduce waste.

### Chemistry<sup>165</sup>

Fluorobenzene is synthesized from benzene, HF, and oxygen with a copper (II) fluoride catalyst. Water is the only by-product because the metal fluoride is regenerated with oxygen and HF. The key to the efficient atom economy of this process is a metal fluoride capable of oxidizing the C-H bond and that could then be readily regenerated. The reaction is as follows:



### Immediate Environmental and Economic Impacts

More than 4,000 metric tons of fluorinated aromatics are used in the synthesis of pharmaceutical products and agricultural chemicals each year. Producing fluorobenzene through the diazotization of an aromatic amine in the presence of tetrafluoroboric acid produces large quantities of waste  $\text{NaBF}_4$  and  $\text{NaCl}$ , while producing it through the use of HF rather than fluoroboric acid results in waste  $\text{HCl}$  or  $\text{NaF}$  and  $\text{NH}_4\text{F}$  salts. Using alternative methods for synthesizing fluorobenzene would eliminate the production of these wastes.

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<sup>165</sup>M. A. Subramanian and L. E. Manzer "A 'Greener' Synthetic Route for Fluoroaromatics via Copper (II) Fluoride," *Science*, No. 297, September 6, 2002, p. 1665; M. A. Subramanian, "Processes for Fluorinating Aromatic Ring Compounds," 2000, U.S. Patent 6,166,273 to E.I. du Pont de Nemours and Company.

## **Long-Term Environmental Significance**

The chemistry for producing alternative methods of synthesizing fluorobenzene provides a starting point for industrial-scale production of fluoroaromatics without the waste products typically associated with current fluorination technologies, although it uses benzene, a known carcinogen, and HF, a highly acidic and corrosive material. The adoption of this technology to synthesizing other fluoroaromatics can provide the atom economy necessary to reduce waste streams.

## **Commercializing Firms**

DuPont no longer makes fluorobenzene. It has donated the relevant patents to the University of Florida, which will seek to commercialize the technology.

## **Incentives to Adopt**

This alternative method of producing fluorobenzene is more economical and results in less wastes requiring disposal.

## **Barriers**

The creation of C-F bonds from C-H bonds is thermodynamically unfavorable. In the case of aromatic hydrocarbon bonds, the formation of H<sub>2</sub>O provides the thermodynamic driving force behind the reaction. Because the C-H bonds are so strong, an equally strong oxidizing metal fluoride compound is needed to break the bond. Because they are very strong oxidizing agents, the oxidative potentials of metal fluorides greater than 1 eV can only be regenerated with costly elemental fluorine. Those less than zero are easily regenerated with HF; however, they are not strong enough to oxidize the C-H bonds. Hence, a barrier to the chemistry is developing a catalyst with an oxidative potential between 0 and 1 and with selectivity to the hydrocarbon being fluorinated.

## 24. Synthesis of 4-aminodiphenylamine

### Introduction

Chlorine is used widely both to produce chlorinated products and to produce intermediate chemicals needed for manufacturing other products. Because the use of chlorine is regulated, intermediate chemicals for other products that do not use chlorine are desirable. The new synthesis of 4-aminodiphenylamine is an example of one way to replace the use of chlorine as an intermediate chemical and also to increase atom economy while reducing the amount of hazardous by-products otherwise formed by the use of chlorine.

### Chemistry<sup>166</sup>

A novel synthesis of 4-aminodiphenylamine (4-ADPA) was accomplished through a class of reactions known as nucleophilic aromatic substitution for hydrogen, or NASH. In this reaction, a base promotes the direct coupling of nitrobenzene and aniline to give 4-ADPA. This new means of producing 4-ADPA has been widely recognized as a breakthrough in nucleophilic aromatic substitution chemistry.

### Immediate Environmental and Economic Impacts

4-ADPA is a key intermediate chemical in the production of 300 million pounds per year of rubber chemicals that are antioxidants, antiozonates, or antidegradants. The previous process involved the chlorination of benzene and resulted aqueous waste with high levels of inorganic salts as well as organic chemicals that are difficult and expensive to treat. The new process reduces organic waste by 74 percent, inorganic waste by 99 percent, and wastewater by 97 percent.

### Long-Term Environmental Significance

Converting just 30 percent of worldwide 4-ADPA production to the new process would eliminate 74 million pounds of chemical waste and 1.4 billion pounds wastewater, each year.

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<sup>166</sup>*The Presidential Green Chemistry Challenge Awards Program: Summary of 1998 Award Entries and Recipients*, p. 5; Michael K. Stern and James K. Bashkin, "Method of Preparing 4-aminodiphenylamine," 1997, U.S. Patent 5,623,088 assigned to Flexsys America L.P.; Michael K. Stern, James M. Allman, James K. Bashkin, and Roger K. Rains, "Method of Preparing 4-aminodiphenylamine," 1997 U.S. Patent 5,608,111 assigned to Flexsys America.

## **Commercializing Firms**

Monsanto Corporate Research and Rubber Chemicals Divisions helped develop this chemistry. Flexsys, a joint venture of the rubber chemicals divisions of Monsanto and Akzo Nobel, has since commercialized it.

## **Incentives to Adopt**

Significant (but unpublished) cost savings are claimed for this process.

## **Government Role**

Governmental scrutiny of chlorine use has led to the development of regulations requiring reduced use of chlorine which have been instrumental to the development of 4-ADPA.

## **Barriers**

Barriers were certainly encountered in doing the research to ultimately find an economically attractive route to 4-ADPA.

## 25. Synthesis of Glyphosate

### Introduction

Glyphosate [N-(phosphonomethyl)iminoacetic acid or N-(phosphonomethylglycine)] is the active ingredient in Roundup<sup>®</sup>, the world's best selling herbicide, introduced in 1976 by Monsanto.<sup>167</sup> It has desirable environmental properties in that it binds to soil particles, making it less likely to move into groundwater, has a lack of residual herbicidal effects in soil, and has low toxicity to humans and animal life.

### Chemistry<sup>168</sup>

The initial process by Monsanto for the first intermediate for glyphosate used the Strecker process, reacting hydrogen cyanide, formaldehyde, and ammonia with a catalyst to produce DSIDA (disodium diiminodiacetate). DSIDA was then reacted with  $\text{PCl}_3$  and formaldehyde to give N-(phosphonomethyl)diiminodiacetic acid, then GI (glyphosate intermediate), which upon catalytic oxidation gave glyphosate.

Monsanto replaced the Strecker synthesis in 1992 when additional manufacturing capacity was needed. Diethanolamine was reacted with sodium hydroxide using a copper catalyst to produce DSIDA. Raney copper was first used, but reaction rates were slow and the catalyst was physically unstable. A second-generation catalyst was subsequently developed; copper was plated upon a platinum/carbon support.

The process for DSIDA was the 1996 winner of the Presidential Green Chemistry Award for an alternate synthetic pathway.<sup>169</sup>

Monsanto has now developed and implemented use of a new heterogeneous catalyst in the oxidation of GI to glyphosate. By-products in the reaction are oxidized by the same catalyst to carbon dioxide.

Most recently a more "atom efficient" route has been developed. N-substituted glycine (R-NHCH<sub>2</sub>COOH) is reacted with phosphoric acid and formaldehyde in the presence of hydrochloric acid. The N-substituted glyphosate is then oxidized with a platinum catalyst to give glyphosate. Studies showed that the isopropyl derivative gave 98 percent selectivity at 79 percent

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<sup>167</sup> Monsanto has 370 issued patents, 1996–2002, related to the preparation and use of glyphosate and the genetically modified plants that tolerate Roundup.

<sup>168</sup> Michael A. Stern, "Environmentally Sound Agricultural Chemistry: From Process Technology to Biotechnology," NRC Workshop on the Environment, November 17–19, 2002, proceedings forthcoming.

<sup>169</sup> See [www.epa.gov/greenchemistry/aspa96.html](http://www.epa.gov/greenchemistry/aspa96.html).

conversion, superior to methyl, n-pentyl, benzyl, or cyclohexyl derivatives. So the complete reaction becomes:

acetone and ammonia are reacted in the presence hydrogen and a catalyst to give isopropylamine, which is converted to N-isopropyl glycine, then as above (Moedritzer-Irani reaction) reacted to give N-isopropyl glyphosate, which is oxidized over platinum to give glyphosate and acetone. The acetone is then recycled to the first step. This chemistry has yet to be implemented.

## **Immediate Environmental and Economic Impacts**

The replacement of the Strecker route to DSIA eliminated the use of hydrogen cyanide, ammonia, formaldehyde, and hydrochloric acid, HCN being of most concern because it requires very special handling to minimize risks to workers and the community. The Strecker route involves exothermic reaction, generation of potentially unstable intermediates, and possibility of a runaway reaction. One pound of waste is generated for each pound of product that requires special treatment for traces of cyanide and formaldehyde.

The environmental benefits from the implemented new catalyst and new process technology:

<b>Resource</b>	<b>Annual Reductions for 2002</b>
Steam, Btus	880 billion
Demineralized water, gallons	380 million
<b>Waste</b>	
Flow to biotreatment, gallons	800 million
SARA 313 deep well injection, lbs	52,000
Biosludge, lbs	8 million
Solid waste to landfill, lbs	1.4 million
SARA 313 air emissions, lbs	17,600
Carbon dioxide emissions, lbs	100 million

The economic benefits have been sizeable. From 1995 to 2002, as capacity increased fourfold, unit costs were trimmed by 40 percent.

## **Incentives to Adopt**

When Monsanto faced the need to expand capacity, the firm was able to adopt a lower-cost process that gave additional environmental benefits. The firm has not adopted the “atom efficient” process. Sales of Roundup leveled off in 2001 and additional capacity might not have

been needed at this time. It is also possible that this newer process does not give sufficient economic return to justify adoption at this time.