Next Generation Environmental Technologies

Benefits and Barriers

Robert J. Lempert, Parry Norling, Christopher Pernin, Susan Resetar, Sergej Mahnovski

Prepared for Office of Science and Technology Policy
The research described in this report was conducted by RAND's Science and Technology Policy Institute for the Office of Science and Technology Policy under Contract ENG-9812731.

ISBN: 0-8330-3417-0

RAND is a nonprofit institution that helps improve policy and decisionmaking through research and analysis. RAND® is a registered trademark. RAND's publications do not necessarily reflect the opinions or policies of its research sponsors.

© Copyright 2003 RAND

All rights reserved. No part of this book may be reproduced in any form by any electronic or mechanical means (including photocopying, recording, or information storage and retrieval) without permission in writing from RAND.

Published 2003 by RAND
1700 Main Street, P.O. Box 2138, Santa Monica, CA 90407-2138
1200 South Hayes Street, Arlington, VA 22202-5050
201 North Craig Street, Suite 202, Pittsburgh, PA 15213-1516
RAND URL: http://www.rand.org/
To order RAND documents or to obtain additional information, contact Distribution Services: Telephone: (310) 451-7002; Fax: (310) 451-6915; Email: order@rand.org
Preface

Next Generation Environmental Technologies (NGETs) focus on the redesign, at the molecular level, of manufacturing processes and products so as to reduce or eliminate the use of hazardous materials. The potential for such technologies suggests that they may play an important role in a new approach to environmental protection. NGETs thus raise important policy questions, including the range of benefits such technologies have already provided and may in the future provide and the types of actions commensurate with these benefits that policymakers might take to encourage their development and adoption. This report examines 25 case studies of such Next Generation Environmental Technologies to begin to address such questions.

For readers unfamiliar with NGETs, this study will provide a survey of their promise and weaknesses. For researchers and practitioners creating new NGETs, this study aims to provide a broader context for their efforts. For policymakers, this study aims to provide the raw materials for a systematic assessment of the range of potential benefits of NGETs and the portfolio of policies needed to move them forward.

About the S&T Policy Institute

Originally created by Congress in 1991 as the Critical Technologies Institute and renamed in 1998, the Science and Technology Policy Institute is a federally funded research and development center sponsored by the National Science Foundation and managed by RAND. The Institute's mission is to help improve public policy by conducting objective, independent research and analysis on policy issues that involve science and technology. To this end, the Institute

1. Supports the Office of Science and Technology Policy and other Executive Branch agencies, offices, and councils

2. Helps science and technology decisionmakers understand the likely consequences of their decisions and choose among alternative policies

3. Helps improve understanding in both the public and private sectors of the ways in which science and technology can better serve national objectives.

In carrying out its mission, the Institute consults broadly with representatives from private industry, institutions of higher education, and other nonprofit institutions.
Inquiries regarding the Science and Technology Policy Institute may be directed to the addresses below.

Helga Rippen, Ph.D., M.D., M.P.H.
Director
Science and Technology Policy Institute
Contents

Preface .......................................................................................................................... iii
Figures ............................................................................................................................. vii
Tables ............................................................................................................................ ix
Summary ........................................................................................................................ xi
Acknowledgments ......................................................................................................... xiii
Acronyms ....................................................................................................................... xv

Introduction .................................................................................................................. 1
What Are Next Generation Environmental Technologies? ........................................... 5
    Assessing the Promise of NGETs ........................................................................... 7
Mechanisms for Gaining the Benefits from NGETs .................................................... 9
    Mechanisms ............................................................................................................ 9
    Cost Reduction ....................................................................................................... 9
    Risk Reduction ..................................................................................................... 10
    Technology Spillover Effects—Technology Transfer ......................................... 11
Lessons from Case Studies ......................................................................................... 13
    Overview of Cases ............................................................................................... 13
    Near-Term Benefits of NGETs and Barriers to Their Adoption ....................... 20
I. NGETs Can Provide Benefits in All the Important Areas Identified in Our Study .......................................................... 20
    Environmental Benefits ..................................................................................... 20
    Security Occupational Safety and Health Benefits ........................................... 25
    Economic Benefits ............................................................................................. 27
II. NGETs Can Eliminate the Use and Generation of Hazardous Substances at Little or No Additional Cost ....................................................... 28
III. NGETs Are Adopted for a Wide Variety of Reasons ......................................... 29
IV. Barriers Are Significant ..................................................................................... 31

Longer-Term Opportunities for NGETs .................................................................. 35
    Responding to Societal Demand Through New Processes and New Chemicals .................................................................................................................... 35
    Opening New Green Pathways—Addressing Uncertain Problems with NGETs .................................................................................................................. 37

Conclusions and Observations .................................................................................. 41
    NGETs Can Provide Benefits in All Areas Studied ........................................... 41
    NGETs Can Address Uncertainties ................................................................... 41
    Firms Adopt NGETs for a Number of Different Reasons ................................. 42
    Policymakers Face a Number of Challenges ................................................... 42

Appendix A: Descriptions of the 25 Case Studies .................................................... A-1
Appendix B: Government Policies and Increased Adoption of NGETs........B-119

Appendix C: Opportunities for Further Study: Additional Cases from the First International Conference on Green & Sustainable Chemistry, Tokyo, March 2003.................................................................C-127
Figures

Figure 1. Science and Technology Landscape. ................................................................. 12

Figure 2. Breakdown of Total TRI Chemical Releases Over All Industries. ........... 21

Figure 3. TRI Release Breakdown of the Chemical and Allied Products Industry (SIC code 28) (% of emissions). ................................................................. 22

Figure 4. Top Ten Chemicals Released Excluding the Mining Industry (% of emissions). ........................................................................................................ 23
Tables

Table 1. Summary of case studies. ............................................................................................. 15
Table 2. Distribution of case studies. Cases as listed in Tables 1 and A1............. 19
Table 3. Top ten chemicals released into the air................................................................. 23
Summary

Next Generation Environmental Technologies (NGETs) represent a set of advanced manufacturing technologies that have the potential to produce environmentally benign products and processes. These technologies offer a new approach to environmental protection: Rather than focusing on the cleanup and control of waste and hazardous materials, they involve the redesign of industrial products and processes to reduce the quantity of material inputs required and to eliminate broad classes of environmentally detrimental outputs. When successfully implemented, NGETs offer the promise of substantial new advances in environmental protection often at low cost and even with a net economic benefit. They also raise important policy issues related to the magnitude and importance of the benefits that can be realized and the types of actions that might be taken to encourage their development and diffusion.

This report examines 25 existing NGETs to begin to address these issues. The technologies considered span the range of development from early research to full deployment in profitable businesses. Those that have been commercialized are offering benefits in a variety of areas, including the environment, national security, occupational safety and health, and the economy. Others that are still in various developmental stages offer similar promise.

Most of the technologies reviewed here draw on applications of the emerging science of green chemistry, an important source for NGETs. For each case study, we describe the underlying chemistry, the commercializing firm(s), the incentives that caused those firms to adopt the technology, and the role played by government support. Particular attention is paid to the identification of both near- and long-term benefits as well as to any barriers to technology adoption.

These case studies provide a review of the benefits and problems associated with NGETs. Taken together, they demonstrate the following:

1. NGETs can provide significant benefits to society in all the areas considered in our study: the environment, national security, occupational safety and health, and the economy.

2. NGETs can in some cases eliminate the use and generation of hazardous substances at little or no additional cost.
3. NGETs can be adopted by businesses for a variety of different reasons: to meet environmental regulations in a cost-effective way; to provide environmentally benign products economically; or to develop profitable new products in new and environmentally beneficent ways. NGETs provide new approaches to competitive advantage.

4. The barriers to the widespread use of NGETs can be technical, economic, and/or societal in nature.

This report represents a first step toward assessing the potential benefits of NGETs, reviewing the barriers to their successful deployment and pointing out where government actions have supported their successful adoption. Our case studies indicate that although green chemistry can be a powerful source of environmentally and economically beneficial technologies, its development is still in its infancy. Substantial work is needed both to create new NGETs and to encourage demand for their use. Much also remains to be learned about the basic science and practical application of green chemistry principles.
Acknowledgments

The authors are especially grateful to the many individuals who provided details or background on specific case studies, including Ruben Carbonell, North Carolina State University; Michael Stern and James Bashkin, Monsanto; Uma Chowdhry, Leo Manzer, Mas Subramanian, and Vasantha Nagarajan, DuPont; Akazu Takahashi, Ube Industries; Eric Beckman, University of Pittsburgh; Jeff Gendler and Ray Ballee, Hydrocarbon Technologies, Inc.; John Cooper, BASF; Nicholas Ashford, Massachusetts Institute of Technology; James Frank, Argonne National Laboratory; Robin Rogers, University of Alabama; David Berkowitz, Global Cooling; Vitaly Pecharsky, Ames Laboratory; Thomas Asmus, DaimlerChrysler; Michael Frenklach, University of California, Berkeley; Fred Cannon, Penn State; Mary Kirchhoff, Green Chemistry Institute; Richard Engler, U.S. Environmental Protection Agency (EPA); Ray Garant, American Chemical Society; Egils Milbergs and Jeff Keuter, National Coalition for Advanced Manufacturing; and Jack Cook, Integrated Manufacturing Technology Initiative.

We appreciated the invitations from the organizers of the 6th Annual Green Chemistry & Engineering Conference, the 2002 Green Chemistry Gordon Research Conference, and the First International Conference on Green & Sustainable Chemistry (Masao Kitajima, Makato Misono, and Shigetoshi Seta), where we could present portions of this report during its preparation.

We also thank colleagues at RAND and the Science and Technology Policy Institute for their helpful suggestions and support in preparing the report: Lisa Sheldone, Terry Kelly, Mihal Gross, Debra Knopman, and David Adamson.

A special thanks to Clifford Grammich, Paul Arends, and Nan Norling for their editing chores.

Finally, we wish to thank Dennis Hjeresen, Green Chemistry Institute; Tracy Williamson, EPA; and Richard Silberglied, RAND, for their thorough reviews and their many thoughtful suggestions for additions, modifications, and corrections.

The statements and conclusions contained in this report are still the sole responsibility of the authors.
<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Aqueous biphasic systems</td>
</tr>
<tr>
<td>ACQ</td>
<td>Alkaline copper quaternary</td>
</tr>
<tr>
<td>ADPA</td>
<td>Aminodiphenylamine</td>
</tr>
<tr>
<td>AND</td>
<td>Adiponitrile</td>
</tr>
<tr>
<td>AO</td>
<td>Advanced oxidation</td>
</tr>
<tr>
<td>AOX</td>
<td>Absorbable organic halides</td>
</tr>
<tr>
<td>API</td>
<td>Active pharmaceutical ingredient</td>
</tr>
<tr>
<td>BAC</td>
<td>Benzyl ammonium chloride</td>
</tr>
<tr>
<td>Btu</td>
<td>British thermal unit</td>
</tr>
<tr>
<td>CCA</td>
<td>Chromated copper arsenate</td>
</tr>
<tr>
<td>CDI</td>
<td>Capacitive Deionization</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Elemental chlorine</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CPA</td>
<td>Chloropropionic acid</td>
</tr>
<tr>
<td>DDAC</td>
<td>Dodecyl dimethyl ammonium chloride</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl ether</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>DSIDA</td>
<td>Disodium diimindociacetate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>ECF</td>
<td>Elemental chlorine free</td>
</tr>
<tr>
<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>EPCRA</td>
<td>Emergency Planning and Community Right-to-Know Act</td>
</tr>
<tr>
<td>FDA</td>
<td>U.S. Food and Drug Administration</td>
</tr>
<tr>
<td>GDP</td>
<td>Gross domestic product</td>
</tr>
<tr>
<td>GI</td>
<td>Glyphosate intermediate</td>
</tr>
<tr>
<td>GSC</td>
<td>Green and Sustainable Chemistry Network</td>
</tr>
<tr>
<td>GSK</td>
<td>GlaxoSmithKline</td>
</tr>
<tr>
<td>GWP</td>
<td>Global warming potential</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>HCF</td>
<td>Hydrofluorocarbon</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>HTI</td>
<td>Hydrocarbon Technologies, Inc.</td>
</tr>
<tr>
<td>IBB</td>
<td>Iso-butyl benzene</td>
</tr>
<tr>
<td>kg</td>
<td>Kilogram</td>
</tr>
<tr>
<td>lbs</td>
<td>Pounds</td>
</tr>
<tr>
<td>MCF</td>
<td>Methyl chloroform</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascals</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>N₂</td>
<td>Elemental nitrogen</td>
</tr>
<tr>
<td>NASH</td>
<td>Nucleophilic aromatic substitution for hydrogen</td>
</tr>
<tr>
<td>NESHAP</td>
<td>National Emission Standards for Hazardous Air Pollutants</td>
</tr>
<tr>
<td>NGET</td>
<td>Next Generation Environmental Technology</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NIH</td>
<td>National Institutes of Health</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Nitrogen oxides</td>
</tr>
<tr>
<td>NSF</td>
<td>National Science Foundation</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Elemental oxygen</td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation for Economic Cooperation and Development</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyaspartic acid</td>
</tr>
<tr>
<td>PCE</td>
<td>Perchloroethylene</td>
</tr>
<tr>
<td>PDC</td>
<td>Polycrystalline diamond compact</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>PMN</td>
<td>Premanufacture notices</td>
</tr>
<tr>
<td>PO</td>
<td>Propylene oxide</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>R&amp;D</td>
<td>Research and development</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
</tr>
<tr>
<td>SCF</td>
<td>Supercritical fluid</td>
</tr>
<tr>
<td>SCI</td>
<td>Chemical Specialties, Inc.</td>
</tr>
<tr>
<td>SiC</td>
<td>Standard Industrial Classification</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>TCF</td>
<td>Totally Chlorine Free</td>
</tr>
<tr>
<td>TRI</td>
<td>Toxics Release Inventory</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
</tbody>
</table>
Introduction

Over the past decade, there has been increasing interest in a fundamentally new approach to environmental protection. Rather than focusing on the control or cleanup of waste and hazardous materials, this new approach emphasizes redesigning industrial products and processes to reduce or eliminate the hazards at their source, reducing the amount and toxicity of chemical reactants, hazards of products and by-products, quantities of waste, and energy consumed, often at reduced costs. Proponents suggest that new science and technology can help produce processes and products that are both more environmentally benign and economically attractive.

Both the “pull” of demand and the “push” of technology drive this new approach. On the demand side, environmental policy has made significant advances over the past 30 years, particularly in controlling end-of-pipe emissions from large industrial facilities and key durable goods such as automobiles. But in some areas the trends have not been positive. In particular, the economies of the United States and other developed countries have not shown any consistent dematerialization, that is, a decrease in the total use and emissions of materials. Nor has there been any systematic reduction in the use of hazardous chemicals. For instance, total chemical emissions in North America have shown little change over the past five years. While manufacturers cut their toxic air emissions by 25 percent (153,000 metric tons) between 1995 and 1999, the improvement was largely offset by a 25 percent increase (33,000 tons) in on-site releases to land, a 35 percent increase (58,000 tons) in off-site releases mostly to landfills, and a 26 percent increase (24,000 tons) in releases to lakes, rivers, and streams.¹ Recent studies have found that in Europe the production and import of dangerous chemicals has grown faster than gross domestic product (GDP) over the past decade.² Many hazardous materials, such as sulfuric acid and chlorine, do not appear in final products but rather are used and dissipated in the production process. While total material use has not dropped in developed economies, there has been a reduction over the past three decades as a percentage of GDP. This comes largely as a result of some input substitution, that is, the use of new materials in place of old ones, increased efficiency of production, and growth of the service and information technologies’ economies. Nevertheless, the amount of material per product and the hazardous material used in their production has remained relatively unchanged.³

Concurrently, traditional approaches to environmental policy, principally command and control regulations but also market-based tools such as emissions trading and pollution taxes, do not

³The trends are often worse in the developing world, where economic growth is often faster and the rates of dematerialization are less.
seem sufficient to address many of these problems. The interest in new approaches stems from several factors. In part, the sources of many of today's most intractable environmental problems are not well addressed by traditional regulatory tools. Additionally, new attitudes about environmental protection may make it increasingly effective for government to focus on enabling rather than compelling environmental performance.

As an example of the first issue, traditional regulatory tools were designed to control large effluent streams from a relatively small number of large facilities such as electric power generation or chemical manufacturing plants. But increasingly, pollution comes from a large number of small sources. For instance, dry cleaners and automobile paint shops have been a significant source of volatile organic compounds (VOCs) that contribute to smog. Again, in the early 1990s, significant quantities of silver were discovered in the sediment and sea life in San Francisco Bay. The source turned out to be dentists' offices. Traditional regulatory tools are not effective for such point sources, spurring interest in alternative tools.

An increased interest in new approaches for environmental protection may also derive in part from significantly changed attitudes about the environment over the past few decades. Many firms now see an increased environmental consciousness as offering the potential for market niches that emphasize the environmental benefits of products and services. More generally, many firms seek to avoid adverse publicity caused by perceived inattention to the environment. Increasing numbers of corporate executives may begin to see environmental protection as an important part of their corporate responsibility. These shifting attitudes offer the potential for government to supplement mandatory requirements. Such additional actions could encourage and enable firms to act proactively in protecting environmental quality when cost-effective methods are available.

In conjunction with this increased demand for new approaches to environmental protection, there are powerful trends that provide a technology push driving new approaches. Across the economy, advances in the sciences of materials and chemical and biological processes increasingly make possible the redesign, at the molecular level, of the basic products and processes that underlie economic activities ranging from chemical manufacture to energy production to transportation to the disposal of household goods. Combined with information technology, these new technologies have the potential to revolutionize many sectors of the economy. The effects are already seen in the proliferation of new materials in everything from automobiles to sporting goods. Bioprocesses increasingly create new drugs. Many technology forecasters see the coming decades as ones where biotechnology and nanotechnology will provide unprecedented control

---


David W. Rejeski and James Salzman, "Changes in Pollution and the Implications for Policy" in Dietz and Stern, 2002.

National survey research suggests that there has not been a significant shift among individual attitudes, but rather individuals educated since the 1970s tend to be much more environmentally conscious than individuals educated before that time. See R. E. Jones and R. E. Dunlap, "The Social Bases of Environmental Concern: Have They Changed Over Time?" Rural Sociology, No. 57, 1992, pp. 28-47, and C. L. Kanagy, "Surging Environmentalism: Changing Public Opinion or Changing Publics?" Social Science Quarterly, No. 75, 1994, pp. 804-819.
over the fundamental building blocks of organic and inorganic matter. These emerging capabilities offer the hope that environmental problems can be increasingly addressed by designing materials and production processes that are intrinsically environmentally benign. Such advances could significantly reduce material use, eliminate reaction with and production of hazardous materials, and offer the promise of substantial new advances in environmental protection at very low cost or even with a net economic benefit. We call the broad class of such technologies “Next Generation Environmental Technologies” (NGETs).

The potential of NGETs to support a new approach to environmental protection raises important questions for both private industry and government policymakers. Can such technologies enable a widespread decoupling of environmental impact from economic growth, or will they remain confined to isolated pockets of success? If the former is indeed possible, what steps must the government and the private sector take to bring NGETs to their full potential? Over the past decade the federal government has pursued a variety of programs to explore the development of these new approaches. These include funding for basic research; partnerships, fellowships, and an awards program in green chemistry; and initial attempts at flexible regulatory reform. Policymakers may now confront the extent to which NGET programs ought to be increased and the extent to which, if possible, environmental policy ought to come to rely more heavily on such a technology-based approach.

Such questions are difficult to answer because many NGETs are relatively young. As with any new technology, future costs and benefits are impossible to predict accurately. To craft policy successfully in this area, policymakers must lay out a range of scenarios for potential impacts, consider a portfolio of potential policy levers, and choose portfolios of policies that will be effective across the range of uncertainty inherent in any new technology program.

This report takes an initial step in framing such a process. It explores 25 case studies of NGETs as a means of surveying the current activity in the field. We examine each technology’s current impact, its potential promise, reasons for its adoption, and the barriers to broader implementation. For readers unfamiliar with NGETs, this report will provide a survey of its promise and weaknesses. For researchers and practitioners creating new NGETs, it aims to provide a broader context for their efforts. For policymakers, it can provide the raw materials for a systematic assessment of the range of potential benefits of NGETs and the portfolio of policies needed to move them forward. The report does not, however, make specific policy recommendations.

---


What Are Next Generation Environmental Technologies?

Traditionally, technology has addressed environmental problems by improving “end-of-pipe” controls, that is, by providing better means to control the release of hazardous substances or to clean up subsequent releases. More recently, technology has been used to enhance pollution prevention, by limiting the use or creation of environmentally hazardous materials. NGETs contribute to this effort by focusing on the redesign, at a molecular level, of manufacturing processes and products. Because such redesign provides other benefits to firms, including increases in production efficiency and reductions in the requirements for raw materials, NGETs may in some cases offer the prospect of environmental protection at no additional manufacturing cost.

The class of NGETs has significant overlap with the emerging scientific discipline of green chemistry. Green chemistry focuses on the design of chemical processes and products that are environmentally benign. It is guided by a set of 12 principles (see box on page 8). The term green chemistry is being used ever more broadly—describing a program within the U.S. Environmental Protection Agency (EPA), designating programs or centers in a number of universities, and providing the name of the Green Chemistry Institute, a partnership of a network of scientists and institutions with the American Chemical Society. Any technology resulting from green chemistry research most likely qualifies as an NGET, and because most environmental hazards stem from chemicals and their effects on society, green chemistry may provide a significant fraction of all NGETs. These technologies are the focus of our review. However, we do not exclude a few technologies dealing with physical processes—such as joining, finishing, or magnetic cooling—that stem from other areas of scientific research. Thus this report focuses on technologies from green chemistry but describes its subject with the more general term: “Next Generation Environmental Technologies.”

Green chemistry is aimed to help practitioners involved in the invention, design, and application of chemical products and processes to reduce or eliminate the use and generation of hazardous substances. The principles promote environmental chemistry at all levels: research, reduction to practice, education, national and international policy, and public perception. They help chemists

---

9We do not consider social processes (such as leasing instead of selling products or video conferencing as an alternative to travel) that can also eliminate or reduce the need for a hazardous product or process.
10To our knowledge, the term “Next Generation Environmental Technologies” derives from the CHEMRAWN XIV Future Actions Committee, which first used the phrase “Next Generation Innovative Environmental Technologies such as green chemistry.”
and chemical engineers design more environmentally benign products and processes through the selection of feedstocks, reagents, alternative synthetic transformations, solvents, reaction conditions, and end products, as well as the design of safer chemicals. For instance, when considering what feedstocks to use in generating a particular compound, the green chemist will explore renewable feedstocks whenever practical. There is no guarantee that such renewable feedstocks are possible for a given reaction nor, if they are, that they will provide a net environmental benefit. Nonetheless, the principles of green chemistry provide a set of design criteria and goals that can help improve the environmental performance of new products and processes.

As they begin to apply the principles of green chemistry, chemists are discovering many pathways toward environmentally greener designs. For instance, synthetic catalysts and biocatalysts such as enzymes offer a variety of alternative synthetic pathways that are consistent with the principles of green chemistry. These catalysts also enable the use of alternative reagents and feedstocks, previously impractical with conventional chemistries. The two crosscutting enabling technologies hold much promise in fulfilling the expectations for green chemistry.

In surveying the field, it is useful to employ a taxonomy of methods that develop NGETs. To that end, we use the seven areas of green chemistry, a taxonomy that has been laid out to help describe green chemistry research:

A. Use of alternative feedstocks that are both renewable and less toxic to human health and to the environment.

B. Use of innocuous reagents that are inherently less hazardous and are catalytic.

C. Employment of natural processes—biosynthesis, biocatalysis, and biotech-based chemical transformations for both efficiency and selectivity.

D. Use of alternative solvents that reduce potential harm to the environment and serve as alternatives to currently used volatile organic solvents, chlorinated solvents, and other hazardous chemicals.

E. Safer chemical design—with principles of toxicology to minimize intrinsic hazards while maintaining needed functionality.

F. Development of alternative reaction conditions that increase selectivity and enable easier separations.

G. Minimization of energy consumption.

---

13Tundo et al., “Synthetic Pathways and Processes in Green Chemistry,” 2000. Posters from the American Chemical Society (www.chemistry.org/education/greenchem) highlight six themes: (1) Use renewable resources; place greater emphasis on renewable starting materials. (2) Find safer solvents; eliminate the use of toxic solvents to dissolve the reacting materials. (3) Economize on atoms; design reactions in which most or all of the atoms end up in the desired product rather than in the waste product. (4) Get off to a good start; identify reactions that use nonhazardous materials to make the desired product. (5) Return safe substances to the environment; produce products that are benign or rapidly biodegradable. (6) Lower energy input; use methods that minimize the energy required for a reaction to take place.
All the case studies considered in this report employ one or more of these methods. More information on how these methods are employed in each case study is covered in Table 1 and Appendix A.

**Assessing the Promise of NGETs**

NGET proponents foresee a promising future based on an increasing awareness of green chemistry and growth in commercial applications over the next two decades. The authors of the chemical industry’s *Vision 2020* are typical in their optimism:

> While the challenges of sustainability are significant, there are also major opportunities. . . . The chemical industry now has the opportunity to accelerate its development of advanced manufacturing technologies and new chemistry and related technologies that use materials and energy more efficiently. U.S. companies also have an opportunity to build on their current dominance in the relatively new field of environmental technology. Environmental technologies make sustainable development possible by reducing risk, improving process efficiency, and creating products and processes that are environmentally beneficial or benign.  

To support this vision, the chemical industry has established goals of reducing feedstock losses to waste and by-products by 90 percent, energy intensity by 30 percent, and emissions and effluents by 30 percent, all by the year 2020.

This report provides a first step toward assessing the potential of NGETs to help meet such goals identified by the chemical and many other industries. We examined 25 existing NGETs in this process. The technologies considered span the range of development from early research to full deployment in profitable businesses. Those that have been commercialized are offering significant benefits. Others that are still in various developmental stages offer similar promise.

In addition to supporting more public and private sector research, policymakers will be considering appropriate mechanisms to express society’s demand for the benefits that NGETs can offer. Even when NGETs can provide such benefits at little or no cost, they must compete inside firms with other investment opportunities. Furthermore, the diversity of potential NGET applications offers both a benefit and a challenge. Policymakers are unlikely to know beforehand the full range of future benefits that are possible. Thus for NGETs to play their full role in a new approach to environmental protection, policymakers will need to determine society’s demand for such benefits, the best ways to achieve them, and the rationale for actions to be taken, communicating these to industry and society at large.

---

14 The *Vision 2020* study, completed in 1996, was in part stimulated by a request from the White House Office of Science and Technology Policy for industry advice on how the U.S. government could better allocate R&D funding to advance the manufacturing base of the U.S. economy. See http://www.ccrhq.org/vision/. *Vision 2020* did not use the term “green chemistry,” but follow-up efforts did.
**Twelve Principles of Green Chemistry**

1. It is better to prevent waste than to treat or clean up waste after it is formed.

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

3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficiency of function while reducing toxicity.

5. The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary wherever possible and innocuous when used.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. A raw material of feedstock should be renewable rather depleting wherever technically and economically practicable.

8. Unnecessary derivitization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

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

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

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

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

---

Mechanisms for Gaining the Benefits from NGETs

The case studies demonstrate that NGETs offer potentially significant benefits over a wide variety of applications, recognizing the uncertainty in any forecast of the ultimate range and scope for any specific technology. This report describes current benefits and then the possible longer-term benefits that depend on further technology advances.

We now look at the mechanisms by which the benefits are delivered.

Mechanisms

A review of our case studies and the literature on environmental technologies suggests that the invention, design, and deployment of NGETs offer four types of benefits—environmental, economic, security, and health and safety. These benefits are delivered by three mechanisms: cost reduction, risk reduction, and broad technology transfer or spillover effects.

Cost Reduction

NGETs can reduce the costs of providing the various benefits. The classic model derived from welfare economics provides a way of thinking about how NGETs might enable a new approach to environmental protection. In this model, one can estimate the costs associated with emitting some pollutants. One also knows the potential costs of reducing these emissions. With this information, policymakers can choose the level of environmental regulation so that the marginal cost of reducing emissions is just balanced by the marginal benefit of further reductions. At this optimal level of reductions, society as a whole has gained a benefit equal to the reduced level of environmental impact less the cost of achieving the necessary reductions.

In this model, technological innovation can play a role by lowering the costs of reducing emissions. Policymakers are then able to choose a higher level of regulation, with an overall increase in the net societal gain. In this model, such research can play its most important role when the current costs of reducing some pollutant are sufficiently high that the optimal level of regulation leaves the pollutant untouched. An opportunity is created for research to make significant cost reductions compared to the alternatives. In cases where costs are already low compared with benefits, innovation may provide little additional gain. Only in cases where innovation makes dramatic improvements in relative costs can it fundamentally change the regulatory calculus.

---

Many of today’s environmental challenges represent cases where the current costs of reductions are high compared with the perceived benefits. One example might be the sequestration of greenhouse gases from electric power generation facilities, where current costs may be high because of the limited or untested technological options available for reductions. NGETs may significantly change the situation by providing technological options that dramatically reduce the costs of reductions relative to the derived social benefits. In such cases the government can set new regulatory standards and achieve previously unavailable social benefits. NGETs may also significantly change the situation if they can lower costs of reductions sufficiently so that firms will make these reductions without the need for traditional regulatory stimulus. This latter case represents the situation where NGETs can indeed provide a new approach to environmental protection.

**Risk Reduction**

Many of today’s environmental challenges also represent cases where the potential benefits of addressing the problem are sufficiently uncertain that it becomes difficult to justify a traditional regulatory remedy. NGETs may provide a powerful tool for managing such risks. For instance, there may be many emerging environmental hazards of which we are only dimly aware. An estimated 100,000 chemicals are used in commerce worldwide, and more than one new chemical is introduced every day, not all of which may be harmless. In addition, the volume of many existing pollutants grows yearly.

The “precautionary principle” represents one approach to addressing such uncertain environmental risks. This principle, embodied in many of the environmental policies of the European Union, suggests that human activities with a potential for serious environmental harm should be limited even in the absence of full scientific certainty. For instance, the principle suggests that some new chemicals ought not be used until proved completely safe. Industry and some policymakers in the United States generally oppose this concept because it can increase the risks to economic growth in exchange for an uncertain benefit. Such growth can create additional wealth that can help pay for enhanced environmental protection, and is a valuable end in itself. To preserve economic growth, many experts argue that hazardous substances should not be regulated until the benefits of doing so clearly outweigh the costs. However, some environmental dangers may not become certain until damages are already significant and emissions control and cleanup have become expensive.

NGETs may help serve as a bridge between these two positions by making a different wager. NGETs can reduce environmental risk by eliminating broad classes of potentially dangerous substances from products and processes. The principles of green chemistry guide firms in designing new products and processes in such a way that their impact on the environment is

---

17. These include industrial chemicals, polymers, pesticides, pharmaceuticals, and food additives. Four times as many premanufacture notices are submitted as chemicals commercially produced.

reduced. While reductions of many new effluents will have little ultimate consequence, NGETs may unknowingly eliminate some critical environmental problems before we ever learn that such problems exist.

**Technology Spillover Effects—Technology Transfer**

Finally, research on NGETs can have broad spillover effects that facilitate the development of subsequent NGETs in the same firm, or across an industry. It is widely understood that society’s scientific and technological advances provide a stock of knowledge that can be repeatedly drawn on by those seeking new innovations. Early NGETs may have had a relatively sparse base on which to draw. As the body of research and practical experience grows, it will become easier and less expensive for firms to make progress in their particular applications. In addition, innovation in new technology areas can be subject to increasing returns. Scientists and engineers can draw more heavily on the principles and lessons of many NGETs and green chemistries as they become more familiar and proven. Constraints may ease as NGETs become more prevalent. Early research efforts can help create the knowledge and resources to make future projects easier and more likely to succeed. Spillover effects also occur when one firm installs technology eliminating a particular pollutant. Competitors may then be pressured through a variety of forces to at least reduce, if not eliminate, that pollutant.

The importance of spillover effects for the development of NGETs is increased by the wide variety of fields from which these technologies derive. Figure 1 shows how advances in many different scientific disciplines, including biochemistry, bacteriology, genetics, catalysis, mathematics, and electrochemistry, have contributed to green chemistry. Disciplines other than those shown can also play a role. These illustrative connections were generated by the authors, observing patterns of citations in the chemical sciences literature and individual histories of the developments in our case studies. This diversity underlies the great promise of NGETs, but it also stresses the difficulty of bringing together all the potentially relevant information while these technologies and their use remain relatively new and unexplored.
Figure 1. Science and Technology Landscape. (Influence diagram showing the information flow from scientific disciplines to green chemistry and engineering and then to NGETs and environmentally benign products and processes.)
Lessons from Case Studies

Tables 1 and 2 summarize the cases in our survey; Appendix A describes them in detail. Each case focuses on a particular NGET and examines the source of the technological innovation, the principles and methods of green chemistry employed, the extent to which it has been commercialized, the motivation of the firm developing the technology, and any government role in its development. The case studies aim to survey the benefits and barriers of NGETs. From our survey we found that:

1. NGETs can provide significant benefits to society in all the areas considered in our study: the environment, national security, occupational safety and health, and the economy.

2. NGETs can in some cases eliminate the use and generation of hazardous substances at little or no additional cost.

3. NGETs can be adopted by businesses for a variety of different reasons: to meet environmental regulations in a cost-effective way, to provide environmentally benign products economically, or to develop profitable new products in new and environmentally beneficent ways. NGETs provide new approaches to competitive advantage.

4. The barriers to the widespread use of NGETs can be technical, economic, and/or societal in nature.

Overview of Cases

We identified potential technologies from a wide variety of sources, including applicants for EPA's green chemistry awards, surveys of the chemical and patent literature, conference proceedings, and suggestions from persons in the field. We chose cases covering a wide range of technologies in varying industrial sectors. We limited our choices to those that have near-term applications (though many may have long-term benefits as well) or had significant potential applications. We did not include work that might be called "fundamental research." We also limited our selection to cases where sufficient information appeared available. As is typical of case analyses, our findings are not based on exhaustive samples but nevertheless portray the

---

Patent searches for NGETs are difficult; "Environmental Technologies" yielded only 116 hits in the U.S. Patent database for 1996-2002, and "green chemistry" yielded 8; many environmental technologies described control or analytical methods. The American Chemical Society commissioned a survey by CHI and reported overall results at the 6th Annual Green Chemistry and Engineering Conference, 2002.
range of NGET examples. New potential cases will continue to appear as progress is made in green chemistry, as is seen in Appendix C.

The case studies vary widely in breadth. Some discuss a specific alternative applied to a given situation while others discuss several alternatives that could be used in a range of applications. Some NGETs, including many bioprocesses and electrochemical processes, are based on the latest science. Others, such as the use of supercritical CO₂ as a solvent and the fermentation routes to vitamins, proteins, and fine chemicals, represent well-studied processes that continue to be improved over the years.

In many cases, near-term benefits will increase as the market penetration of the product and process continues to grow, leading to further cost reduction and performance improvements relative to competing products and processes.
<table>
<thead>
<tr>
<th>Case Study</th>
<th>Comments</th>
<th>Environmental/Energy Benefits</th>
<th>Security/ Safety Benefits</th>
<th>Performance/ Economics Benefits</th>
<th>Principles and Areas Addressed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Processes using supercritical CO₂ solvent</td>
<td>Applications in cleaning, coffee decaffeination, polymerization solvent</td>
<td>Elimination of chlorinated solvents</td>
<td>Reduced exposure to solvent vapors</td>
<td>Improves economics and performance</td>
<td>4, B, D</td>
</tr>
<tr>
<td>2 3 steps for ibuprofen</td>
<td>Example of &quot;atom economy&quot; principle</td>
<td>Elimination of 35 million lbs of waste</td>
<td>Reduced investment and operating costs</td>
<td></td>
<td>1, 8, F</td>
</tr>
<tr>
<td>3 Converting polymers to monomers for recycle: PET and Nylon 6</td>
<td></td>
<td>Elimination of up to 100 million lbs per year PET from landfills; 200 million lbs of nylon 6 diverted from landfills; air emissions reduced 89%</td>
<td></td>
<td></td>
<td>1, 9, G</td>
</tr>
<tr>
<td>4 Bio-based processes</td>
<td>47 processes (examples) studied (see Appendix A)</td>
<td>Average 20% reduction in waste (improved yields); elimination of hazardous chemicals in mining, pulp and paper, specialty chemicals</td>
<td>Reduced exposures; reduced critical metals; reduced storage of Cl₂</td>
<td>Implemented where superior economics prevailed; provided improved performance and entry to new markets</td>
<td>1, 2, 7, 8, 9, 12, A, B, C, F, G</td>
</tr>
<tr>
<td>5 Dimethyl carbonate</td>
<td>Manufacture and use of DMC</td>
<td>Could eliminate use of phosgene in the manufacture of multibillion pounds of polycarbonates and polyurethanes</td>
<td></td>
<td></td>
<td>2, 3, 4, 10, B, E</td>
</tr>
<tr>
<td>6 Direct production of hydrogen peroxide from hydrogen and oxygen</td>
<td>Not yet commercialized; uses carbon dioxide as solvent</td>
<td>Eliminates waste streams; reduces energy use by eliminating three energy-intensive units: oxidation reactors, stripping column, and distillation train</td>
<td>Safety a continuing concern in any manufacturing process for hydrogen peroxide</td>
<td>Cheaper hydrogen peroxide could find greater use in &quot;green chemistry&quot;</td>
<td>3, 5, 9, B, D</td>
</tr>
<tr>
<td>7 Advanced oil and gas exploration and production</td>
<td>CO₂, sand fracturing, modern drilling bits; synthetic drilling muds</td>
<td>Reduced waste and energy use; no harm to groundwater</td>
<td>Increased worker safety</td>
<td>Lower-cost operation</td>
<td>1, 3, 4, 6, 10, B, E</td>
</tr>
<tr>
<td>8 Various approaches to water purification</td>
<td>Chemical, membrane, ultraviolet, and more</td>
<td>Eliminate use of chlorine</td>
<td>Enhanced security</td>
<td>Lower costs; availability when otherwise not possible</td>
<td></td>
</tr>
<tr>
<td>9 Wood preservation</td>
<td>Replace chromated copper arsenate with alkaline copper quaternary</td>
<td>Virtually eliminates the use of arsenic in the U.S., use of 64 million lbs of hexavalent chromium, and RCRA hazardous wastes from production/treating facilities</td>
<td>Avoids worker exposures in wood treatment</td>
<td>Replacement at a somewhat increased direct cost</td>
<td>3, 4, 10, B, E</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>Benefits</td>
<td>Relevant References</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------</td>
<td>---------------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Sentricon® termite colony elimination system</td>
<td>More than 300,000 structures are now being safeguarded.</td>
<td>3, 4, 10</td>
<td>B, E</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Inert anodes</td>
<td>Example of green electrochemistry; collaborative program—DOE and Alcoa</td>
<td>Avoids potential worker exposure</td>
<td>Nonenergy savings of $20 million</td>
<td>3, 6</td>
</tr>
<tr>
<td>12</td>
<td>Process for production of Cytovene® antiviral agent</td>
<td>Elimination of 1.1 million kg/year liquid waste and 25,000 kg/year solid waste</td>
<td>Reduced costs with yield increase of 25% and 100% increase in throughput</td>
<td>1, 2</td>
<td>F</td>
</tr>
<tr>
<td>13</td>
<td>High-yield melting of Al</td>
<td>In alliance with Praxair, Alcoa is testing high-yield melting</td>
<td>Safer work environment</td>
<td>Reduced natural gas use and reduced wastes translate to reduced costs</td>
<td>6</td>
</tr>
<tr>
<td>14</td>
<td>Elimination of ozone-depleting chemicals</td>
<td>Completely eliminated the use of CFCs and other ozone-depleting substances</td>
<td>Eliminated potential exposure to methyl chloroform</td>
<td>Replacing CFCs with water or “no-solvent” processes translate to cost savings</td>
<td>3</td>
</tr>
<tr>
<td>15</td>
<td>Delignification and bleaching of pulp in paper manufacture</td>
<td>Eliminates use of chlorine or chlorine dioxide; using air in place of sulfur and chlorine</td>
<td>Eliminate formation of dioxin and other organo-chlorine waste products</td>
<td>Elimination of use of chlorine</td>
<td>2, 3</td>
</tr>
<tr>
<td>16</td>
<td>Clean solvent extraction using polyethylene glycol-based aqueous biphasic systems</td>
<td>In aqueous biphasic systems (ABS) the major component in each of the two immiscible phases is water, and thus a liquid-liquid extraction</td>
<td>Technology can be envisioned that completely eliminates the use of volatile organic compounds</td>
<td>Immediate environmental and economic impacts</td>
<td>3</td>
</tr>
<tr>
<td>17</td>
<td>Room-temperature ionic liquids</td>
<td>Liquids composed entirely of ions can be good solvents for catalytic reactions eliminating many side reactions</td>
<td>No commercialized applications yet as a separation or reaction medium; concerns on potential toxicity and environmental impact need to be studied</td>
<td>Potential to reduce worker exposure to volatile solvents</td>
<td>3</td>
</tr>
<tr>
<td>18</td>
<td>Environmentally friendly refrigerants, new refrigeration processes</td>
<td>(1) Trifluoro methyl iodide, blended as a combustion inhibitor, (2) hydrofluorocarbons have been developed by 3M, (3) non-chemical related cooling principles</td>
<td>10% P with 20% market penetration by 2010; CO₂ emissions down by 4 million tons per year, particulates down 12,000 tons, NOx down 16,000 tons, and sulfur dioxide down 24,000 tons</td>
<td>10</td>
<td>E</td>
</tr>
</tbody>
</table>
| 19 | Clean diesel breakthrough with compact advanced polymer membrane | Three changes to engine operating conditions: (1) increased oxygen content in the engine air supply, (2) retarded timing of fuel injections, and (3) increased fuel flow—made practical by compact advanced polymer membrane | Reduces NOx by 15% and particulates by 60%. Concern has been raised that benefits may be obtained by other means. | 3  
F |

| 20 | Biodegradable polymers | Host of polymers have been developed over the past 20 years | Benefits of all biodegradable materials: eliminates litter; energy savings need to be determined by a life cycle analysis | 4, 7, 10  
B, E |

| 21 | Capture of nitrous oxide in adipic acid manufacture to use in new phenol process | Adipic acid manufacture gives 2 billion lbs of nitrous acid (greenhouse gas 300x the global warming potential of CO2)—10% of annual releases | Solutia can recycle 250 million lbs of nitrous oxide on start up of the full-scale plant. Competitors have found other ways to eliminate nitrous oxide emissions. Startup delayed. | 2, 3, 6 |

| 22 | Advanced oxidation process for the metal casting industry | When the coal and adheres experience high temperatures at the molten metal surface, they can emit VOCs. However, a novel advanced oxidation process has been installed in five full-scale foundries | Decreased emissions by 20–75%; diminished by 15–40% the amount of clay, coal, and sand needed to produce castings; and decreased casting defects by up to 35% while increasing mold strength; prevents pollution; reduces waste to landfills; broadens foundries' opportunities; and creates jobs. | Worker exposures decreased  
Cost savings are claimed for the process | 3  
F |

| 23 | Process for fluoro benzene | Synthesized from benzene, HF and oxygen with a copper fluoride catalyst, with catalyst regeneration | Major reduction of waste potential; DuPont not pursuing; patent donated to University of Florida | Potential cost savings | 9  
B |

| 24 | Synthesis of 4-aminediphenylamine | NASH reaction gives major cost reduction and elimination of chlorine. | Elimination of chlorine; major reduction in wastes | Eliminated worker potential exposure to chlorine | Significant cost savings | 4  
F |

| 25 | Synthesis of glyphosate | “Zero-waste” process replaced Strecker process in producing Roundup™ by Monsanto | Eliminated production of 1 kg waste for each kg of disodium iminodiacetate—key intermediate; waste contained cyanide and formaldehyde | Eliminated worker exposure to hydrogen cyanide and formaldehyde | Cost reduced by 40% from 1995 to 2002 | 1, 2, 6, 9  
B, G |

Note: Principles and areas as listed previously on pages 6 and 8.
Table 2 lists the case studies according to the primary type of benefit they provide and their current state of development. The columns categorize technologies by three stages of development: (1) Research and Development (R&D), where the technology is being developed in the laboratory; 2) Market and Product Development, where the commercial firm is investing to bring a specific product and/or service based on the technology to a well-defined market; and 3) Sustainable Business, where the technology supports a product or service that makes money and has significant market penetration in some market or niche. 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 rows provide benefits demanded by society, often through regulations, that cost the firm money to provide. However, the technologies 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.

The case studies include examples of each type of primary benefit and each stage of development, although most of our cases address primarily environmental and economic benefits. In general, firms will adopt an NGET for one of three reasons. First, the new technology may be the least expensive means to produce an existing product, irrespective of any broader social benefits. Second, the new technology may be the least expensive means for the firm to meet environmental, health, or safety regulations. Third, the new technology may enable the firm to offer new products or services with novel or improved qualities, which may include improved environmental performance that the firm’s customers find attractive.
<table>
<thead>
<tr>
<th>Environmental</th>
<th>Security</th>
<th>Health and Safety</th>
<th>Economic</th>
</tr>
</thead>
<tbody>
<tr>
<td>6: H₂O₂ production</td>
<td>8: Water purification</td>
<td>5: DMC production</td>
<td>23: Fluorobenzene production</td>
</tr>
<tr>
<td>16: ABS</td>
<td></td>
<td></td>
<td>4aa: Enzyme optimization</td>
</tr>
<tr>
<td>17: Ionic liquids</td>
<td></td>
<td></td>
<td>4r: Complex carbohydrates</td>
</tr>
<tr>
<td>4g: Ammonium acrylate</td>
<td></td>
<td></td>
<td>11: Inert anodes</td>
</tr>
<tr>
<td>4s: Bioconversion of CO₂</td>
<td></td>
<td></td>
<td>4h: Polyesters</td>
</tr>
<tr>
<td>4u: p-Hydroxybenzoic acid</td>
<td></td>
<td></td>
<td>4q: Oil well completion</td>
</tr>
<tr>
<td>4v: Polyhydroxyalkanoates</td>
<td></td>
<td></td>
<td>4t: Cross-linked enzyme crystals</td>
</tr>
<tr>
<td>4w: Adipic acid</td>
<td></td>
<td></td>
<td>4bb: Ascorbic acid</td>
</tr>
<tr>
<td>4ee: Terephthalic acid</td>
<td></td>
<td></td>
<td>4cc: 1,3-Propanediol</td>
</tr>
<tr>
<td>4vv: Biorefinery</td>
<td></td>
<td></td>
<td>4tt: Succinic acid</td>
</tr>
<tr>
<td>1a: CO₂ cleaning</td>
<td></td>
<td></td>
<td>11: Inert anodes</td>
</tr>
<tr>
<td>3: Polymers to monomers</td>
<td></td>
<td></td>
<td>4h: Polyesters</td>
</tr>
<tr>
<td>13: High yield aluminum</td>
<td></td>
<td></td>
<td>4q: Oil well completion</td>
</tr>
<tr>
<td>15: Delignification</td>
<td></td>
<td></td>
<td>4t: Cross-linked enzyme crystals</td>
</tr>
<tr>
<td>18: Non-CFC refrigerants</td>
<td></td>
<td></td>
<td>4bb: Ascorbic acid</td>
</tr>
<tr>
<td>19: Clean diesel membranes</td>
<td></td>
<td></td>
<td>4cc: 1,3-Propanediol</td>
</tr>
<tr>
<td>20: Biodegradable polymers</td>
<td></td>
<td></td>
<td>4tt: Succinic acid</td>
</tr>
<tr>
<td>22: Advance ox process</td>
<td></td>
<td></td>
<td>2: Ibuprofen</td>
</tr>
<tr>
<td>4p: Ethanol from biomass</td>
<td></td>
<td></td>
<td>7: Oil and gas production</td>
</tr>
<tr>
<td>4pp: Levulinic acid from biomass</td>
<td></td>
<td></td>
<td>12: Cytovene production</td>
</tr>
<tr>
<td>4uu: Biodiesel</td>
<td></td>
<td></td>
<td>24: Aminodiphenylamine production</td>
</tr>
<tr>
<td></td>
<td>9: Wood preservation</td>
<td></td>
<td>25: Synthesis of Glyphosate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4a: Riboflavin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4d: Amino acids</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4c: Cephalexin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4x: 5-Cyanovaleramide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4z: Acetic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4dd: Nicotinamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4ff: Aspartame</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4gg: 6-Aminopenicillanic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4hh: L-lysine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4ii: L-threonine/L-methionine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4jj: Roundup Read* soybeans</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4kk: Vitamin B-12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4ll: Vitamin C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4mm: Vitamin F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4nn: D-p-hydroxyphenyl glycine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4oo: Feed enzymes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4qq: Citric acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4rr: High-fructose syrups</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4ss: Monosodium glutamate</td>
</tr>
</tbody>
</table>
Near-Term Benefits of NGETs and Barriers to Their Adoption

Proponents for NGETs and associated green chemistry research suggest that this new approach to environmental protection will have major impacts in the decades ahead. We use our case studies to see to what extent this may be true. In particular, we examine in the case studies how NGETs, to date, have helped reduce the use of hazardous substances, the benefits NGETs provide, why NGETs are adopted, and the barriers to their greater adoption.

A key challenge in such an assessment is that NGETs represent new technology. The federal R&D support for green chemistry programs is only about a decade old, relatively young to have had significant societal impact. Accordingly, two-thirds of our case studies represent technologies not yet embodied in sustainable businesses (roughly half our case studies shown in Table 2 represent sustainable businesses if the 47 bioprocesses examples are counted separately). Despite their infancy, our case studies demonstrate that NGETs have already provided important societal benefits.

I. NGETs Can Provide Benefits in All the Important Areas Identified in Our Study

Our case studies demonstrate that NGETs can provide benefits across the full spectrum considered in this study—environmental, security, occupational safety and health benefits, and economic. As is clear from Table 2, the vast majority of our case studies primarily offer environmental or economic benefits. This distribution owes in part to our selection, which focused on NGETs that offer environmental benefits at low or no cost. However, this distribution of cases also reflects the significant interest over the past decade in developing new technologies to enhance environmental protection. The next decade may also see increased technological activity directed toward national security.

Environmental Benefits

Environmental benefits from NGETs arise from a variety of techniques that either reduce or eliminate the use of hazardous materials, or replace environmentally sensitive materials with less-damaging chemicals. NGETs offer improved environmental quality in a range of areas, including reduced resource depletion, ecosystem damage, ozone depletion, and levels of toxic pollutants, as well as greater material efficiency, waste minimization, and climate improvements.

---

20NGETs may also help save energy. We include such energy savings as means to provide other more tangible benefits, such as environmental, security, and economic.
As the use of different chemicals has expanded to include many thousands of specialty chemicals across the economy, so too have the means of tracking these chemicals. However, this is done with some difficulty.

The Emergency Planning and Community Right-to-Know Act (EPCRA) was enacted in 1986 as a result of pressure from public and environmental organizations' demands to know what chemicals were being released into communities without their knowledge. EPCRA Section 313 requires EPA and the states to collect annually information on a list of chemicals that industrial facilities may be releasing into the environment. These data, known as the Toxics Release Inventory (TRI), are collected on only a small portion (about 650 chemicals) of the total number of chemicals used in society. However, the Inventory may be used as a barometer for the fate of some of the more commonly used chemicals and a gauge for understanding the use of some of the more dangerous and highly pervasive materials.

The number of chemicals for which data are compiled each year has increased from 343 chemicals in 1994 to more than 650 chemicals in 30 categories today. The top six two-digit Standard Industrial Classification (SIC) code industries comprise more than 92 percent of the total releases (see Figure 2).

![Pie chart showing the breakdown of TRI chemical releases by industry.]

Figure 2. Breakdown of Total TRI Chemical Releases Over All Industries.

The mining industry (SIC codes 10 and 12) releases the bulk (56 percent) of the TRI chemicals, nearly 4 billion pounds of the total 7.1 billion pounds, and almost all (99 percent) is released on site. Only a couple of case studies focused on the mining industry, and none of them directly addressed the largest problem there, which is the removal of underground material left on the surface. Paper and allied products releases 18 percent, and primary metals 5 percent. The chemicals and allied products industry (SIC code 28) releases approximately 600 million pounds.

---

*See "Toxics Release Inventory (TRI) Program," at http://www.epa.gov/tri/.*

*Toxics Release Inventory (TRI) Program.*
of chemicals (8 percent) into surface water, over land, underground, and into the air. These compounds are widely dispersed and the top ten chemicals account for only 64 percent of total releases (Figure 3). The bulk of the case studies mentioned in the report address chemicals used in this industry sector.

![Figure 3. TRI Release Breakdown of the Chemical and Allied Products Industry (SIC code 28) (% of emissions).](image)

The top ten chemicals released into the air across all industries are largely comprised of solvents and cover 77 percent of the total released into the air.
Table 3. Top ten chemicals released into the air.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent of Total Air Emissions</th>
<th>Total (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid</td>
<td>33</td>
<td>666,193,514</td>
</tr>
<tr>
<td>Methanol</td>
<td>9</td>
<td>184,820,191</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>9</td>
<td>179,848,171</td>
</tr>
<tr>
<td>Ammonia</td>
<td>7</td>
<td>150,901,368</td>
</tr>
<tr>
<td>Toluene</td>
<td>4</td>
<td>89,911,659</td>
</tr>
<tr>
<td>Hydrogen Fluoride</td>
<td>4</td>
<td>72,700,182</td>
</tr>
<tr>
<td>Xylene (mixed isomers)</td>
<td>3</td>
<td>66,634,179</td>
</tr>
<tr>
<td>N-Hexane</td>
<td>3</td>
<td>56,070,510</td>
</tr>
<tr>
<td>Styrene</td>
<td>3</td>
<td>54,744,130</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2</td>
<td>49,371,156</td>
</tr>
</tbody>
</table>

The top ten chemicals released from all industries excluding mining are shown in Figure 4. These comprise nearly 3.2 billion pounds of chemicals released, indicating the impact of manufacturing facilities.

![Figure 4. Top Ten Chemicals Released Excluding the Mining Industry (% of emissions).]
NGETs have the potential to address many of the large-volume chemicals released by the chemical industry and other industries. Some technologies replace chlorinated solvents with more benign alternatives that could have an effect on the large amount of chlorofluorocarbons (CFCs) included in the TRI (for example, Cases 1, 14, and 18). Chlorine is one of the most released TRI chemicals, and the case studies having to do with the pulp and paper industry (Case 4m and 15) and water purification (Case 8) aim to reduce the use of this chemical. Some cases supply alternatives to many solvents, such as through the development of ionic liquids. However, replacing well-known solvents with these new chemicals is not yet fully understood.

Not all the chemicals in the TRI are exceptionally dangerous to the environment. Methanol, for example, has a relatively low toxicity, and none of the case studies addresses its removal. However, methanol's heightened persistence and widespread occurrence may be a cause for concern. The Twelve Principles of green chemistry call for reducing both the risk and the exposure to chemical substances whenever possible, regardless of the known risks.

The three-stage conversion of cleaning processes at an IBM plant in Austin, Texas (Case 14), for printed wiring board and electronic card assembly and test processes produced a substantial environmental benefit. This conversion eliminated the need for two CFCs that had been previously used at the plant: CFC-113 (430,000 pounds in 1988) and methyl chloroform (308,000 pounds in 1988).

The use of carbon dioxide as a cleaning solvent (Case 1) is an example of an NGET that can eliminate an entire class of emissions and that is currently finding an ever-growing list of applications. Carbon dioxide, which is just beginning to be used in the dry-cleaning industry, replaces older technologies that use the chlorinated solvents trichloroethane, trichloroethylene, or perchloroethylene.23 Only a small fraction of commercial dry-cleaning machines currently use the new technology, but such machines have the potential to terminate the use of chlorinated solvents at nearly 35,000 dry-cleaning establishments in the United States. This would eliminate nearly 51,000 tons of organic solvent emissions and 95,000 tons of other hazardous air pollutants every year.24

Biochemie (a division of Novartis) developed a green chemistry process for an antibiotic intermediate, 7-amino-cephalosporanic acid (Case 4e). A reaction pathway involving two enzymes replaced a chemical process that used N,N-dimethylaniline, trimethylchlorosilane, phosphorous pentachloride, methylene chloride, and zinc salts. The bio-based process uses no toxic ingredients, is an aqueous room temperature process, and biological waste treatment can be used. Taxes on incinerated wastes from the former process provided an incentive for development of this NGET.

23 Nearly 85 percent of all dry cleaners use perchloroethylene as the solvent in their process. See Footnote 4.
Significant environmental benefits come, as a number of cases indicate, when NGETs are developed for fine chemicals or pharmaceuticals. This is readily understood from the work of Roger A. Sheldon, chemistry professor at Delft University in the Netherlands. He developed the “E-factor” measuring the efficiency of chemical processes—the ratio of chemical waste to intended product (see Table A8). Sheldon found that commodity chemicals have an E-factor of between 1 and 5, while for fine chemicals the ratio is between 5 and greater than 50, and for pharmaceuticals 25 and greater than 100.

Security Occupational Safety and Health Benefits

NGETs provide health and safety benefits for workers in chemical and related production plants. Although the chemical industry has an excellent safety record, NGETs, to the extent that they reduce the need for toxic or otherwise dangerous materials during production, may reduce undue worker exposure. Many of the new processes, by operating at lower temperatures and pressures than conventional synthetic processes, can reduce further the dangers from potential accidents. The safe production of end-use chemicals provides one area of risk reduction. A second is the production and manufacturing of new benign materials that pose fewer health and safety risks altogether. Many compounds produced today are known to cause problems to the users. For example, while the health and safety risks of producing the pesticides used in agriculture are relatively low, the application of pesticides poses an acute hazard to hundreds of thousands of farm workers, particularly in developing countries. The production of safer pesticides may reduce such problems.

NGETs also offer the workplace elimination of chlorine (Cases 8, 15, 24), chlorinated solvents (Cases 1, 4b, 4c), and ethylene oxide plus acrolein from the bio-based process for 1,3-propanediol, an intermediate for a new polyester (Case 4cc).

NGETs can also provide national security benefits. They can, for example, reduce U.S. dependence on critical materials (including oil and precious metals) from potentially unstable regions and reduce the hazards from chemical plants, storage facilities, and transport vehicles, eliminating potential targets for terrorists. Shortly after the September 11, 2001 attacks, EPA reported that at least 123 U.S. chemical plants contained enough chemicals to result in a million casualties in nearby communities if attacked. Sudden changes took place in the way businesses perceived their exposures to chemical catastrophes. As an example, the Blue Plains Wastewater

---


26 United Nations Environment Programme press release, February 21, 2002, www.unep.org. A committee of government-appointed experts concluded that three widely used pesticides and all forms of asbestos should be added to an international list of chemicals subject to trade controls.

27 James V. Grimaldi and Guy Gugliotta, “Chemical Plants Feared as Targets,” Washington Post, December 16, 2001, p. A1. In March 2003, the General Accounting Office released a report saying that the nation’s chemical plants have not undergone comprehensive security assessments and are still vulnerable. The country has 123 industrial plants that could release enough toxic gas to kill more than a million people in nearby areas, 700 that could kill 100,000 or more and 3,000 that endanger 10,000 or more (www.gao.gov/new.items/d03439.pdf).
Treatment Plant (Washington, D.C.) swapped its 90-ton railcars filled with toxic chlorine for safer sodium hypochlorite to reduce the risk. Proposed legislation also created new incentives to reduce the use of hazardous chemicals. Over the past year there has been considerable interest among policymakers in reducing the risks chemical facilities might pose as targets for potential terrorist attacks. Legislation proposed in the 107th Congress sought to prevent, control, and minimize the potential consequences of chemical releases by requiring firms to: (1) identify hazards that may result from an accidental or criminal release; (2) ensure safer design and maintenance of that source; and (3) minimize the consequences of any such release. The legislation did not directly encourage the long-term phase-out of dangerous chemicals. However, the costs of meeting the required security levels associated with some chemicals might cause the chemical industry to consider the use of less-risky chemical alternatives. Opponents of the legislation argued that additional oversight by the government could be costly and would not ensure safety. NGETs could provide a means to address security risks by removing the need to use and store some dangerous substances. Although Senate Bill 1602 was not enacted, such initiatives provide incentives for accelerating development of NGETs and related inherently safer processes.

One target chemical could be phosgene, a well-known chemical warfare agent that was used in World War I and is designated in several agency regulations as an acute hazardous substance. It can cause short-term irritation to the eyes, skin, and breathing passages. Repeated exposures can cause permanent lung damage. Accidents, spills, or terrorist attacks at sites using phosgene can affect surrounding areas. Reducing the use of phosgene can help reduce this security and occupational safety hazard. Alternative dimethyl carbonate (DMC) synthesis methods (Case 5) will displace large volumes of phosgene with materials such as methanol and urea, two relatively benign substitutes.

In some cases, process changes aimed at environmental improvement may have resulted in inherently less safe designs that introduce workers to greater health and safety risks. The Environment, Health and Safety Committee of the Royal Chemical Society points to the collection of vent discharge gases for incineration or for absorption, which resulted in explosions when the composition of the gases in the vent system entered the flammable range. Ashford examined eight cleaner technologies in the International Cleaner Production Information Clearinghouse. He found that four worsened occupational safety and health, and four could have been further improved to provide greater safety and health benefits. One of the cases that worsened safety and health, "rapeseed oil extraction by enzymes," is related to the Biodiesel Case 4uu. The message is

---

27 Senate Bill 1602, introduced by Sen. Jon Corzine (D-N.J.) and referred to as the Chemical Security Act of 2001, was not passed during the last session of Congress. It mandated programs in "inherently safer processes."
that process engineers must consider workers as part of the production process in designing NGET-based processes.

**Economic Benefits**

NGETs may provide economic benefits to firms and society at large by reducing the cost of meeting existing and future environmental and safety standards and security goals. In addition, firms may adopt NGETs in order to deploy new processes and offer new products that are economically beneficial to the firm in their own right, without consideration of their environmental, security, or health and safety benefits. This situation is particularly interesting because it suggests a potential for NGETs to play a broader role in environmental protection.

A good example is found in aluminum smelting. Energy accounts for approximately one-fourth of the costs to smelt aluminum. New inert anodes developed for aluminum smelting (Case 11) have enabled a reduction in the anode-cathode distance from 1.75 inches to 1 inch, in turn reducing the energy required for aluminum smelting by more than 25 percent. Potentially, this could translate into a U.S. energy savings of 6 trillion Btus annually by 2010, at a value of nearly $90 million per year. Environmental benefits resulting from this NGET include the elimination of carbon and fluorocarbon emissions as well as organic matter generated during anode manufacture and consumption, and the reduction of cyanide formation and dust emissions. In addition, nonenergy cost savings amount to $20 million per year. Test cells are operating in Europe and North America.

A novel synthesis of 4-aminodiphenylamine (4-ADPA) used in the production of rubber chemicals can replace previous processes that involve the chlorination of benzene (Case 24). The new process eliminates more than 70 percent of organic wastes and more than 90 percent of inorganic wastes and wastewater. Although societal demands to eliminate chlorine were a factor in the development of 4-ADPA, the process yields significant cost savings to Monsanto and Flexsys, the joint venture of Monsanto (now Solutia) and Akzo Nobel, the firms that have commercialized it.

Monsanto, in producing the environmentally benign, nonselective herbicide Roundup® (Case 25) replaced the synthetic route to the key intermediate disodium iminodiacetate with a copper-catalyzed reaction that eliminated the use of hydrogen cyanide and formaldehyde. This reduced the waste flow to biotreatment by 800 million gallons per year while reducing manufacturing costs by more than 40 percent. Additional savings are still possible.

The alternative synthetic process for ibuprofen (Case 2) provides another commercially viable example. This process uses hydrofluoric acid as a catalyst and achieves a 77 percent atom economy, as opposed to the 40 percent achieved using the traditional manufacturing process.  

---


The greater throughput requires less capital expenditure and generates less waste. This process was deployed by BASF in 1992 at one of the largest ibuprofen manufacturing facilities in the world, in Bishop, Texas, which produces 7 million pounds per year, nearly one-fourth of world’s supply. The new process helped eliminate nearly 8.2 million pounds of waste per year; adopting it for all ibuprofen production, displacing the other five routes, could help eliminate 25 million pounds of waste each year.

II. NGETs Can Eliminate the Use and Generation of Hazardous Substances at Little or No Additional Cost

NGETs fully manifest themselves as a new approach to environmental protection when they provide environmental or other societal benefits at little or no cost. In such cases, firms may adopt the new technologies without the need for regulations or other mandatory measures. Ideally, government policy would then only focus on the R&D and information dissemination policies that promote the supply of NGETs. We have just seen cases where some environmental benefits are delivered with a net economic benefit.

Additional cases show instances where NGETs provide environmental benefits at minimal or no additional cost. Such situations are, of course, not unprecedented. The United States’ 100-year decarbonization trend that has reduced the amount of CO₂ produced per unit GDP is largely a result of efficiency increases and fuel changes driven by economic forces. Nonetheless, NGETs offer the potential of extending such improvements to sectors where it has been lacking heretofore.

Many of the bioprocesses (Case 4) provide environmental benefits at little or no cost. Some products such as specific stereoisomers of vitamins, amino acids, fine chemicals, and pharmaceutical intermediates would be difficult or nearly impossible to synthesize by costly and inefficient traditional chemistry. Typical is the synthesis of Riboflavin or Vitamin B2 (Case 4a) which reduced gas emissions by 50 percent and water emissions by 66 percent while cutting operating costs in half. Eastman and Genencor have developed a one-step fermentation process for the ascorbic acid (vitamin C) intermediate 2-ketogluconic acid (Case 4bb), replacing a four-step conventional process and cutting plant investment in half. New biological processes helped a Chilean copper mine leach metals of value, such as copper, zinc, and cobalt, from a sulfide mineral (Case 4c). Bioleaching involves the use of bacteria, principally *Thiobacillus ferroxidans*, *Leptospirillum ferroxidans*, and certain thermophilic (high temperature) bacteria. During oxidation, bioleaching places copper (or the metals of interest) in the solution phase; the oxidation residues are then handled to maximize recovery of the solution (within the volume and solution grade constraints of downstream processes), and the solid residue is discarded. Operators claim that bioleaching has environmental and economic benefits not available in more conventional processing technologies such as roasters, smelters, and pressure autoclaves. Environmental

---

3 Most developed countries have shown a similar trend. Nonetheless, the economy has grown faster than carbon emissions per unit GDP have dropped, so total emissions have increased.
benefits include the generation of environmentally stable residues and the elimination of noxious gases and toxic effluents. Economic benefits include quicker and less-onerous environmental permit and reporting processes and simpler and safer operations. Bioleaching also allows smaller projects to be developed more economically.

Case 9 provides an example of NGETs that have helped eliminate some incompletely understood health and safety risks at an additional cost acceptable to the market. Until very recently, nearly all pressure-treated wood in the United States was preserved using chromated copper arsenate (CCA). CCA contains two known human carcinogens: hexavalent chromium and arsenic. While EPA has not concluded at this time that CCA-treated wood poses an undue risk, it is widely believed that reduced exposures to arsenic, which could be dislodged or leached from the wood, is desirable. Treated wood is used in decks, playground equipment, picnic tables, boardwalks, fencing, and landscaping, putting children especially at risk. Public concerns about arsenic in drinking water, the desire of consumers for more environmentally benign products, and potential new regulations have all stimulated interest in an NGET that can eliminate the need for CCA-treated wood. A new alternative wood preservative, alkaline copper quaternary (ACQ) provides the same level of protection as CCA against decay fungi and termites at a competitive cost. Unlike CCA, none of the components of ACQ (copper, dodecyl dimethyl ammonium chloride, or alkyl dimethyl benzyl ammonium chloride) are known to be carcinogens, and quaternary ammonium compounds have low mammalian toxicity. Other environmental benefits include reducing the use of arsenic in the United States by 90 percent and eliminating the use of 64 million pounds of hexavalent chromium, as well as eliminating hazardous waste generation as designated by the Resource Conservation and Recovery Act (RCRA) along with the problems of disposing of CCA-treated wood.

Advanced oil and gas exploration technologies (Case 7) provide an example of advances in material technology that offer environmental benefits at little or no cost. Improved drill bits have cut drilling times in half and reduced the time drilling rigs must be on site, and thus their environmental impact.

III. NGETs Are Adopted for a Wide Variety of Reasons

Firms adopt NGETs because these technologies may help lower costs; however, a lower cost may be a necessary but not sufficient condition for adoption. In many of our case studies, there was some specific reason, often idiosyncratic, that the technology was adopted or not adopted. This suggests that there is no single set of government policies that might speed or encourage a broad range of NGET.

In particular, it is not always sufficient for an NGET to provide environmental benefits at no cost. Firms have many demands on their investment capital. They cannot invest in every option that saves them money. Rather, they seek the opportunities that promise the highest rate of return. The case studies here suggest that the existence of NGETs themselves is rarely the driver of a firm’s decision to redesign its production processes. Firms instead may use available NGETs when they choose to upgrade or build new production facilities for other reasons. As a result, the
adoption rates and timing of investments in NGETs will often be driven by factors external to the quality and performance of the NGETs themselves.

For example, the new process for making ibuprofen (Case 2) was not developed until the expiration of the Boots Company patent, which opened the market to generic competition. The loss of the patent spurred the firm (eventually to be BASF) to consider new, more-efficient manufacturing processes, including "greener" processes to fend off the new competition.

Companies, either the ones with patented drugs or those seeking to enter the market, will develop options as a drug comes off patent. One important option is to lower production costs. This is done by process improvements or by moving production to lower cost sites, often in developing countries. NGETs can in some cases offer a different route to lower costs, as was the case in the manufacture of ibuprofen. Although 20 percent of ibuprofen supply comes from Shansun Chemicals and Drugs Ltd. in India, the green chemistry–based process has allowed BASF to maintain a market share while remaining in Texas.

Likewise, the decision by Ube Industries to develop an alternative process for synthesizing DMC (Case 5) was a business decision to move downstream in the value chain and to take advantage of the corporate expertise in nitrite chemistry and the availability of ammonia, a raw material for DMC synthesis. Because this process bypasses the use of phosgene, Ube Industries has also gained recognition as a leader in dealing with environmental, worker health, and safety issues. Should a market for DMC as a fuel additive develop, Ube Industries would also be able to capitalize on it through production at a recently constructed plant using its new synthetict process.

Governmental regulations and other efforts to promote the demand for environmental protection have played a role in advancing many NGETs. Firms can seek NGETs to lower the cost of meeting actual or anticipated regulations. Regulations can also speed the adoption of low- or no-cost NGETs because firms will invest in response to the timing of the government requirements. For instance, regulations have stimulated investments in NGETs to avoid the use of banned substances, such as the use of chlorine in pulp bleaching, or to reduce the cost of compliance with environmental and worker health and safety regulations. The desire of firms to cut tax payments, including, for example, those in 15 states on perchloroethylene emissions, may also lead to further NGET innovation. Recycling programs, take-back legislation, and recycled content standards also help to stimulate NGET markets. Some states have created incentives for NGET use; Nebraska and North Carolina, for example, provide incentives for dry cleaners to use the supercritical CO₂ process (Case 1). Taxes on incinerated wastes led Biochemie to develop a new route to an antibiotic intermediate (Case 4b). When use of chlorine was prohibited in the pulp and paper industry, various other oxidants were adopted (Cases 4m and 15), and when the storage of contaminated gypsum was prohibited in the Netherlands, Budel Zink adopted a bio-based zinc refining process (Case 4n).

38. Personal interview with Akazu Takahashi, Ube Industries, June 2002.
On occasion, the cost savings offered by NGETs may drive firms to invest in the absence of other external factors. For instance, volatility in the world sugar market created an incentive to seek domestic replacements for sucrose. Significant work on recombinant thermostable enzymes led eventually to the $3 billion high-fructose corn syrup industry (Case 4rr). Alternatively, an NGET may offer a firm the opportunity to enter new markets. For instance, Cargill-Dow invested $750 million to develop a family of biodegradable polymers based on lactic acid (Cases 4i and 20) to replace such materials as polystyrene and acrylics.

DuPont licensed the DeSimone technology to use liquid carbon dioxide (Case 1) rather than CFCs or water as the polymerization solvent for producing a number of Teflon® fluoropolymer products for reasons other than cost. 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.

IV. Barriers Are Significant

Economic models suggest that private firms often underinvest in the development of new technologies because they cannot capture the full benefits that accrue from such research. The knowledge they generate might be useful copied or extended by other firms, benefiting society but not sufficiently helping the originating firm. In practice, firms will also fail to invest in some new technologies that would clearly save them money. In many cases a firm may have existing capital stock that, while more expensive to operate, costs less overall than new technology primarily because of sunk capital. In addition, firms focus their scarce investment resources on technologies central to their core business strategy, often those expected to give them the highest rate of return. Thus, it is often insufficient for an NGET to merely save money for a firm; the technology must make the firm more money than some other competing investment.1

Some NGETs promise significant benefits, but many have to date found only limited commercial applications, in niche or smaller markets. Societal benefits will be limited until they can be diffused more widely. Many studies have addressed barriers to the adoption of new environmental technologies. For instance, the Environment, Health and Safety Committee of the Royal Society of Chemistry provided one recent summary of the barriers to developing green chemistry: (1) the lack of global harmonization on environmental regulations; (2) rigid notification and authorization processes hindering new product and process development; (3) need for speed and certainty of results caused by short-term planning; (4) economics—the green chemistry approach may be more costly, though this is not invariably the case; (5) accounting practices which do not consider all costs; (6) difficulty in getting research funding; (7) insufficient guidance on best practice for green chemistry; (8) the low profile of more sustainable chemistry in schools

---

and universities; and (9) a culture geared to looking at the product itself rather than the overall process and life cycle. 38

We observed many of these barriers and others in the case studies. Four types of barriers were especially evident in the cases:

1. Need for additional research, technology development, or process engineering

In nearly all instances when a technology is initially developed and then commercialized, additional research or technology improvements will be needed to gain or maintain competitive advantage. Two competing groups, Cool Clean Technologies and Global Technologies, are introducing dry-cleaning systems using liquid carbon dioxide (Case 1), and each seeks to improve the economics and the performance of the washing systems, especially the surfactants.

DuPont is piloting a bio-based process for 1,3-propanediol (Case 4cc). While doing this, the firm is using a chemical-based process to supply enough diol to react with terephthalic acid and commercialize Sorona® polypropylene terephthalate [PPT, or poly(3-GT)]. Both chemical engineering and metabolic engineering efforts are required to continue the scale-up of the bio-based process. In some situations a significant barrier may be in the gaining of resources or funding to do such additional research or development.

There will be instances when research on an NGET conducted in a university or government lab is not continued by or transferred to an industrial laboratory. The firm may not want to allocate R&D funds to the development; it may feel that even though the technology is promising, the risk is too great versus other R&D targets; or it may feel the technology is still untested. Case 4w, the bio-based process for adipic acid is one example. In some situations, promising research on NGETs fails to receive federal funding. Some argue that priorities for environmental research often fall below those for research in the life sciences or other research funded by numerous agencies through congressional appropriation committees. 39 There is no coordinated effort, for example, to eliminate the top volume pollutants; the emissions come from many different firms, each with its own control mechanisms, related economics, and incentives for research, with no coordinated federal effort to tackle such major common problems.

2. Need to surmount infrastructure and integration barriers

Solutia (formerly Monsanto) plans to use by-product nitrous oxide from the adipic acid process to manufacture phenol (Case 21), but matching the output of the two processes becomes a challenge. When quantities of nitrous oxide are limiting, other routes to phenol or other sources of nitrous oxide must be found; this could greatly affect the economics of the phenol process. Startup of this process has been delayed, indicating the extent of these barriers.

38Note on Green Chemistry Version: 5 April 02, www.rsc.org.
39This was a major topic of discussion at the Workshop on the Environment, one of the NRC workshops on “Challenges for the Chemical Sciences in the 21st Century” November 17–19, 2002, Irvine, Calif.; proceedings forthcoming.
Systemic barriers have also limited NGET diffusion for the depolymerization of recycled plastics, particularly polyethylene terephthalate (PET) and nylon 6 (Case 3). About 750 million pounds of PET are used in the United States each year, particularly for soft-drink bottles and other food containers. Nylon is prevalent in carpeting and is increasingly used in automobiles, but its use results in large amounts of currently nonrecyclable carpeting “fluff.” One key hurdle to plastics recycling is the difficulty in separating the different components of the waste stream so that they can compete with virgin materials. At present, only a small fraction of plastics is returned to high-grade uses. The rest is used for low-grade applications and does not replace much raw material. The lower cost of virgin materials in particular can limit NGETs for plastics recycling. A joint venture of DSM Chemicals and Honeywell International to depolymerize recycled carpeting and produce 100 million pounds of caprolactam each year from 200 million pounds of recycled carpet, shut down after two years of operation when plummeting prices for virgin nylon made operation of the plant uneconomical.

This failure indicates some of the problems NGETs often face when moving beyond recycling markets or niche markets in general. It is difficult to compete in commodity markets dominated by large existing producers where prices can fluctuate strongly. NGET plastics recycling also relies on a less certain source of supply than that of its competitors using virgin material, who typically buy from a small number of large petroleum firms. In boom times, it is straightforward to quickly garner the supplies needed to expand production. In contrast, plants such as Evergreen (for nylon 6 recycle) rely on a diffuse network of households and commercial office buildings willing to deliver their old carpets. While Evergreen suffers along with its larger competitors during periods of low prices, it cannot as easily scale up its needed raw materials when boom times offer large profits to increased production.

3. Need to make the up-front investment

The use of CO₂ as a solvent in the dry-cleaning industry also requires higher up-front capital costs and specially trained operators. While the operating costs of the new technology may be lower and the payback periods are similar, the CO₂ machines are twice as expensive as the traditional machines that use perchloroethylene. These significant up-front costs pose a barrier to its use. Working with supercritical carbon dioxide necessitates lower temperatures and higher pressures that go beyond the capacity of normal dry-cleaning machines. Special care is also needed to prevent the release during cleaning of large quantities of CO₂ which can inhibit breathing by machinery operators.⁹⁰

4. Regulatory barriers

While regulations can stimulate NGETs, the design and implementation of regulations can often hinder implementation of NGET-based processes. When strict timetables are required to meet new emission limits, there is little incentive to develop a greener process. DuPont manufactures phosgene at its Chambers Works plant in New Jersey. The New Jersey EPA placed strict

⁹⁰This demonstrates that green chemistry may introduce other hazards to be faced.
requirements on carbon tetrachloride emissions which would require a $2 million incinerator. Negotiations led to an extension of two years. In that time, work on new catalysts reduced emissions to less than the required level while promising to reduce the emissions ultimately to zero.\textsuperscript{4}\textsuperscript{4} Such regulatory flexibility is not always forthcoming.

The way in which patents are enforced greatly impacts the incentive to develop new routes to an "active pharmaceutical ingredient" (API). As we saw in Case 2, the incentive for developing the new route to ibuprofen was the expiration of the fundamental product patent. In parts of Europe, companies cannot develop generic versions of brand-name products that still have patent protection. In the United States, however, because of the Hatch-Waxman Act, manufacturers of an API can develop a new route before the patent has expired.\textsuperscript{4}\textsuperscript{4} Thirty-five blockbuster drugs are coming off patent between now and 2007. The combined sales of $82 billion for these 35 can create incentives for process research. For example, the patent protection for Zocor, Merck's cholesterol-lowering drug (annual sales of nearly $7 billion), expires in 2005. Hovine in Portugal has teamed with a Korean firm to develop a fermentation process to supply the API to displace Merck.\textsuperscript{4}\textsuperscript{5}


\textsuperscript{5}Rouhi, 2002, pp. 46-48.
Longer-Term Opportunities for NGETs

In addition to the important but limited near-term benefits noted above, NGETs have the potential to provide broad and significant benefits over the coming decades, through further development, greater diffusion, and the introduction of new applications. It is of course difficult to estimate with accuracy the long-term benefits offered by advances in technology, particularly when effective application involves adoption by firms in competitive markets. When policymakers consider the role new technologies can play in helping to achieve long-term goals, it is useful to present a range of possibilities. In this report we provide indications of these possibilities.

Over the long-term, NGETs and green chemistry offer many promises, including substantial reductions in the environmental footprint of many chemical processes, improvements in the health and safety of those exposed to chemicals, and enhanced security at facilities with hazardous materials. These and other benefits of NGETs will arise from a combination of technology innovation and investments in new processes. The case studies suggest a range of paths that environmentally friendly chemistries will follow as they make their way into the marketplace. Some paths emphasize market pull. Demand for new environmental processes, driven either by regulation or societal pressure, will spur the development and deployment of NGETs. Demand pull need not generate new research; often well-known technology can be used in new applications. In paths emphasizing technology push, new research or new applications demonstrated in one area may suggest other applications where a potential need was previously unrecognized or seemed impossible to address effectively. The combination of demand pull and technology push will create the long-term opportunities offered by NGETs.

Responding to Societal Demand Through New Processes and New Chemicals

In many cases, known and sometimes long-standing environmental and other problems can be addressed by new science and technology or novel applications of known technology. Our case studies show a wide variety of NGETs developed in response to new regulations or other pressures signaling a societal demand for new levels of environmental performance. Many of these have significant longer-term possibilities.

As has been noted, the chemicals and allied products industry (SIC code 28) is responsible for more than 600 million pounds of waste included in the TRI compiled by EPA. Many of these

4For a discussion of the types of information about unpredictable technology futures that can be most useful to policymakers, see Lempert and Schlesinger, “Adaptive Strategies for Climate Change,” in Watts, 2002, p. 468.

4See “Toxics Release Inventory (TRI) Program.”
chemicals are manufactured with processes that utilize older synthetic pathways fine-tuned over many years without significant consideration given to environmental impacts. Our case studies demonstrate that in some cases NGETs, often applying existing science, can prove more cost effective than even these older highly optimized processes. The new synthetic pathway used by BHC to manufacture ibuprofen (Case 2) provides the most well-known example.

In the future, an NGET that eliminated phosgene from the creation of DMC could have broad benefits (Case 5). By reducing the environmental as well as the economic costs of phosgene in the synthesis, such an NGET might enable DMC's use in a variety of synthetic processes as a methylating agent, replacing less environmentally friendly reagents such as methyl chloride and dimethylsulfate. The potential substitution of DMC for phosgene in the synthesis of polyurethanes, polyamides, and polycarbonates, processes that account for more than 90 percent of the demand for phosgene, could result in an expanded market for DMC, thus lowering its cost while significantly reducing the demand for phosgene with its attendant hazards. In this case, environmental benefits occur both when a new nontoxic biodegradable chemical (DMC) is produced and when it is used in the synthesis of other products.

The fuel additive market provides another example of the potentially dramatic benefits of substituting greener chemicals for others currently in common use. When used as a fuel additive, DMC has a higher oxygen content than methyl tertiary-butyl ether and is less toxic and biodegradable. However, at present, DMC suffers from a prohibitively higher cost. If technology can reduce these costs through a new greener synthetic procedure, DMC could reduce CO, NOx, VOCs, and particulates beyond the levels with existing fuel additives.

NGETs might also provide broad, long-term benefits by enabling use of new environmentally friendly refrigerants in response to the push to rid the environment of CFCs. Case 18 suggests that new compounds are available to reduce energy use substantially through more efficient, environmentally friendly refrigerants. Such compounds could potentially remove the CFCs and recently developed CFC alternatives currently used in refrigeration while at the same time increasing the efficiency of refrigeration and thus reducing the use of energy. Reductions in energy use for refrigeration obviously constitute an additional benefit to the environment.

Other NGETs based on greener paths to hydrogen peroxide and hydrogen peroxide activation could potentially replace the use of chlorine in the pulp and paper industry (Case 15). This industry currently bleaches pulp with a five-step process alternating with different oxidants. \( \text{H}_2\text{O}_2 \) has the potential to replace some of the steps in the process that use \( \text{Cl}_2 \). But \( \text{H}_2\text{O}_2 \) alone cannot

---


6It can be argued that a more economical process for the production of DMC would provide many of the same benefits regardless of the environmental implications. However, in this case, the marginal costs of DMC may be driven indirectly by health and safety and the public sentiment against storing phosgene associated with DMC production. Finding a greener synthetic pathway that obviates the need for phosgene is the only way to produce a chemical that costs less than phosgene and hence can compete in some of those markets.
replace ClO₃ in the final steps. Case 15a suggests that the activation of H₂O₂ with the use of a chelated iron compound can make the use of hydrogen peroxide more efficient and competitive with the ClO₃-based process. The societal interest in the removal of chlorine from the bleaching process has spurred new interest in using small molecule activation by inorganic catalysts. If successful, these NGETs could remove the chlorine from circulation and thus the toxic chemicals resulting from its use. To capture many of these long-term benefits, new inorganic catalysts need to be tailored to the specific hydrogen peroxide applications.

A better and cheaper synthesis of H₂O₂ (Case 6) could have important spillover effects for a host of industries. Such greener oxidants would benefit the pulp and paper industry as well as the chemicals industry, where demand has grown steadily over the decade. For example, the demand for H₂O₂ as an oxidant in printed circuit board etching and semiconductor manufacturing and in wastewater treatment has increased substantially in recent years. Water purification (Case 8) highlights the need and potential for displacing the chlorine currently used in 98 percent of all water treatment plants. More than 13 million pounds of chlorine are currently used in water purification, posing not only health risks but security risks as well.

Replacing current processes in competitive markets can of course be difficult even with NGETs based on well-understood science. For instance, the chemistry for returning polymers to monomers has been known for quite some time. In principle, this technology could significantly enhance the level of plastics recycling (Case 3) and could yield broad social benefits. The rubber and plastic industry accounts for nearly 100 million pounds of waste, of which more than 99 percent is emitted to the atmosphere. Increased recycling could reduce the amount of virgin materials used by the chemicals industry to supply the rubber industry. Landfills could also be reduced. Carpets for example, account for nearly 1 percent of all landfill, or more than 4 billion pounds of nonbiodegradable annual waste consisting largely of potentially recyclable polymers. However, NGETs for returning this waste to monomers that can serve as raw materials to the rubber and plastics industry have been unable to compete in the marketplace because of the large price swings and significant investment needs of commodity markets for raw materials. In particular, firms can find virgin raw materials a preferred source of supply because of ready availability even in times of increased demand.

Opening New Green Pathways—Addressing Uncertain Problems with NGETs

In addition to situations where known societal problems spur the application of NGETs, there are also many cases where new green chemistries offer the promise of preventing potential environmental problems that have not yet been identified or risen to the level of a serious problem. Research in significant areas such as catalysis and biotechnology can suggest

---

Footnotes:

86 Information on the product stewardship program for carpets from the EPA can be found at http://www.epa.gov/epaanswer/non-hw/reduce/epr/products/carpet.html.
unexpected environmental, health and safety, and security benefits. The use of supercritical carbon dioxide as solvent (Case 1), genetically modified enzymes as effective biocatalysts (Case 4), or nucleophilic aromatic substitution for hydrogen (NASH) (Case 24) all provide examples. The long-term benefits of such new solvents, reagents, and reaction conditions may provide substantial environmental, security, and health and safety benefits and avoid a range of heretofore unrecognized problems. In many of these cases, significant research remains to be done before these benefits can be fully realized.

As one important example, organic solvents are used across many industries for precision cleaning, medical device fabrication, and the dry cleaning of garments. These industries use more than 30 billion pounds of halogenated and other organic solvents per year. Some of the environmental impacts of solvents are well known. Solvent use in general is a leader in the TRI, and solvents comprise eight of the top ten TRI chemicals that are sent off site for remediation (Table 3). The worldwide solvent market has been in decline for some time because of the restrictions on many of the more popular VOCs and chlorinated products. While the markets for oxygenated solvents have seen recent expansion, especially in the Far East, other areas of solvent use have been curtailed. Regulatory pressures on VOCs in general, and specifically on those used in paints and coatings, will constrain these solvent markets. Nonetheless, not all potential impacts of solvent use are known with confidence. For instance, some of the solvents in the TRI list are not necessarily toxic nor do they pose serious immediate environmental risks. However, because such large volumes of these chemicals are used across industries, the effects of the combined releases are not completely understood.

---


Table 3. Top ten chemicals transferred off site for further waste management

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Sum of Total Transferred Off Site for Further Waste Management (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>46,438,705</td>
</tr>
<tr>
<td>Toluene</td>
<td>29,932,942</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>21,046,481</td>
</tr>
<tr>
<td>Xylene (mixed isomers)</td>
<td>18,338,223</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>13,311,876</td>
</tr>
<tr>
<td>Nitrate compounds</td>
<td>10,356,824</td>
</tr>
<tr>
<td>Styrene</td>
<td>9,562,186</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>9,018,540</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>8,266,837</td>
</tr>
<tr>
<td>N-Hexane</td>
<td>7,468,617</td>
</tr>
</tbody>
</table>

The general principles of green chemistry call not only for removing the toxic and dangerous compounds from syntheses but also for reducing the total amount of compounds released into the environment regardless of the toxicity, as a hedge against unknown effects. To that end, several new technologies offer promising alternatives, including the aqueous biphasic systems and room temperature ionic liquids highlighted in Cases 16 and 17. Supercritical carbon dioxide has the potential to develop into a useful solvent to replace some of the TRI chemicals. Carbon dioxide has unique characteristics as a solvent, but a variety of technical barriers must first be overcome for it to be used ever more broadly. For example, carbon dioxide has a wide range of potential applications, but each application requires a good understanding of the ideal pressures and temperatures that can be used for specific solute. Firms must invest in research to determine the optimal conditions for each case. Carbon dioxide will become more pervasive as each new success encourages other firms to explore the technology.

The movement of synthesis toward better control of smaller molecules through catalysis is a common theme among many of our case studies and is an area of technology development with the potential for substantial long-term environmental implications. Both the safer production processes and potential markets of DMC and H₂O₂ provide examples. For instance, new iron catalysts (Case 15a) will activate the small molecules of H₂O₂ to provide the oxidation potential needed to bleach wood pulp. Without the catalysts, the hydrogen peroxide may not be able to reach the same levels of bleaching power as conventional chlorine-based bleaching. Many of the iron catalysts under development as activators mimic the type of biological processes found in
nature, where natural enzymes activate hydrogen peroxide for use in oxidation reactions (Case 4m). Developing technologies to exploit natural processes may provide far-reaching environmental implications.

The development of better synthetic pathways has increasingly exploited the spillover of biological concepts into chemical science and engineering. The bioprocesses highlighted in this study were developed with the hope of moving closer to what biological systems do well—manipulating a relatively small number of starting materials (e.g., O₂, N₂, CO₂) and transforming them into a multitude of complex compounds. Many of the toxicity, health and safety issues, and environmental problems associated with current synthetic pathways stem from the complex starting materials and intermediate compounds produced throughout a synthetic pathway. Starting with simple and easily found materials, such as those already present in the atmosphere—N₂, O₂, CO₂—and manipulating them in single steps into complex compounds may enable the atom economy necessary to decouple society’s chemical processes from environmental impacts. Moving from the complex starting materials and simple reactions to simple starting materials and complex, highly specific reactions may afford the renewable feedstocks and reduced footprint necessary to ensure that the environmental, security, and health and safety risks can be reduced.

Bioprocesses highlighted in this report have shown promise as greener synthetic pathways (Case 4). The benefits stem from the complex reactions that biological systems are efficient at performing compared with conventional chemical technologies. Bioprocesses reduce energy use, quantities of feedstocks, and the amount of waste generated compared with alternative nonbiologically driven processes. Regulatory pressures have promoted the use of biobleaching and biopulping in the pulp and paper industry for environmental reasons, and advances in biocatalysis (especially in enzyme development) have significantly increased yields and the economics of many processes. Bioprocesses have also enabled the manufacture of many chemicals and pharmaceuticals previously very difficult to produce while leading to reduced waste and improved economics. Enzyme developer Maxispan believes that $50 billion of the $800 billion global commodity, specialty, and fine chemical markets are readily addressable by bioprocesses. It also says that another $200 billion has been identified as potentially addressable by biological approaches in the next 10 to 20 years. Much of the research performed to date on bioprocesses is now more readily distinguished as part of the cadre of NGET tools. The reduced energy requirements, specificity of reactions, and benign reagents typically involved may address the inherent problems with traditional synthetic pathways.

Conclusions and Observations

This section presents conclusions based on our case study results and observations based on the analyses of barriers.

NGETs Can Provide Benefits in All Areas Studied

NGETs have the potential to make a significant contribution to a new approach to environmental protection. NGETs represent an important class of pollution prevention technology that redesigns products and processes at the molecular level to reduce or eliminate the use of hazardous materials. Our case studies demonstrate that NGETs have already provided a wide range of environmental, security, health and safety, and economic benefits. In some cases, NGETs can provide these benefits for no additional cost or even at a lower cost compared with today’s practices. And because NGETs are relatively new technologies, they may help policymakers ensure environmental quality with less reliance on costly regulations as they mature.

The nation’s economy increasingly relies on a wide variety of chemical products and processes. Progress in slowing the use of potentially hazardous substances has not kept pace with other positive environmental trends over the past 30 years. Finding new ways to ensure that needed chemicals pose no or little risk requires new thinking into the means by which they are produced and employed. Over the past decade, green chemistry, an important source of NGETs, has begun to provide alternatives to chemicals that are known to be dangerous or to potentially pose risks. The case studies suggest that green chemistry technologies also have potential to expand beyond their current niches and provide significant long-term benefits spanning the four areas highlighted in this study. NGETs may help eliminate emissions from broad classes of chemicals through inventive solvent choices; toxic reagents may be nearly completely displaced by an environmentally benign alternative; the security risks of dangerous chemicals may be avoided through the creation and adoption of less hazardous alternatives; and synthetic processes may be more readily adapted to take into consideration environmental concerns.

NGETs Can Address Uncertainties

In addition to addressing currently known risks, NGETs can also help address those that are imperfectly understood. The principles of green chemistry guide scientists and engineers toward processes that intrinsically embody more of the process inputs in the final product and thus are more efficient and generate less waste. Such principles can eliminate potential environmental problems before they arise.
Firms Adopt NGETs for a Number of Different Reasons

Driven by technology push alone, however, NGETs are unlikely to reach their full potential. The case studies demonstrate that firms adopt NGETs for many reasons, ranging from business decisions to pursue new production processes or product lines to the need to respond to regulatory pressures. Firms adopt NGETs because they are the most cost-effective means to meet some particular end. In each firm, however, NGETs must compete for resources with a host of other investment opportunities. To garner scarce investment dollars, it is rarely sufficient for a new technology to merely save the firm money. It must be among the options that move the firm most aggressively toward its corporate goals.

Policymakers Face a Number of Challenges

This report made no attempt to assess the need for or the types of policies the federal government might implement in response to the potential offered by NGETs and the barriers to their implementation. Nonetheless, the report suggests several observations about potential policy actions.

A number of different types of government policies can help NGETs reach their full potential. One such policy area is that of information dissemination. Our case studies suggest that there are important spillovers across and among different areas of green chemistry. Applications of broad processes such as biocatalysis in bioprocessing in one area may suggest applications in another. When a firm develops some new product or process, it does not generally scan the full range of possibilities but rather tends to scan a more narrow range close to current practice. In part, research and design is expensive, so innovators will focus the majority of their efforts on those design choices where they expect to find promising answers. Publicizing the scientific principles and successful applications of green chemistry may cause firms to guide their internal research toward innovations that become NGETs. Examples of such information dissemination policies include partnerships involving industry to develop environmentally benign processes, such as those with the Department of Energy’s (DOE’s) Office of Industrial Technologies; awards programs such as EPA’s Presidential Green Chemistry Challenge Awards; fellowships and other funding for green chemistry at the nation’s universities; and encouraging the work of professional, scientific, and engineering societies in education and training related to green chemistry.

The government also has an important role to play in supporting basic research. New areas of chemistry and other sciences, still in their relative infancy, may lead to significant changes in a vast number of processes across the economy. Basic research may help to unlock their potential. At present the federal government funds a range of research potentially relevant to NGETs such as the EPA/NSF (National Science Foundation) Technology for a Sustainable Environment program. (See Appendix B for a list of examples of federal policies that can affect the development and adoption of NGETs.) Additional relevant programs have been proposed. The
National Coalition for Advanced Manufacturing\textsuperscript{55} has called for a three-year, $5 billion basic manufacturing science and technology initiative, which includes research on manufacturing technologies for energy efficiency and environmental quality. We have not made an attempt to survey what the government is funding relevant to NGETs and then to assess this funding against the most promising avenues and areas of greatest need. Such a complete survey of federal funding is difficult to do given the diverse funding sources, the variety of programs and objectives, and the uncertainty that energy, life sciences, or chemical engineering programs will result in green chemistry or NGET advances.\textsuperscript{56}

Finally, the widespread diffusion of NGETs may require policymakers to also address demand pull by providing appropriate incentives for the adoption of NGETs. Crafting such incentives will be an important challenge. On one hand, NGETs present policymakers with questions common to environmental policy. For instance, NGETs may diffuse relatively slowly if internal cost savings are the only incentive the firms have to adopt them. Policymakers will need to determine whether the potential benefits of NGETs warrant other incentives to speed their adoption. However, there are opportunity costs to encouraging firms to allocate their capital and technical personnel to develop NGETs. Resources spent on such pursuits are not available to develop other products and processes. Policymakers will need therefore to gauge what level and type of effort seems appropriate to further the development of NGETs. Should the approach be technology push or demand pull, fund research, increase the extent of regulation, or some combination?

There are also some areas where NGETs pose particular challenges. These include the focus on process technology, the uncertainty of future process applications, and the extent to which technology spillovers broaden the adoption of new manufacturing processes. For example, the focus on process technology is often invisible to consumers and thus relatively decoupled from any emerging market demand for cleaner products. Many government policies also focus on industrial products rather than processes that produce them. For instance, the EPA premanufacture notices (PMN) required of chemical manufacturers focus on the potential toxicity and hazards of new products rather than the greenness of the process by which they will be made.\textsuperscript{57}

NGETs also present policymakers with a problem of information asymmetry. There are a vast number of products and processes for which the adoption of NGETs might provide important environmental, security, safety, and economic benefits. Only firms have the information that can allow them to discover which products and processes offer the most gains from NGETs. But society as a whole may reap a large fraction of the gains from such applications. Some of these benefits come through reducing risks that are presently imperfectly understood or that seem too

\textsuperscript{55}www.naciam.org

\textsuperscript{56}However, in discussions with the Office of Science and Technology Policy (on March 26, 2002) we estimated that green chemistry federal funding was most likely in the $20–100 million range with all manufacturing technologies about $100 million (database at www.imit21.org/); industrial R&D related to NGETs might be 1 percent of chemical R&D or $260 million per year.

\textsuperscript{57}EPA had for a short period provided advice to PMN submitters on ways the processes could be made more environmentally benign; discussion with Richard Engler, EPA, December 3, 2002.
costly to control. Clearly, policymakers should not threaten to regulate in every area where NGETs might provide some benefits, but many potential benefits may remain undiscovered without some expression of societal demand. Thus, policymakers must devise means to appropriately enable and encourage chemists, chemical engineers, and other potential innovators to explore the effective new scientific tools at their disposal and bring them to bear most effectively on the array of applications for NGETs.
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. 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. 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.

\[^{1}\text{Articles and books in the Green Chemistry General Reference Annotated Bibliography (http://center.acs.org/applications/greencem or www.chemistry.org/education/greencem) discuss the chemistry of many of these cases.}\]

\[^{2}\text{EPA’s Presidential Green Chemistry Challenge Awards represent a significant effort in publicizing green chemistry-based technologies and helping developers of some technologies recognize that they are indeed members of the green chemistry community.}\]
<table>
<thead>
<tr>
<th>Case Number</th>
<th>Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Supercritical or Liquid CO₂ as Solvent</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Ibuprofen Synthesis</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>Recycling for PET and Nylon: Converting Polymers to Monomers</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>Bio-Based Processes</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>Dimethyl Carbonate</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>Production of Hydrogen Peroxide (H₂O₂) Directly from Hydrogen and Oxygen</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>Advanced Oil and Gas Exploration and Production Technology</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>Approaches to Water Purification</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>Wood Preservation</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>Sentricon® Termite Colony Elimination System</td>
<td>71</td>
</tr>
<tr>
<td>11</td>
<td>Inert Anodes in Aluminum Smelting</td>
<td>73</td>
</tr>
<tr>
<td>12</td>
<td>Process for Production of Cytovene® Potent Antiviral Agent</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>High-Yield Melting of Aluminum</td>
<td>77</td>
</tr>
<tr>
<td>14</td>
<td>Elimination of Ozone-Depleting Chemicals in the Printed Wire Board and</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Electronic Assembly and Test Processes</td>
<td></td>
</tr>
<tr>
<td>15a</td>
<td>Delignification and Bleaching of Pulp in Paper Manufacture Without the Use</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>of Chlorine or Chlorine Dioxide</td>
<td></td>
</tr>
<tr>
<td>15b</td>
<td>Trees to Paper Using Air in Place of Sulfur and Chlorine</td>
<td>81</td>
</tr>
<tr>
<td>15c</td>
<td>TAML™ Oxidant Activators for Hydrogen Peroxide</td>
<td>82</td>
</tr>
<tr>
<td>16</td>
<td>Aqueous Biphasic Systems for Liquid-Liquid Extractions</td>
<td>83</td>
</tr>
<tr>
<td>17</td>
<td>Room Temperature Ionic Liquids</td>
<td>86</td>
</tr>
<tr>
<td>18</td>
<td>Environmentally Friendly Refrigerants: New Refrigeration Processes</td>
<td>90</td>
</tr>
<tr>
<td>19</td>
<td>Clean Diesel Breakthrough with Compact Advanced Polymer Membrane</td>
<td>99</td>
</tr>
<tr>
<td>20</td>
<td>Biodegradable Polymers</td>
<td>102</td>
</tr>
<tr>
<td>21</td>
<td>Capture of Nitrous Oxide in Adipic Acid Manufacture to Use in New Phenol</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>Process</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Advanced Oxidation Process for the Metal Casting Industry</td>
<td>109</td>
</tr>
<tr>
<td>23</td>
<td>Fluoroaromatics via Copper (II) Fluoride Chemistry</td>
<td>112</td>
</tr>
<tr>
<td>24</td>
<td>Synthesis of 4-aminodiphenylamine</td>
<td>114</td>
</tr>
<tr>
<td>25</td>
<td>Synthesis of Glyphosate</td>
<td>116</td>
</tr>
</tbody>
</table>
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.³

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:³⁴

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

---


• Reduce quantity needed

4. Alternative synthetic transformations
  • Additions are good:
    \[ A + BC \rightarrow ABC \]
  • Substitutions are not so good:
    \[ AB + BC \rightarrow AC + BD \]
  • Eliminations are probably the worst:
    \[ AB \rightarrow A + B \]

5. Selection of solvents and reaction conditions
  • Five of the top ten chemicals released are solvents (methanol, toluene, xylene, methyl ethyl ketone, and MeCl₂), 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.

<table>
<thead>
<tr>
<th>Green Chemistry Area → Benefit</th>
<th>Alternative Feedstocks</th>
<th>Natural Processes; Biocatalysis, Fermentation</th>
<th>Alternative Reagents; Improved Catalysis</th>
<th>Alternative Synthetic Pathway</th>
<th>Alternative Solvent or Reaction Condition</th>
<th>Selection of Products and the Design of Safer Chemicals</th>
<th>Minimize Energy Consumption</th>
</tr>
</thead>
</table>
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.

<table>
<thead>
<tr>
<th>Green Chemistry Area → Industry</th>
<th>Alternative Feedstocks</th>
<th>Natural Processes, Biocatalysis, Fermentation</th>
<th>Alternative Reagents; Improved Catalysis</th>
<th>Alternative Synthetic Pathway</th>
<th>Alternative Solvent or Reaction Condition</th>
<th>Selection of Products and the Design of Safer Chemicals</th>
<th>Minimize Energy Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Mining</td>
<td></td>
<td>4-n,y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric, Oil, Gas, and Sanitary Services</td>
<td></td>
<td>4-q,s</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Chemicals and Allied Products (pharmaceuticals)</td>
<td>4-c,d,e,f,g,h,p</td>
<td>3,4,5,7,11,12</td>
<td>10,12</td>
<td>2,5,21,23,24,25</td>
<td>1,16,17</td>
<td>9,18,20</td>
<td></td>
</tr>
<tr>
<td>Primary Metals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>Paper and Allied Products</td>
<td></td>
<td>4-m</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Food and Kindred Products</td>
<td></td>
<td>4-a,j,k,r,dd,ff,hh,ii,ij,kk,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>mm,oo,qq,rr,ss</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. Supercritical or Liquid CO₂ 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 CO₂ is about 1,100 pounds per square inch (psi), and the critical temperature is about 31 degrees C. Supercritical applications using CO₂ 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, CO₂ has properties between those of a liquid and a gas, particularly a lack of surface tension. This means supercritical CO₂ (SCCO₂) 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. SCCO₂ now is being used in many separation and cleaning applications.⁶⁷⁸

Carbon dioxide is just beginning to be used in the dry-cleaning industry. There are still few machines (60 from Micell by 2001) using SCCO₂ 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 SCCO₂ 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.⁹

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 CO₂ and other technologies. Using SCCO₂ in dry cleaning, for example, results in a net increase of energy use owing to the power needed for equipment to generate liquid CO₂. We consider these issues in the use of CO₂ 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.

---

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. 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 CO₂ 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. 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 CO₂ compounds soluble for such cleaning applications.

These cleaning additives may have to be specially formulated for use with liquid CO₂. Surfactants designed by Joseph M. DeSimone, for example, have increased the solubility of various materials for

---

polymerizing fluoromonomers. The following table summarizes the characteristics of CO₂ and other cleaning solvents.

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

**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 CO₂ 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.

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.

---


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, 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 CO₂ cleaning technology (although these estimates of current releases will be

Figure A1. Comparison of a Model Facility’s Emissions of PCE (SCCO₂ = supercritical carbon dioxide; CA = carbon absorber; RC = refrigerated condenser)\(^{16,17}\)

---


\(^{17}\)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).²⁹

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.³¹ 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 nation³² and targeted for cleanup.³³ 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 CO₂ emissions to the atmosphere, as CO₂ is stable, nontoxic, unreactive, and can be produced from renewable resources.

**Commercializing Firms**

Two competing dry-cleaning systems have been developed. Applying CO₂ 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-cleansing technology developed by Raytheon has now been applied to dry cleaning.³⁴ 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.³⁵ 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 CO₂ challenge the entrenched position of hydrocarbons and PCE in the dry-cleaning solvents market. Washpoint combines liquid CO₂ with an

---

³⁴Including Alliance Laundry Systems, largest commercial laundry company in North America; Chart Applied Technologies, division of world's largest cryogenic equipment manufacturer: Electrolux Vascator, 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® system, a dry-cleaning process and manufacturing equipment that use liquid CO₂ just below ambient temperature (or 18 to 22 degrees C) and vapor pressure (or approximately 50 millibars). Micell adapted the basic research on CO₂ 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 CO₂ technology ranging from electronics to metal cleaning.

A process using liquid CO₂ is being developed for fabric cleaning. Liquid CO₂ appears to be adequate for dry-cleaning garments; ongoing research is examining all the capabilities of dry cleaning with liquid CO₂.

Other commercial applications of CO₂ 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.26 Researchers at Sandia National Laboratory have reported the cost for large-scale manufacturers to convert to a “no-clean” process using CO₂ technology would be about $25,000 but result in savings of $100,000 to $200,000 per year.”

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.27

Incentives to Adopt

Tightening environmental regulations and fluctuating petroleum costs provide incentives for adopting CO₂ 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.

---

**Government Role**

Beyond the environmental regulations noted above, governmental bodies affect the use of dry-cleaning technologies and the adoption of CO₂ 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 CO₂ 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 CO₂ in chip manufacturing cleaners received the R&D [Research and Development] 100 Awards Programs in 2001.

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 CO₂ 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. Two states also have incentives for dry cleaners to purchase equipment using liquid CO₂ technology. 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 CO₂ 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 CO₂ does not escape during cleaning. Although CO₂ is relatively nontoxic and unreactive, large quantities of the gas can inhibit the ability of an operator to breathe. Second, typical detergents used

---

in conventional dry cleaning do not work in a liquid CO₂ 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).”

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 CO₂ 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 SCCO₂.

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 (MeCl₂), 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 CO₂ rather than a volatile organic compound
such as MeCl₂ used to extract the caffeine.

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

Replacing any methods using volatile organic compounds such as MeCl₂ with those using SCCO₂ would
have an immediate beneficial environmental impact.

---

32 According to Laidlaw Corp., they have stopped producing these detergents. Additional information available at
www.laidlawcorp.com. Other participants in the Global Technologies group such as Caled, however, are producing the surfactants.
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.34

Incentives to Adopt

A significant marketing or economic incentive for using SCCO₂ is the fact that CO₂ decaffeination produces more flavorful coffee products. Carbon dioxide, unlike organic compounds, does not lead to residual aftertastes and bitterness when used for decaffeination. Using SCCO₂ 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 SCCO₂ for decaffeination are European Union regulations that first limited MeCl₂ residue to 2 parts per million in decaffeinated coffee and now ban the solvent in decaffeination altogether. There are no such restrictions for CO₂ (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 CO₂ 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.

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:

- 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® 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.™

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.

---


™Carbonell, “CO2-Based Technologies.”
Fahlman\textsuperscript{7} 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.

\textit{Long-Term Environmental Significance}

Using CO\textsubscript{2} 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\textsubscript{2}, used in this process can be extracted from and released back into the air with no net addition of it to the atmosphere.

\textit{Commercializing Firm}

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


**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

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 synthesis was a six-step process that used AlCl₃ 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:

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.

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).

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.

---

6) 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-isobutylphénylacetonitrile 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. ⁴ Acylation of IBB with propionyl chloride gives isobutypropiophenone. Halogenation with copper bromide gives 2-bromo-4-isobutypropiophenone. 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-isobutyacetophenone, which is then converted to 3-methyl-3-(p-isobutylphenyl)glycidenitrile 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”⁴⁴ and utilized the most “cost effective manufacturing process” for ibuprofen. It is not known which of these processes is used in its operation, but the firm holds improvement patents related to route D⁴ 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.”

---

Figure A2. Routes to Ibuprofen. (Dubeck and Searns, 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. This process uses hydrogen fluoride rather than AlCl₃, 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 AlCl₃ 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 AlCl₃, 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

---

*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 AlCl₃ 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

The processes for recycling plastics can be challenging. Polymers 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 Petretex 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

---

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. 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).

---

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-nomer” 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 Petretic process and the barriers:

**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.

---

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 sp2-hybridized carbon), isomerases (for
isomerization), and ligases (for forming carbon-oxygen, carbon-sulfur, carbon-nitrogen, carbon-carbon, and phosphoric ester bonds).\textsuperscript{51}

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:\textsuperscript{52}

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.


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.

\section*{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

---

\textsuperscript{51}See http://us.expasy.org/enzyme.

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 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 H₂S 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 comparing enzyme pulp bleaching with elemental chlorine free (ECF) bleaching found a 16 percent reduction in carcinogens as well as 12 percent

---


54 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.
reduction in heavy metals in conjunction with the kraft process. The study 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. 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.

e. Total waste

---


• 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 hydralases)\(^{(5)}\) 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\(_2\)S is generated on-site by the bacteria rather than being transported and stored.

c. Reduced energy use

• 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:
  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-
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.

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.\(^1\)

- Of the three processes for refining gold—roasting, pressure oxidation, and bacterial oxidation\(^2\)—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\(^3\) sees the development of efficient “biorefineries” (Example 4vv)\(^4\) that could replace petrochemical refineries throughout the 21st century and produce current petrochemicals plus many other products that oil refineries cannot—food, 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.\(^5\)


\(^{5}\)This 48th example is not included in the count of examples because a biorefinery represents many of the 47 examples.

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. 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. Significant barriers are evident.

---

66DuPont 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).

Table A5. Needed Investments in Bio-Based Processes.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td></td>
<td>3,658</td>
<td>1,350</td>
</tr>
<tr>
<td>Acetone</td>
<td>7</td>
<td>2,462</td>
<td>1,221</td>
</tr>
<tr>
<td>Butanol</td>
<td></td>
<td>1,328</td>
<td>1,157</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td></td>
<td>424</td>
<td>230</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>11</td>
<td>556</td>
<td>484</td>
</tr>
<tr>
<td>Isopropanol</td>
<td></td>
<td>1,236</td>
<td>1,084</td>
</tr>
<tr>
<td>Butanediol</td>
<td></td>
<td>200</td>
<td>196</td>
</tr>
<tr>
<td>Adipic acid</td>
<td></td>
<td>760</td>
<td>230</td>
</tr>
<tr>
<td>Lactic acid</td>
<td></td>
<td>10,063</td>
<td>2,208</td>
</tr>
</tbody>
</table>

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."

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.

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.

---


<table>
<thead>
<tr>
<th>Example 4-</th>
<th>Product/Description</th>
<th>Development Stage</th>
<th>Benefits—Primary and Secondary</th>
<th>Details</th>
<th>Industry-Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Riboflavin (Vitamin B2) Fermentation of glucose</td>
<td>Commercial—Hoffmann La Roche</td>
<td>1. economic 2. environmental</td>
<td>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.</td>
<td>Food 1</td>
</tr>
<tr>
<td>b</td>
<td>7-Amino-cephalosporanic acid (antibiotic intermediate); involves reactions using two enzymes</td>
<td>Commercial—Biochemie (Novartia)</td>
<td>1. environmental 2. economic 3. health/safety</td>
<td>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.</td>
<td>Medicine 1</td>
</tr>
<tr>
<td>c</td>
<td>Cephalxin (antibiotic) four-step process; fermentation followed enzymatic reactions; further reduction in steps anticipated</td>
<td>Commercial—DSM</td>
<td>1. economic 2. environmental</td>
<td>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).</td>
<td>Medicine 1</td>
</tr>
<tr>
<td>d</td>
<td>Amino acids—use immobilized enzymes,</td>
<td>Commercial—Tanabe</td>
<td>1. economic</td>
<td>International amino acid markets were completely</td>
<td>Medicine</td>
</tr>
<tr>
<td></td>
<td>continuous process replaced batch enzymatic process</td>
<td>(Japan) (see comment in column 5)</td>
<td>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.</td>
<td>food, animal feed 1</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------------------------------------------</td>
<td>-----------------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>S-Chloropropionic acid (CPA) (agricultural intermediate); racemic CPA enzymatically dechlorinated R-enantiomer only; S-CPA isolated by solvent extraction; development of enzyme was critical</td>
<td>Commercial—Avecia</td>
<td>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.</td>
<td>Agrochem 1</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>Acrylamide; reaction of acrylonitrile with nitrile hydratase enzyme (immobilized whole cell catalyst)</td>
<td>Commercial—20,000 metric tons Mitsubishi Rayon</td>
<td>Replaces copper catalyzed reaction that produces range of by-products, both processes produce only minor amounts of waste; energy savings for new process.</td>
<td>Chemicals (water treatment) 1,8</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>Ammonium acrylate; acrylonitrile hydrolyzed by nitrilase to ammonium acrylate</td>
<td>Demonstration—Ciba (not to be commercialized)</td>
<td>Replaced sulfuric acid hydrolysis, reducing hazards and wastes; but neutralization of purchased acrylic acid became favored route.</td>
<td>Chemicals (water treatment) 1</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>Polyesters; diols and diacids polycondensation with lipase enzyme</td>
<td>Demonstration—Baxenden</td>
<td>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.</td>
<td>Potential: Adhesives 1</td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>Polylactic acid; fermentation of dextrose gives two chiral isomers of lactic acid; chemically cracked to form three lactide</td>
<td>Commercial—Cargill Dow</td>
<td>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</td>
<td>Chemicals, plastics, fibers</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 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. |
| 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. |
| 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. |
| 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. |

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.
<table>
<thead>
<tr>
<th>n</th>
<th>Zinc, refining, roasting, oxidation</th>
<th>Commercial—Budel Zink (Netherlands),</th>
<th>1. environmental</th>
<th>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.</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>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 H2S to precipitate heavy metals as sulfides that can be recycled from the waste streams to the process</td>
<td>Commercial—Billiton, others</td>
<td>1. environmental, 2. safety, 3. economics</td>
<td>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 (As2O3 and SO2); 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.</td>
</tr>
<tr>
<td>p</td>
<td>Ethanol from biomass; fermentation of biomass rather than corn</td>
<td>Demonstration—Iogen; research, Purdue</td>
<td>1. environmental (potential)</td>
<td>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.</td>
</tr>
<tr>
<td>q</td>
<td>Oil-well completion; enzymes to remove filter cake</td>
<td>Commercial demonstration—BP Exploration</td>
<td>1. economics, 2. environmental</td>
<td>Little benefit in using nondamaging drilling muds if the chemicals used to remove their residue (&quot;break&quot; the polymers in the filter cake) damage lifetime productivity of the well. Enzymes replace acids and oxidizing agents; may need</td>
</tr>
</tbody>
</table>

Fuels

1.2(1998)
<table>
<thead>
<tr>
<th>Column</th>
<th>Description</th>
<th>Institution/Source</th>
<th>Benefit</th>
<th>Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>Using enzymes in large-scale organic reactions: oligosaccharides (and complex carbohydrates for clinical evaluation);</td>
<td>Research—Scripps Research Institute</td>
<td>Enables syntheses of materials not available by other routes.</td>
<td>Food</td>
</tr>
<tr>
<td></td>
<td>hydroxy compounds, and novel monosaccharides</td>
<td></td>
<td></td>
<td>2(1999)</td>
</tr>
<tr>
<td>s</td>
<td>Bioconversion of CO₂ to chemicals; converts waste power carbon dioxide into</td>
<td>Research; University of Cincinnati</td>
<td>More than 98 percent removal efficiency was achieved for carbon dioxide from a typical coal fired power plant stack gas effluent.</td>
<td>Fuels</td>
</tr>
<tr>
<td></td>
<td>algae then fermented into a variety of organic feedstocks—methane and acetic</td>
<td></td>
<td></td>
<td>2(1999)</td>
</tr>
<tr>
<td></td>
<td>acid. A marine algae is used in a photobioreactor using light-emitting diodes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>with a wavelength of 68 nm and gas residence time of 3 seconds at ambient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>temperatures and pressures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>Cross-linked enzyme crystals, formulation of enzymes in cross-linked</td>
<td>Pilot plant—Altus Biologics</td>
<td>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.</td>
<td>Chemicals</td>
</tr>
<tr>
<td></td>
<td>crystalline form</td>
<td></td>
<td></td>
<td>2(1997)</td>
</tr>
<tr>
<td>u</td>
<td>p-hydroxybenzoate contacting an active cell mass with toluene that is</td>
<td>Research—North Carolina State</td>
<td>Replaces two-step carboxylation of phenol, reduces generation of waste by-products; nuld reaction conditions for safety to human health and the environment.</td>
<td>Chemicals</td>
</tr>
<tr>
<td></td>
<td>transformed through a series of intracellular enzymatic reactions</td>
<td></td>
<td></td>
<td>2(1999)</td>
</tr>
<tr>
<td>v</td>
<td>Polyhydroxyalkanoates in green plants; studying the transformation of plants</td>
<td>Research—Monsanto</td>
<td>Potential biodegradable plastics; poly(beta-hydroxybutyrate-co-beta-hydroxyvalerate (PHBV) is currently produced by fermentation of the</td>
<td>Chemicals</td>
</tr>
<tr>
<td></td>
<td>with four separate transgenes and a novel</td>
<td></td>
<td></td>
<td>2(1999), 3</td>
</tr>
<tr>
<td>Cell</td>
<td>Application</td>
<td>Location</td>
<td>Environmental</td>
<td>Economic</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>----------</td>
<td>----------------</td>
<td>----------</td>
</tr>
<tr>
<td>w</td>
<td>Adipic acid; glucose to cis,cis-muconic acid with a single genetically engineered microbe; hydrogenation gives adipic acid; catechol also synthesized</td>
<td>Research—Michigan State</td>
<td>1. environmental (potential)</td>
<td>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.</td>
</tr>
<tr>
<td>x</td>
<td>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</td>
<td>Commercial—DuPont</td>
<td>1. economics</td>
<td>The bioprocess gave 99 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.</td>
</tr>
<tr>
<td>y</td>
<td>Lead mine water treatment; sulfate reducing bacteria produce hydrogen sulfide and precipitate metals from the mine water, also removes nitrates</td>
<td>Commercial—Asarco</td>
<td>1. environmental</td>
<td>No chemicals used; no sludge produced; water quality standards met.</td>
</tr>
<tr>
<td>z</td>
<td>Acetic acid</td>
<td>Commercial</td>
<td>1. economics</td>
<td>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.</td>
</tr>
</tbody>
</table>

A-47-
<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
<th>Research/Source</th>
<th>Development/Factors</th>
<th>Notes</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>bb</td>
<td>Ascorbic acid (vitamin C)</td>
<td>Pilot plant—Eastman/Genencor</td>
<td>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.</td>
<td></td>
<td>Chemicals 1</td>
</tr>
<tr>
<td>cc</td>
<td>1,3-propanediol</td>
<td>Pilot plant—DuPont</td>
<td>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.</td>
<td></td>
<td>Chemicals, Fibers 1</td>
</tr>
<tr>
<td>dd</td>
<td>Nicotinamide (Vitamin B3)</td>
<td>Commercial—Lonza Guangzhou Fine Chemicals (China)</td>
<td>Chemoenzymatic process: 2-methyl-1,5-diaminopentane is converted to 3-methyl pyridine, then ammoxidized and resulting 3-cyanopyridine is hydrolyzed to nicotinamide using immobilized Rhodococcus rhodochrous J1 cells (acrylonitrile catalyst).</td>
<td></td>
<td>Food 7,8</td>
</tr>
<tr>
<td>ee</td>
<td>Terephthalic acid and isophthalic acid</td>
<td>Research—DuPont</td>
<td>Process described in U.S. Patent 6187569.</td>
<td></td>
<td>Chemicals 8</td>
</tr>
<tr>
<td>ff</td>
<td>Aspartame</td>
<td>Commercial—600 metric tons</td>
<td>Included in table of reference.</td>
<td></td>
<td>Food 7</td>
</tr>
<tr>
<td>gg</td>
<td>6-aminopenicillanic acid</td>
<td>Commercial—6,000 metric tons</td>
<td>Included in table of reference.</td>
<td></td>
<td>Medicine 7</td>
</tr>
<tr>
<td></td>
<td>Ingredient</td>
<td>Quantity</td>
<td>Category</td>
<td>Notes</td>
<td>Page</td>
</tr>
<tr>
<td>---</td>
<td>-----------------------------------</td>
<td>-----------------------</td>
<td>-----------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>hh</td>
<td>L-lysine</td>
<td>280,000 metric tons; $700 million, 7 percent/year growth; improvements by Degussa</td>
<td>1. economics</td>
<td>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.</td>
<td>7</td>
</tr>
<tr>
<td>ii</td>
<td>L-threonine/L-methionine</td>
<td>10,000/200 metric tons</td>
<td>1. economics</td>
<td>Included in table of reference.</td>
<td>7</td>
</tr>
<tr>
<td>jj</td>
<td>Roundup Ready® Soybeans, Corn, Cotton</td>
<td>Major business for Monsanto</td>
<td>1. economics</td>
<td>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.</td>
<td>12</td>
</tr>
<tr>
<td>kk</td>
<td>Vitamin B-12</td>
<td>12 metric tons</td>
<td>1. economics</td>
<td>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.</td>
<td>7</td>
</tr>
<tr>
<td>ll</td>
<td>Vitamin C (see bb for improvements)</td>
<td>70,000 metric tons</td>
<td>1. economics</td>
<td>Included in table of reference.</td>
<td>7</td>
</tr>
<tr>
<td>mnn</td>
<td>Vitamin F</td>
<td>1,000 metric tons</td>
<td>1. economics</td>
<td>Included in table of reference.</td>
<td>7</td>
</tr>
<tr>
<td>nn</td>
<td>D-p-hydroxyphenyl glycine</td>
<td>3,000 metric tons</td>
<td>1. economics</td>
<td>Included in table of reference.</td>
<td>7</td>
</tr>
</tbody>
</table>
| pp | 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 Aspergillus niger. | 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 produced from renewable feedstocks. | Chemicals 3 |
| 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) |

References
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. 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. Producing DMC from methanol, carbon monoxide, molecular oxygen, and cuprous

---


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."

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."

The CDTech patent application for producing DMC notes that it could replace halogenated solvents such as chlorobenzene,” 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

---

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). 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 NO₂ emissions more than ethanol. DMC could also be used to convert natural gas to a liquid transportation fuel.

Commercializing Firms

Patent activity on DMC has increased in recent years. Most address copper chloride catalysts. 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.

In 1983, EriChin 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.

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. Ube developed a catalyst that increases the production efficiency of DMC. This process maintains a high level of catalyst activity for a long period of time under mild reaction conditions. 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. 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. 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

---

81 Personal interview with Akazu Takahashi, Ube Industries, June 2002.
82 “Ube Bares Low-Cost Catalyst for DMC,” Japan Chemical Week, March 28, 1996, p. 3.
85 “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. 

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 CDTeX 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. “

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

**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

---

Technology Development Organization have helped to publicize the benefits and applications of the Nippon GE and Ube Industries work.
6. Production of Hydrogen Peroxide ($H_2O_2$) 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. 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.

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.

---

88 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.

89 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 autooxidation 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." 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.\(^9\)

---

\(^9\) [http://sbir.er.doc.gov/sbir/Awards_AbSTRACTS/sbirstr/cycle19/phase1/172.htm](http://sbir.er.doc.gov/sbir/Awards_AbSTRACTS/sbirstr/cycle19/phase1/172.htm).

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

<table>
<thead>
<tr>
<th>Unit</th>
<th>Traditional AQ Process</th>
<th>Novel Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Description</td>
<td>CO₂ Solvent</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>Working solution hydrogenated over palladium catalyst in three-phase reactor (solid catalyst, liquid solution, gaseous hydrogen)</td>
<td>No AQ used.</td>
</tr>
<tr>
<td>(AQ + H₂ → AQH₂)</td>
<td></td>
<td>Issue is catalyst robustness.</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Anthrahydroqui-none oxidized in two-phase reactor without catalyst</td>
<td>No AQ used.</td>
</tr>
<tr>
<td>(AQH₂ + O₂ → AQ + H₂O₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extraction</td>
<td>H₂O₂ stripped from organics into water in countercurrent column</td>
<td>Cross-contamination of aqueous and organic phases; H₂O₂ must be further purified</td>
</tr>
<tr>
<td>Drying</td>
<td>Vacuum distillation (several in series, depending on concentration desired)</td>
<td>Large capital cost, energy cost, safety issues; most industrial processes do not require such high concentration.</td>
</tr>
</tbody>
</table>
Commercializing Firm

Most procedures for direct synthesis of \( \text{H}_2\text{O}_2 \) 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. BASF and Solvay recently announced a joint venture for a PO plant that will use in-situ direct synthesis of \( \text{H}_2\text{O}_2 \). Direct synthesis of \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) 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.

By enabling industrial production of hydrogen peroxide at the site it is used, alternative methods may reduce manufacturing and distribution costs. 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 \( \text{H}_2\text{O}_2 \) 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

---

93 Personal communication with Prof. Eric Beckman, University of Pittsburgh, July 18, 2002; Jeff Gendler, Hydrocarbon Technologies, Inc., July 19, 2002; and Ray Ballew, Hydrocarbon Technologies, Inc.
eliminate dioxin and furan formation in pulp and paper effluent. This environmental benefit, however, is currently offset by the fact that H₂O₂ 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 H₂O₂ 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.⁷

**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.⁸ 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.

---


⁸ 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 to see if any qualified as NGETs. No mention was made of the concept of green chemistry. Three technologies were selected. All were in the drilling and completion processes, and all involved chemistry.

Chemistry

Improved drill bits. 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.

---


100The complete list of technologies: Drilling and completion: (a) CO2 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.

Advanced synthetic drilling fluids. 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. 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, CO₂-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.

---

102 DOE, Office of Fossil Energy, p. 40; note also Case 4, Example 4-q.
103 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 Bricor® 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, 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. 104

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. 105 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. 106

3. The Eka Chemicals process to produce ClO₂ from NaClO₃ and H₂O₂ obviates the need for gaseous or liquid chlorine feeds and chloride ion addition. It also reduces byproduct chlorine production, thereby reducing the formation of trihalomethanes and chloroform disinfection by-products. 107

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.

104. etdl.libl.gov/sep/archive/uv[0]/.
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.

**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.

---

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. 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.

---

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

In the 1980s the electrowinning of aluminum involved the electrolysis of a cryolite-alumina (NaAlF₄ + Al₂O₃) melt using a carbon anode and an aluminum cathode to yield aluminum: 2 Al₂O₃ + 3C gives 4Al + 3 CO₂ and by-products from the cryolite. 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 NiO-NiFe₂O₄-Cu and the cathode with TiB₂-Al₂O₃.

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

References:
The Aluminum Association Inc. in conjunction with DOE, "Inert Anode Roadmap" February 1998, prepared by Nancy Margolis and Jack Eisenhauer, Energetics Inc., Columbia, Md.
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 (CF₃ and CF₂); 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® 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

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.

\[\text{Garry B. Semoes, Sam L. Nguyen, J. D. Yuen-Kweil Han, Eric Lodewijk, and George Schloemer, "The Development of an Environmentally Friendly, Cost Effective Process for the Production of Cytovene® Antiviral Agent," prepared for presentation at the 2000 Spring AIChE Meeting, Atlanta, Ga., March 5-10; available at www.aspentech.com/publication_files/AICHE2000.pdf; also described in U.S. Patent 5,565,565.}\]
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®) and ganciclovir monovalinate (Cymeven®).115

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” 2000.116

115 Described in U.S. Patent 5,567,816 and Application No. 09/127,380, now allowed.
13. High-Yield Melting of Aluminum

In alliance with Praxair, Alcoa is testing High-Yield Melting. 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.

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

Chemistry

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.

---

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 (H₂O₂) and ozone (O₃), 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

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 ClO₂-based process. (EPA banned the use of Cl₂ 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.

References:


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

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) O₂ is added, and the same polyoxometalate catalyzes the complete conversion (mineralization) of the dissolved lignin fragments to CO₂ 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.

---

126 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 lead 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. 112

Immediate Environmental and Economic Impacts

As discussed in 15a and 15b above.

---

112 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. 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.

---

Aqueous biphasic systems were first discovered in 1896 by Beijerinck, who noticed the formation of two phases upon mixing agar with gelatin. 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 non-denaturing 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. 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. 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$_4$ from simulated Hanford waste tanks. 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.

---

123http://www.sbu.ac.uk/water/biphasic.html.
124Private communication with Robin Rogers, October 25, 2002.
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.177

<table>
<thead>
<tr>
<th>Industry</th>
<th>Production (tons/year)</th>
<th>E-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Refining</td>
<td>$10^8$–$10^{10}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Bulk Chemicals</td>
<td>$10^4$–$10^6$</td>
<td>1–5</td>
</tr>
<tr>
<td>Fine Chemicals</td>
<td>$10^3$–$10^4$</td>
<td>5–50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10^1$–$10^3$</td>
<td>25–100</td>
</tr>
</tbody>
</table>

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.

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, 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. According to Rogers, 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.

---

126 http://www.ch.qub.ac.uk/resources/ionic/ionic.html.
128 http://bama.ua.edu/~rdrogers/webdocs/ionicliquids.html.
129 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. 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) has commercialized an ionic liquid process (DIFASOL) for the conversion of butene into isoctane. Solvent Innovation and Sachem have also reported commercialization efforts for RTILs.

Chemical Week reported:

Solvant 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.

Solvant 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-methylimidazolium 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).

133 http://quill.qub.ac.uk/pdf/ti.pdf.
136 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.

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. 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. Of particular interest to the refrigeration community today is the phase-out schedule of the relatively more benign 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.

---

1 Some industrial refrigerators utilize absorption or steam jet cycles. *Perry's Chemical Engineers' Handbook*, 1997, p. 11–76.
2 A Class I Substance has an ozone depletion potential of 0.2 or higher.
3 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®, 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®, 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 species cycle to refrigeration was revived by researchers at Global Cooling, who used a free-piston design. 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

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

Refrigerant Replacement

Ikon B is a 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. 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, CO₂ emissions would be down by 4 million tons per year, particulates down 12 thousand tons, NO, down 16,000, and sulfur dioxide down 24,000.\textsuperscript{112}

\textsuperscript{111} Environmental Technology and Education Center: http://www.etec-nm.com/library/ikonbcut.htm.

\textsuperscript{112} 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. 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, 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).

---

143 Private communication with David Berkowitz, September 27, 2002.
144 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. 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. 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.

---

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\textsubscript{x}) 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\textsubscript{x} levels. Conventional strategies for reducing NO\textsubscript{x}, such as exhaust gas recirculation and retarded injection timing, increase particulate emissions. Spark ignition engines have catalytic converters that can handle NO\textsubscript{x} levels, but diesel engines contain high levels of oxygen and particulates that limit the effectiveness of catalytic NO\textsubscript{x} reduction to nitrogen and oxygen.

Researchers at Argonne National Laboratory have developed a process for reducing NO\textsubscript{x} and particulate emissions\textsuperscript{137} 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\textsubscript{x}. 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.

\textsuperscript{137}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\textsubscript{x} emissions by 15 percent while increasing gross engine power by 18 percent.\textsuperscript{18} 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.\textsuperscript{18}

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


\textsuperscript{19} 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. 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. 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.

---

186 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."

187 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

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

Three representative materials are:

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

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™

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™ 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.

---

152 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.

---

Barriers™

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.

---

10. Sentricon® 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.

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.

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,\textsuperscript{186} nitrous oxide (N\textsubscript{2}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).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure-a3.png}
\caption{Industrial N\textsubscript{2}O Emissions from the U.S. Industrial Sector.}
\end{figure}

\textsuperscript{186}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 N₂O 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 N₂O 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 process developed by Solutia may reduce the cost of producing adipic acid by 20 percent¹⁵⁶ and N₂O emissions by 90 to 98 percent.¹⁵⁷

Long-Term Environmental Benefits

While N₂O 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).¹⁵⁷ 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

---


¹⁵⁷These forecasts assume a rate of capacity growth of 3 percent per year and N₂O 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. 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 N₂O is sent to a captive phenol
plant producing at low cost, which would produce low-cost feedstock for the adipic acid plant.

**Government Role**

During the 1990s, manufacturers implemented N₂O controls because of EPA regulations.

---

140 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

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. Cannon says at least one foundry using the process has

\[1\text{http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/2177/report/0; http://www.oit.doe.gov/metalcast/environmental.shtml.}\]
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.¹⁰²

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.¹⁰³ 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.

¹⁰² es.epa.gov/ncer_abstracts/grants/01/sustain/cannon.html.
¹⁰³ Private communication with Professor Fred Cannon, October 24, 2002.
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 NaBF₄ and NaCl. Some efforts have been made to increase the atom economy of fluorobenzene synthesis so as to reduce waste.

Chemistry

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:

\[ \text{M–F} + \text{C–H} \rightarrow \text{M–F} \rightarrow \text{C–F} + \text{HF} \]

\[ 2\text{HF} + \text{O}_2 + \text{M–F}_x \rightarrow \text{M–F}_x \]

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 NaBF₄ and NaCl, while producing it through the use of HF rather than fluoroboric acid results in waste HCl or NaF and NH₄F salts. Using alternative methods for synthesizing fluorobenzene would eliminate the production of these wastes.

---

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 H₂O 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

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.

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)iminodiacetic acid or N-(phosphonomethylglycine)] is the active ingredient in Roundup®, the world’s best selling herbicide, introduced in 1976 by Monsanto. 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

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 PCI, and formaldehyde to give N-(phosphonomethyl)diminodiacetic 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.

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-NHCH₂COOH) 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

---

107 Monsanto has 370 issued patents, 1996–2002, related to the preparation and use of glyphosate and the genetically modified plants that tolerate Roundup.
109 See 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:

<table>
<thead>
<tr>
<th>Resource</th>
<th>Annual Reductions for 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam, Btus</td>
<td>880 billion</td>
</tr>
<tr>
<td>Demineralized water, gallons</td>
<td>380 million</td>
</tr>
</tbody>
</table>

**Waste**

<table>
<thead>
<tr>
<th>Resource</th>
<th>Annual Reductions for 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow to biotreatment, gallons</td>
<td>800 million</td>
</tr>
<tr>
<td>SARA 313 deep well injection, lbs</td>
<td>52,000</td>
</tr>
<tr>
<td>Biosludge, lbs</td>
<td>8 million</td>
</tr>
<tr>
<td>Solid waste to landfill, lbs</td>
<td>1.4 million</td>
</tr>
<tr>
<td>SARA 313 air emissions, lbs</td>
<td>17,600</td>
</tr>
<tr>
<td>Carbon dioxide emissions, lbs</td>
<td>100 million</td>
</tr>
</tbody>
</table>

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.
Appendix B

Government Policies and Increased Adoption of NGETs
The mechanisms through which government policy can affect the rate of adoption of Next Generation Environmental Technologies fall into four broad categories:

1. Direct funding and/or performance of research and development activities.

2. Economic incentives, including both tax incentives and subsidies.

3. Information dissemination, including direct dissemination, industry consultations, and voluntary programs.

4. Infrastructure support, including direct investment in infrastructure, creating an appropriate institutional environment, and education and training.

Government policies intended to affect adoption rates will generally include elements from more than one category. Particular mechanisms will be more or less appropriate as technologies mature.¹⁷⁹

Policy options, some examples of these policies that have affected NGETs, and a number of issues related to the use of these policies are summarized in the following table.

### Table B1. Policy Options Affecting NGETs.

<table>
<thead>
<tr>
<th>Policy or Action</th>
<th>Intended Effects</th>
<th>Examples</th>
<th>Issues Associated with Policy Success</th>
</tr>
</thead>
<tbody>
<tr>
<td>Funding R&amp;D</td>
<td>Enhance scientific understanding that can lead to new technologies.</td>
<td>1. NSF Center at University of North Carolina/North Carolina State.</td>
<td>1. Level of federal funding vs. other initiatives may be insufficient.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. DOE’s support to develop a biorefinery.</td>
<td>2. Little coordination between funding agencies or focus.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. DOE’s Office of Industrial Technologies.</td>
<td>3. Multidisciplinary efforts receive less funding.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. EPA/NSF Technology for Sustainable Environment.</td>
<td>4. Responsibility for environmental R&amp;D is dispersed; no analogy: National Institutes of Health is to the FDA as X is to EPA.</td>
</tr>
<tr>
<td>Purchases/procurement</td>
<td>Provide early markets that can speed commercial development of new technologies.</td>
<td>Government purchases of “green” power or recycled materials.</td>
<td>Can be difficulty in defining that products and processes should be defined as “green.”</td>
</tr>
<tr>
<td>Tax incentives/disincentives</td>
<td>Provide market signal to help firms internalize costs of hazards, encourage new investment.</td>
<td>1. Landfill costs.</td>
<td>A targeted approach difficult to use for promoting NGETs in general; can be difficult to set and/or adjust appropriate tax levels; can distort efficient economy.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Depreciation rules favoring certain types of investment.</td>
<td></td>
</tr>
</tbody>
</table>

---

171 Most examples are found throughout the case studies in Appendix A.

<table>
<thead>
<tr>
<th>Subsidies</th>
<th>Encourage greater adoption of environmentally friendly processes.</th>
<th>Agricultural subsidies that encourage use of renewables (ethanol).</th>
<th>As with tax incentives, lobbying efforts for entrenched technologies may distort objective or make it difficult to encourage certain NGETs.</th>
</tr>
</thead>
</table>

| Regulations: workplace/ emissions/ products | Increase costs or eliminate processes and products that cause harm to the environment, workers, or those using a product. | 1. Various acts administered by EPA—from the Clean Air Act to Clean Water, Superfund, and TSCA; banning use of some chemicals in certain applications.  
2. Rules enacted by the Occupational Safety and Health Administration.  
3. Limits set by the FDA.  
4. Labeling requirements. | 1. Permit limits may not be tight enough to encourage development of new environmental benign or inherently safer process.  
2. Regulations may favor the established vs. the new process; hurdles for the new process.  
3. Products banned in one country may still be exported to others (tetraethyllead, various pesticides).  
4. Small and “nonpoint” sources are difficult to regulate and enforce.  
5. Targets are single chemicals or one work practice where harm comes from collective effects.  
6. Negotiations with regulators can lead to commitment to develop NGETs. |

| Patent law | Encourage investment in new technologies by | 1. Several statutes such as the 1980 Bayh-Dole Act allowing federally funded research to yield patents | 1. Process chemistry may be best protected as trade secrets; some process patents are more difficult to enforce than product patents. |
| Information dissemination | protecting firms’ intellectual property; can enable technology transfer of proprietary green chemistry. | for those doing the work—enabling intellectual property to be licensed to industry.  
2. Extensions or limitations on patent protection such as Waxman-Hatch Act. | 2. Intellectual property can be a barrier to wide diffusion of NGETs. |
|---------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
|                      | Encourage adoption by providing a wide range of technology and cost. Performance information on green chemistry–based technologies. | 1. EPA’s Presidential Green Chemistry Awards.  
2. Sponsoring conferences and workshops by EPA, DOE, and NSF.  
3. Sponsoring studies by National Research Council and others.  
4. Books, papers by government or academic scientists.  
5. Standard setting.  
7. Availability of Toxics Release Inventory with sources. | |
| Industry consultations | Encourage adoption of NGETs by industry by providing information on the cost and performance of new technologies. | 1. Government and academic scientists as consultants to various firms or industry associations.  
2. Nonprofit Zero Waste Alliance provides industry consultations. | Those in industry may not know they are “doing” green chemistry, may not call for assistance, or may not want to disclose proprietary information. |
| Voluntary programs | Encourage adoption through behavior change; perceptions of good citizenship. | 1. Recycling programs.  
2. Encourage nongovernmental standard setting.  
3. Encourage initiatives of associations: Responsible Care® (American Chemistry Council), Inherently Safer Processes (American Institute of Chemical Engineers).  
4. Firms publishing environmental annual reports with commitments on emissions, energy reductions.  
5. “Green consumerism” may promote voluntary actions. | 1. Backup of regulation or anticipation of future regulation may be an important driving force for voluntary programs.  
2. Programs may not be accepted broadly across an industry. |
|-------------------|---------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Infrastructure support and development | Enables diffusion through provision of necessary foundation. | 1. Establishment of recycling centers.  
2. Support for networks, user facilities at National Laboratories. | |
| Education and training | Accelerated diffusion by increased knowledge of principles and approaches of NGETS. | 1. Support for green chemistry programs at universities.  
2. Support for many workshops around the world. | Green chemistry programs in universities may be drawing more talent into the study of chemistry. |
Appendix C

Opportunities for Further Study: Additional Cases from First International Conference on Green & Sustainable Chemistry, Tokyo, March 2003
Introduction

The First International Conference on Green & Sustainable Chemistry was held March 13–15, 2003, at the Waseda University International Conference Center, Tokyo. During the conference a number of additional developments were discussed that either added information on cases we have studied or pointed to possible additional cases. There were also discussions in measuring the benefits of green and sustainable chemistry.

Information on Cases

Details are given in Table C1.

Measuring Benefits

At the conference there was also considerable discussion on measuring the benefits of green and sustainable chemistry, or the “metrics for green and sustainable chemistry” or metrics for sustainability.

We can measure the benefits of one process or chemistry at a time, as we have done in this report.

The pharmaceutical firm of GlaxoSmithKline (GSK) has identified a set of core “sustainability metrics”: mass, energy, toxic dispersion (greenhouse gas, toxicity, eutrophication, Total Organic Carbon, acidification, and ozone precursors), natural resource utilization (oil), solvents, “chemistry greenness,” and economics. Evaluation of GSK chemistries and processes using such metrics revealed:

- From an economic standpoint, yield remains a very good metric, especially for high value added materials such as pharmaceuticals, and exerts significantly more influence on cost than poor atom economy, at least in the short term.

- Atom economy may be useful as an organizing concept or in combination with other metrics, but at this time it is not considered to be useful as a standalone metric.

- Reaction mass efficiency combines key elements of chemistry (including atom economy) and process and represents a simple, objective, easily derived and understood metric for use by scientists and focuses attention away from waste toward the use of materials.

---

173 See Abstracts, The First International Conference on Green & Sustainable Chemistry, Green & Sustainable Chemistry Network Secretariat, Japan Chemical Innovation Institute, 1-3-5 Kanda Jinbo-cho, Chiyoda-ku, Tokyo 101-0051, Japan.
• Mass productivity is a good metric for businesses because it highlights resource utilization.

• It is important that we have “green processes,” not just “green chemistries,” and this will require the integration of technology and chemistry.

GSK has a range of tools on the company intranet to help researchers develop green processes and determine some of these metrics: a green chemistry guide, a fast life-cycle evaluation of synthetic routes, a materials selection guide (especially solvents), and a green packaging guide.

In Japan, the Green and Sustainable Chemistry (GSC) Network, in evaluating nominations for the Japanese GSC award, uses four categories: (1) energy consumption (or carbon dioxide emissions), (2) virgin resource consumption, (3) consumption of landfill sites, and (4) environmental emissions. These are plotted on a radar chart. 175

In making these measurements, one must consider to what extent are they relative. Do we consider the process the green process is actually replacing, or for a new product do we consider a hypothetical alternative process based on traditional chemistry that would never be commercialized for a variety of reasons?

Eventually one might sum the benefits over all newly installed processes to get the total impact of green chemistry on the environment and society. Alternatively we can measure the decrease in overall emissions, reduction in energy use, waste reduction, reduced hazard chemical storage, and increased use of renewable feedstocks. 176

Subhas Sikdar, director of the sustainable technology division at National Risk Management Research Laboratory, EPA, discussed the scope and limitation of “sustainability metrics” for products and processes. He pointed for the need to quantify benefits in three areas: economic development, ecological preservation, and social good. In some areas, benefits are more difficult to quantify. 177

We have not discussed the potential benefits of green chemistry itself—the attraction of more students into the discipline of chemistry, the improvement of the public’s appreciation of

175 Abstracts, pp. 87–88.
176 This problem is somewhat similar to that encountered in modeling the impact of technologies on global climate change. Bottom-up or engineering systems models take one technology at a time (microeconomics); top-down or macroeconomic models look at the overall impact. See http://www.iea.org/pubs/studies/files/mapping/fig4.pdf.
177 Abstracts, pp. 71–73.
chemistry, seeing chemistry as part of the solution rather than the problem, and the improvement in the image of the chemical industry.
<table>
<thead>
<tr>
<th>Case</th>
<th>Description</th>
<th>Comments</th>
<th>Benefits</th>
<th>Speaker or Reference</th>
</tr>
</thead>
</table>
| 1    | Supercritical carbon dioxide as solvent | Cleaning semiconductor wafers with supercritical carbon dioxide gives increased penetration as device dimensions approach the nanoscale. Development involving industry, government, and academia is being commercialized. | Eliminate 4 million gallons of waste water that are produced and thousands of gallons of chemicals used on an average day in a single semiconductor manufacturing facility. | Laura.rothman@scfluids.com
SC Fluids, Inc. 472 Amherst St. Nashua NH 03063 p. 55 of abstracts |
| 5    | Dimethyl carbonate | 1. Vapor-phase reaction of methanol and CO with copper chloride catalyst in fluid bed; optimization.  
2. National Institute of Advanced Industrial Science and Technology (AIST), Japan, developed a cyclic carbonate process using supercritical carbon dioxide and ionic fluids. | 1. Eliminates problems from liquid phase reactions.  
2. 100% yield and 100% selectivity “expected to significantly accelerate the development of production methods for environmentally friendly engineering plastics.” | 1. ito.hirofumi@jgc.co.jp p 127 of abstracts.  
2. See www.aist.go.jp/index_en.html for “What’s New” 2/26/03; good website for a number of green chemistry developments. |
| 17   | Room Temperature Ionic Liquids | A representative sample of research studies that were reported:  
—Application of Ionic Liquids to extractive fermentation of lactic acid (p. 112).  
—Enzymatic esterification in green solvents: application of ionic liquids in bioconversions (p.115).  
—Electrochemical fluorination of oxygen-containing heterocycles | None to the point of process development and commercialization. | See abstracts as noted. |
<table>
<thead>
<tr>
<th>18</th>
<th>New refrigeration processes</th>
<th>Greenfreeze refrigeration technology based on hydrocarbons; collaborative work involving Greenpeace</th>
<th>Eliminates CFCs; discussed as “controversial.”</th>
<th>J. Michael Fitzpatrick, President and Chief Operating Officer, Rohm and Haas; <a href="mailto:ebush@rohmhaas.com">ebush@rohmhaas.com</a></th>
</tr>
</thead>
</table>
| 20 | Biodegradable polymers      | 1. BASF has developed a biodegradable plastic, Ecoflex®, which is enjoying “double-digit growth rates.”
  2. A series of biodegradable polymers are being developed in China with the Polymer Material Engineering Lab, Changchun Institute of Applied Chemistry; the polymers are manufactured from carbon dioxide and various epoxides. | 2. The new biodegradable plastics cost less than $1/lb have mechanical properties comparable to polyethylene, low oxygen and water permeability approaching that of PVDC. BioCO2™ 3000 uses cyclohexene as the epoxide. Another product uses ethylene and propylene oxides with carbon dioxide. | 1. Dietmar Nissen, President BASF East Regional Headquarters; nissend@basf-east-asia.com.hk
  p. 7 of abstracts
  2. Xianhong Wang; xhwang@ciac.jl.cn
  p. 54 of abstracts |
| 26 | Thermal green chemistry     | Higher temperatures than normal offer opportunities for efficiencies in time and energy, and some batch reactions can be made continuous. At 200 degrees C and pressures of 2–3 MPa reactions in traditional solvents can be carried out in shorter time periods and at higher yields. A microwave batch reactor and continuous microwave reactor were used. Reactions were also carried out in high temperature water. | Additional work will be needed to scale-up for commercial applications. | C. R. Straus, Center for Green Chemistry, Monash University, Australia strauss@sci.monash.edu.au
  Abstracts pp. 43–46 |
| 27 | New routes to vinyl acetate and ethyl acetate | Acetic acid, oxygen, and ethylene are reacted in a fixed bed reactor which “fluidizes” the catalyst to produce vinyl acetate; the use of the fluidized bed saved 30% of capital costs and x-ray imaging eliminated the need for a $20–30 million demonstration plant and three to four years in development time. Acetic acid is added to ethylene with a heteropolyacid as catalyst. | Allowed plant consolidation, improved economics, reduced energy in transportation of raw materials, reduced water use, and 35% less raw materials. The two processes received industrial awards, one (ethyl acetate) being the AstraZeneca Award for excellence in Green Chemistry and Engineering. | Ian Dobson, General Manager BP Chemicals, Sunbury on Thames, Middlesex UK. Abstracts pp. 47–51. |
| 28 | Recyclable waterborne coating system | Nippon Paint develop a waterborne coating and a system that collects uncoated waste paint for recycle. | Eliminates VOCs and reduces waste in industrial coating operations | Sakuichi Konishi: konishi_NP2060@npc.nipponpaint.co.jp Abstracts pp. 31–33 |
| 30 | Safer insecticide | CONFIRM™—selective caterpillar control agent. The product acts by strongly mimicking a natural substance found within the insect’s body that is the natural “trigger” that induces molting and regulates development in insects. CONFIRM™ disrupts the molting process causing insects to stop feeding; they then die. Related Selective Insect control agents were also described. | Inherently safer to non target organisms, lower use rates. | Mentioned by J. Michael Fitzpatrick at the conference. Winner of 1998 Green Chemistry Presidential Challenge Award: see www.epa.gov/greenchemistry/docs/award_recipients_1996_2002.pdf pp. 52–53 |
| 31 | Use of solid acid catalysts | DuPont has developed a solid acid (poly-perfluorosulfonic acid, or Nafion®) on silica sol-gel network for polymerization of tetrahydrofuran to polytetramethylene ether glycol, which is used to manufacture Lycra® spandex fiber. | Eliminates use of fluosulfonic acid and allows recovery of the acid. Activity increased 1,000x by use of the support; solids reduced 99.5% and biological oxygen demand to almost zero. | Mentioned by Thomas Connelly, Chief Science and Technology Officer at DuPont, abstracts p. 98 |
| 32 | Supersolids clear coat | DuPont created a very high solids automotive coating—reduced molecular weight that crosslinks when drying. | Won an EPA Clean Air Award; improved properties (scratch resistance, higher gloss) with 25% less solvent emissions. | Mentioned by Thomas Connelly, Chief Science and Technology Officer at DuPont, abstracts p. 99; Note: he also mentioned Tyzor Polyester catalysts, titanium-based catalysts that eliminate the Sb and Ge heavy metal catalysts. Can be used when a light coloring is permitted. |
| 33 | New route to caprolactam | Clean production of caprolactam without production of significant quantities of ammonium sulfate is accomplished by combining a process developed by Sumitomo Chemical with one developed by Eni Chem. Cyclohexanone is reacted with ammonia, hydrogen peroxide and TS-1 catalyst; the resulting oxime is converted to caprolactam via the Beckmann rearrangement in the vapor phase. | The only by-product is water; commercial operation begins in 2003. | Akio Kosi, Chairman, Sumitomo Chemical Company 27-1, Shinkawa 2-chome, Chuo-ku, Tokyo 104-8260; abstracts p. 11 Note: He mentioned without details the catalytic oxidation of HCl back to chlorine; a commercial plant to begin operation in “the near future” and a new route to a rubber intermediate ethylidene norborne. |