

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.⁴⁴ 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.⁴⁵ Many of these

⁴⁴For 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.

⁴⁵See "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.⁴⁶ 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,⁴⁷ 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, NO_x, VOCs, and particulates beyond the levels with existing fuel additives.⁴⁸

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. H₂O₂ has the potential to replace some of the steps in the process that use Cl₂. But H₂O₂ alone cannot

⁴⁶Pietro Tundo "Dimethyl Carbonate as a Green Reagent," in *Collection of Lectures of the Summer Schools on Green Chemistry*, Venice 1998, 1999, 2000, INCA 2001, <http://helios.unive.it/inca>.

⁴⁷Michael A. Pacheco and Christopher L. Marshall, "Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive," *Energy & Fuels*, No. 11, 1997, pp. 2-29.

⁴⁸It 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 ClO_2 in the final steps. Case 15a suggests that the activation of H_2O_2 with the use of a chelated iron compound can make the use of hydrogen peroxide more efficient and competitive with the ClO_2 -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 H_2O_2 (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 H_2O_2 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.⁴⁹ 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.⁵⁰ 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

⁴⁹Toxics Use Reduction Institute, www.turi.org.

⁵⁰Information on the product stewardship program for carpets from the EPA can be found at <http://www.epa.gov/epaoswer/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.⁵¹ 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.⁵² 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.

⁵¹Cann and Connelly, "Real World Cases in Green Chemistry," 2000.

⁵²Kerri A. Walsh, "Oxygenated Products Survive Global Slump," *Markets and Economics*, February 13, 1996, p. 38.

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

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

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).⁵³ 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 Maxygen 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.⁵⁴ 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.

⁵³J. L. Pierrel and M. Fontecave, "Iron and Activated Oxygen Species in Biology: The Basic Chemistry," *BioMetals*, No. 12, 1999, pp. 195–199.

⁵⁴Ann M. Thayer, "Biocatalysis: Chemical and Pharmaceutical Makers Seek More Efficient and Often Cleaner Routes to Making Old and New Products," *Chemical & Engineering News*, May 21, 2001, pp. 27–34.