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,[19] 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

[19] 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 CO_2 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 1. Summary of case studies.

	Case Study	Comments	Environmental/Energy Benefits	Security/ Safety Benefits	Performance/ Economics Benefits	Principles and Areas Addressed
1	Processes using supercritical CO_2 solvent	Applications in cleaning, coffee decaffeination, polymerization solvent	Elimination of chlorinated solvents	Reduced exposure to solvent vapors	Improves economics and performance	4 B, D
2	3 steps for ibuprofen	Example of “atom economy” principle	Elimination of 35 million lbs of waste		Reduced investment and operating costs	1, 8 F
3	Converting polymers to monomers for recycle: PET and Nylon 6		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%			1, 9 G
4	Bio-based processes	47 processes (examples) studied (see Appendix A)	Average 20% reduction in waste (improved yields); elimination of hazardous chemicals in mining, pulp and paper, specialty chemicals	Reduced exposures; reduced critical metals; reduced storage of Cl_2	Implemented where superior economics prevailed; provided improved performance and entry to new markets	1, 2, 7, 8, 9, 12 A, B, C, F, G
5	Dimethyl carbonate	Manufacture and use of DMC	Could eliminate use of phosgene in the manufacture of multibillion pounds of polycarbonates and polyurethanes			2, 3, 4, 10 B, E
6	Direct production of hydrogen peroxide from hydrogen and oxygen	Not yet commercialized; uses carbon dioxide as solvent	Eliminates waste streams; reduces energy use by eliminating three energy-intensive units: oxidation reactors, stripping column, and distillation train	Safety a continuing concern in any manufacturing process for hydrogen peroxide	Cheaper hydrogen peroxide could find greater use in “green chemistry”	3, 5, 9 B, D, F
7	Advanced oil and gas exploration and production	CO_2 sand fracturing, modern drilling bits; synthetic drilling muds	Reduced waste and energy use; no harm to groundwater	Increased worker safety	Lower-cost operation	1, 3, 4, 6, 10 B, E
8	Various approaches to water purification	Chemical, membrane, ultraviolet, and more	Eliminate use of chlorine	Enhanced security	Lower costs; availability when otherwise not possible	
9	Wood preservation	Replace chromated copper arsenate with alkaline copper quaternary	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	Avoids worker exposures in wood treatment	Replacement at a somewhat increased direct cost	3, 4, 10 B, E

10	Sentricon® termite colony elimination system	More than 300,000 structures are now being safeguarded.	Employs an integrated pest management approach using monitoring and targeted delivery of a highly specific bait	Avoids worker exposure to insecticides	Economics being tested in the marketplace	3, 4, 10 B, E
11	Inert anodes	Example of green electrochemistry; collaborative program—DOE and Alcoa	Possible savings of 6 trillion Btus / year in the U.S. by 2010 ($90 million); elimination of carbon and fluorocarbon emissions; reduction of cyanide formation and dust emissions, elimination of polycyclic organic matter generated during anode manufacture and consumption	Avoids potential worker exposure	Nonenergy savings of $20 million	3, 6 B, F
12	Process for production of Cytovene® antiviral agent		Elimination of 1.1 million kg / year liquid waste and 25,000 kg / year solid waste		Reduced costs with yield increase of 25% and 100% increase in throughput	1, 2 F
13	High-yield melting of Al	In alliance with Praxair, Alcoa is testing high-yield melting	Project received the Indiana Governor's Award for Excellence in Pollution Prevention.	Safer work environment	Reduced natural gas use and reduced wastes translate to reduced costs	6 F, G
14	Elimination of ozone-depleting chemicals	In the printed wire board and electronic assembly and test processes at IBM	Completely eliminated the use of CFCs and other ozone-depleting substances	Eliminated potential exposure to methyl chloroform	Replacing CFCs with water or "no-solvent" processes translate to cost savings	3 F
15	Delignification and bleaching of pulp in paper manufacture	Eliminates use of chlorine or chlorine dioxide; using air in place of sulfur and chlorine	Eliminate formation of dioxin and other organo-chlorine waste products	Elimination of use of chlorine		2, 3 B, F
16	Clean solvent extraction using polyethylene glycol-based aqueous biphasic systems	In aqueous biphasic systems (ABS) the major component in each of the two immiscible phases is water, and thus a liquid-liquid extraction	Technology can be envisioned that completely eliminates the use of volatile organic compounds Immediate environmental and economic impacts			3 D
17	Room-temperature ionic liquids	Liquids composed entirely of ions can be good solvents for catalytic reactions eliminating many side reactions	No commercialized applications yet as a separation or reaction medium; concerns on potential toxicity and environmental impact need to be studied	Potential to reduce worker exposure to volatile solvents		3 D
18	Environmentally friendly refrigerants, new refrigeration processes	(1)Trifluoro methyl iodide, blended as a combustion inhibitor, (2) hydrofluoroethers have been developed by 3M, (3) non-chemical related cooling principles	Ikon® B with 20% market penetration by 2010: CO_2 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			10 E

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 NO_x 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 CO_2)—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 adhesives 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 fluorobenzene	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-aminodiphenylamine	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 2. Distribution of case studies. Cases as listed in Tables 1 and A1.

	Research and Development	Market and Product Development	Sustainable Business
Environmental	6: H_2O_2 production 16: ABS 17: Ionic liquids 4g: Ammonium acrylate 4s: Bioconversion of CO_2 4u: p-Hydroxybenzoate 4v: Polyhydroxylalkanoates 4w: Adipic acid 4ee: Terephthalic acid 4vv: Biorefinery	1a: CO_2 cleaning 3: Polymers to monomers 13: High yield aluminum 15: Delignification 18: Non-CFC refrigerants 19: Clean diesel membranes 20: Biodegradable polymers 22: Advance ox process 4p: Ethanol from biomass 4pp: Levulinic acid from biomass 4uu: Biodiesel	1b: Decaffeinating 10: Sentricon 14: Eliminate CFCs in printed wireboard 21: N_2O capture 4m: Pulp bleaching 4n: Zinc refining 4o: Copper, gold bioleaching 4y: Lead mine water treatment
Security		8: Water purification	
Health and Safety		5: DMC production	9: Wood preservation
Economic	23: Fluorobenzene production 4aa: Enzyme optimization 4r: Complex carbohydrates	11: Inert anodes 4h: Polyesters 4q: Oil well completion 4t: Cross-linked enzyme crystals 4bb: Ascorbic acid 4cc: 1,3-Propanediol 4tt: Succinic acid	2: Ibuprofen 7: Oil and gas production 12: Cytovene production 24: Aminodiphenylamine production 25: Synthesis of Glyphosate 4a: Riboflavin 4d: Amino acids 4e: S-Chloropropionic acid 4f: Acrylamide 4i: Polylactic acid 4j: Vegetable oil degumming 4k: Waste water recovery 4l: Peroxide bleach residue 4b: 7-Amino-cephalosporanic acid 4c: Cephalexin 4x: 5-Cyanovaleramide 4z: Acetic acid 4dd: Nicotinamide 4ff: Aspartame 4gg: 6-Aminopenicillanic acid 4hh: L-lysine 4ii: L-threonine / L-methionine 4jj: Roundup Read® soybeans 4kk: Vitamin B-12 4ll: Vitamin C 4mm: Vitamin F 4nn: D-p-hydroxyphenyl glycine 4oo: Feed enzymes 4qq: Citric acid 4rr: High-fructose syrups 4ss: Monosodium glutamate

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.[20] 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.

[20]NGETs 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.[21] The top six two-digit Standard Industrial Classification (SIC) code industries comprise more than 92 percent of the total releases (see Figure 2).

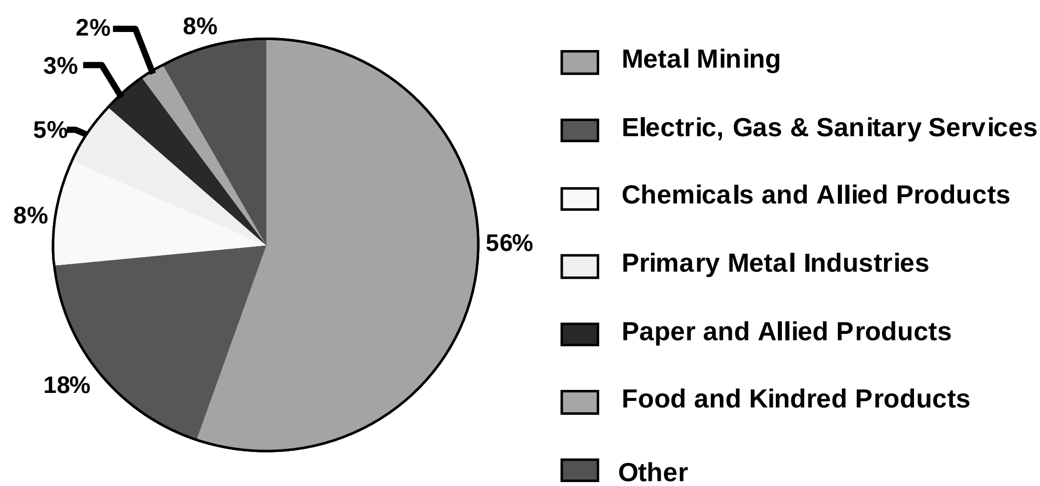

Figure 2. Breakdown of Total TRI Chemical Releases Over All Industries.[22]

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

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

[22] "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.

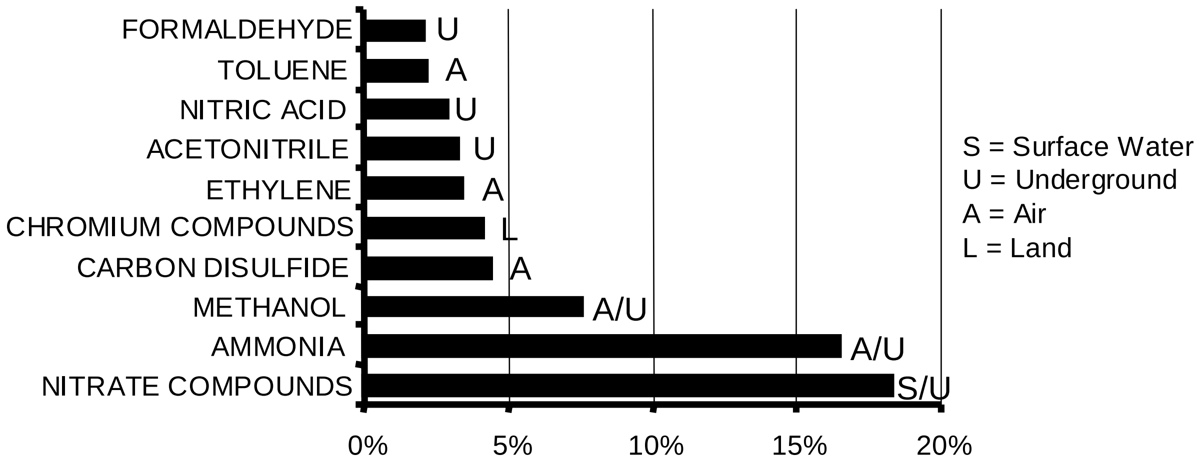

Figure 3. TRI Release Breakdown of the Chemical and Allied Products Industry (SIC code 28) (% of emissions).

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.

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

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.

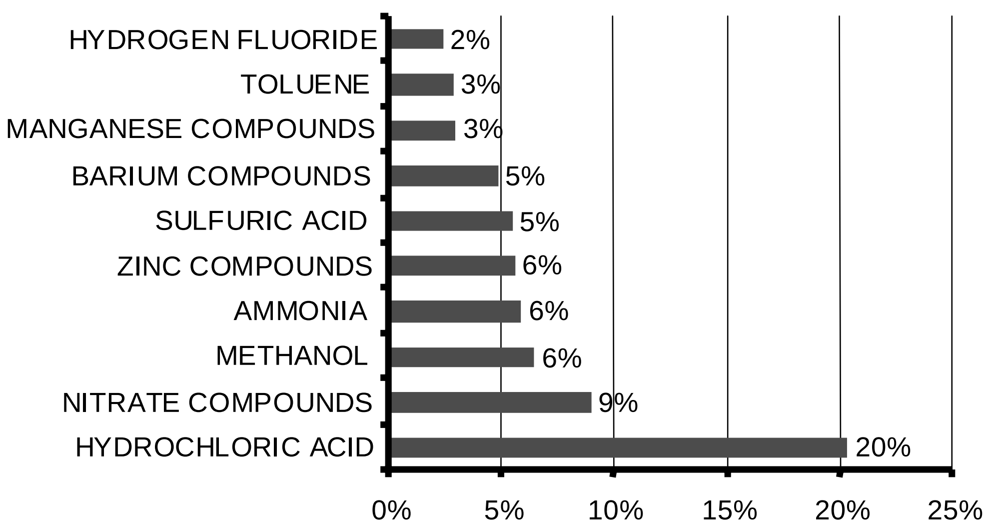

Figure 4. Top Ten Chemicals Released Excluding the Mining Industry (% of emissions).

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.

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[23] Nearly 85 percent of all dry cleaners use perchloroethylene as the solvent in their process. See Footnote 4.

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

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.[25]

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.[26] 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.[27] Sudden changes took place in the way businesses perceived their exposures to chemical catastrophes. As an example, the Blue Plains Wastewater

[25] Celia M. Henry, "Drug Development: Process Chemistry Results in Pharmaceutical Manufacturing Routes That Are Safe, Efficient, and Scalable," *Chemical & Engineering News*, Vol. 80, No. 21, May 27, 2002, p. 57, and R. A. Sheldon, "Atom Efficiency and Catalysis," *Chemistry Review*, May 2000, pp. 10–13.

[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.[28] 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.[29]

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.[30] Ashford examined eight cleaner technologies in the International Cleaner Production Information Clearinghouse.[31] 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

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[28]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.”

[29]See T. A. Kletz, *Process Plant: A Handbook for Inherently Safer Design*, 2nd edition, Philadelphia: Taylor and Francis, 1998, and R. E. Bollinger et al., “Inherently Safer Chemical Processes: A Life Cycle Approach,” American Institute of Chemical Engineers, 1996.

[30]Note on Inherently Safer Chemical Processes, www.rsc.org.

[31]Nicholas A. Ashford, “Industrial Safety: The Neglected Issue in Industrial Ecology,” *Journal of Cleaner Production*, Vol. 5, Nos. 1/2, March–June 1997.

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.[32] 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.[33]

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[32] Michael K. Stern, “Environmentally Sound Agricultural Chemistry: From Process Technology to Biotechnology,” NRC Workshop on the Environment, November 17–19, 2002, proceedings forthcoming.

[33] Michael C. Cann and Marc E. Connelly, *Real World Cases in Green Chemistry*, Washington, D.C.: American Chemical Society, 2000.

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 CO_2 produced per unit GDP is largely a result of efficiency increases and fuel changes driven by economic forces.[34] 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 4o). Bioleaching involves the use of bacteria, principally *Thiobacillus ferrooxidans, Leptospirillum ferrooxidans,* 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

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[34] 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.[35] 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.[36] 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 synthetic 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 CO_2 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).

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[35] Personal interview with Akazu Takahashi, Ube Industries, June 2002.

[36] 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 usefully 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.[37]

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

[37] Robert J. Lempert, Steven W. Popper, Susan A. Resetar, and Stuart L. Hart, *Capital Cycles and the Timing of Climate Change Mitigation Policy*, Washington, D.C.: Pew Center on Global Climate Change, October 2002.

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.

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[38]Note on Green Chemistry Version: 5 April 02, www.rsc.org.

[39]This 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 CO_2 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 CO_2 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 CO_2, which can inhibit breathing by machinery operators.[40]

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

[40]This 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.[41] 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.[42] 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.[43]

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[41] Uma Chowdhry, "Sustainable Growth in the Chemical Industry," in *Challenges for the Chemical Sciences in the 21st Century: The Environment* (proceedings of the "Challenges for the Chemical Sciences in the 21st Century"), Washington, D.C.: National Academies Press, forthcoming.

[42] A. Maureen Rouhi, "Generic Tide is Rising: Expiring Patent Protections and Pressures on Makers of Brand-Name Drugs Bode Well for the Generic Pharmaceutical Industry," Chemical & Engineering News, Vol. 80, No. 38, 2002, p. 44.

[43] Rouhi, 2002, pp. 46–48.