How Industrial Applications in Green Chemistry Are Changing Our World

A white paper examining the newest developments in the industrial applications and reduced environmental impact of green chemistry across many areas of manufacturing and industry.

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TABLE OF CONTENTS

ABOUT THIS REPORT

ABOUT THE AUTHOR

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I. INTRODUCTION

Green chemistry has now been around for two decades, and it has been making a real difference in our world. The well-known companies and organizations that have embraced the discipline include Nike, BASF, Hewlett-Packard, the National Aeronautics & Space Administration, Eastman Chemical, United Soybean Board, Pfizer, the Environmental Protection Agency, Bayer MaterialScience, Codexis, Johnson & Johnson, Amgen, DuPont, and World Wildlife Fund. The global market for green chemistry is predicted to grow exponentially in the coming years, to $98.5 billion by 2020. The young discipline has produced thousands of scientific papers. Research networks in more than 30 countries on every settled continent have been formed along with at least four new international scientific journals. Green chemistry has been credited for decreasing the amount of chemical waste released to the air, water, and land. It has also spawned new areas of research including green solvents, bio-based transformations and materials, alternative energy science, molecular self-assembly, next-generation catalyst design, and molecular design for reduced hazard. Some industry reports predict green chemistry as the future of all chemistry.

II. HISTORY

Green chemistry is built upon advances in areas and disciplines that existed prior to the field's inception including catalysis, atom-economical synthesis, degradable materials, and alternative solvents. When green chemistry was founded in the early 1990s, there was widespread concern over potential adverse impacts on human health and the environment from the processes, by-products, waste, pollution, and industrial chemicals in people's daily lives. "Rather than continue deferring to litigators, legislators, and regulators to reactively handle these critical problems, members of the chemistry community unified around a common goal: to design chemical products and processes that reduce or eliminate the use and generation of hazardous substances," says Paul Anastas of Yale University, one of green chemistry's founders.[1] The 1990s were also the decade when the sustainability field was created and the Pollution Prevention Act of 1990 was passed, marking a regulatory policy change from pollution control to pollution prevention as the most effective strategy for dealing with many environmental issues. [1, 2]

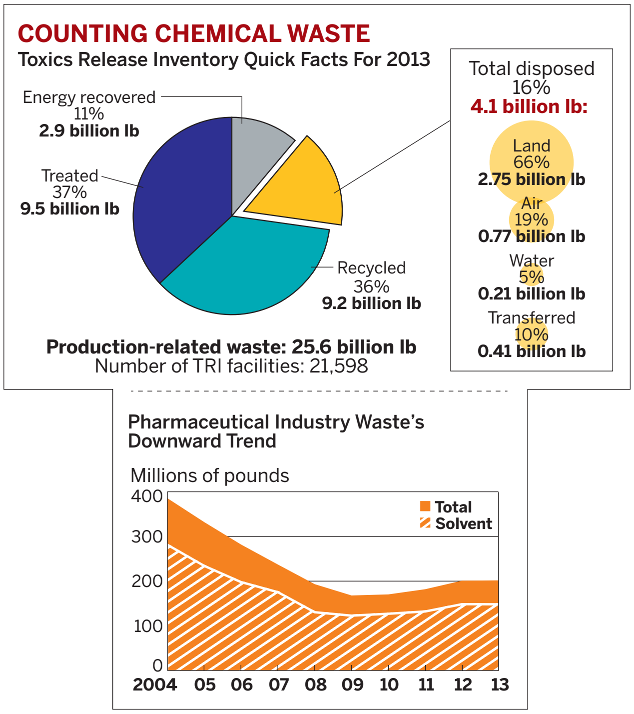
In 1995, the U.S. Environmental Protection Agency (EPA) received support from President Bill Clinton to establish an annual awards program highlighting scientific innovations in academia and industry that advanced green chemistry.[2] This created the annual

Presidential Green Chemistry Challenge Awards, which have been a major platform for promoting awareness about green chemistry.[3] In 1997, the University of Massachusetts at Boston established the field's first green chemistry Ph.D. program.[4] In that same year, in cooperation with the EPA, Dr. Joe Breen, a retired 20-year staff member of the EPA, and chemist Dennis Hjeresen co-founded the Green Chemistry Institute (GCI) as an independent nonprofit with a staff devoted to working exclusively toward the advancement of green chemistry.[2]

Paul Anastas and John C. Warner co-authored the groundbreaking book, *Green Chemistry: Theory and Practice* in 1998.[5] The "12 Principles of Green Chemistry" outlined within this work declared a philosophy that motivated academic and industrial scientists at the time and continues to guide the green chemistry movement.[2] The movement received a boost in 2005 when three scientists – Yves Chauvin of France, and Robert Grubbs and Richard Schrock of the U.S. – won the Nobel chemistry prize for simplifying the process of synthesizing carbon compounds.[6,7] Another green chemistry milestone occurred in 2008, when California's governor, Arnold Schwarzenegger, backed legislation to tighten restrictions on toxic chemicals in household goods. The state's Safer Consumer Products law took effect in 2013, and an initial 164 chemicals were targeted for scrutiny in 2014.[8]

III. IMPACTS

Between 2004 and 2013, the amount of chemical waste released to land, air, and water has decreased by 7%, according to data collected by the EPA's Toxics Release Inventory (TRI). These data show that releases for some chemicals, including hydrochloric acid, trichloroethylene, and methyl isobutyl ketone, have decreased by more than 60% over that time. The releases reported by the pharmaceutical industry, which has long generated the most chemical waste per kilogram of product to produce complex molecules of high purity, have dropped by about half. An EPA analysis points to green chemistry and engineering practices as being behind much of this improvement.[9]



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However, David J. C. Constable, the current director of the Green Chemistry Institute (which is now part of the ACS), says that he believes the reductions highlighted by EPA are still largely related to process changes, and don't necessarily indicate that the underlying synthetic chemistry has changed significantly. "The chemistry changes more in second- or third-generation commercial processes," Constable explains. "It will be then that we can expect to see even greater decreases in wastes, toxics, and emissions."[9]

Green chemistry can play an important role in designing new chemicals to use in place of ones that have been proven to be problematic, according to a recent report by the U.S. National Research Council.[20] Many chemical manufacturers, such as DuPont, now have staff dedicated to exploring green chemistry and incorporating life-cycle analysis to products and manufacturing processes, not just with pollution prevention in mind, but also with the expectation that those changes can positively impact the companies' bottom lines.

The European Union's regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) chemicals legislation is seen as a very powerful promoter of sustainable innovation and green chemistry. REACH favors innovative new materials and processes by granting potential exemptions from registration for five years for substances used in research and development. Experts believe that the REACH authorization process is the main instrument promoting green chemistry and sustainable innovation, by facilitating the phasing out of hazardous chemicals and substituting them with safer alternatives.[11]

In the U.S., California's initiative for safer consumer products is proposing that manufacturers eliminate hazardous chemicals from consumer products, either by removal or reformulation with safer chemicals.[12] While the law only applies within California, experts predict that it will influence manufacturing nationwide due to the state's importance to the broader U.S. economy. Some believe it could become a template for legislation elsewhere.[14]

As interest in green chemistry has grown, the number of academic courses specifically tailored to sustainable chemistry has also burgeoned at the undergraduate and graduate levels.[13] The first college-level course in green chemistry was taught by Prof. Terry Collins at Carnegie Mellon University in Pittsburgh, PA.[14] The ACS website now lists more than 40 academic programs that offer green chemistry coursework in the U.S. and Puerto Rico and over 30 more internationally.[15] Classes are offered by many institutions, ranging from small four-year colleges to major research universities.[16] In the U.S., the institutions that have launched graduate programs in green chemistry include Yale University, the University of Toledo (Ohio), the University of Massachusetts, Lowell; and the University of California, Berkeley. European universities with programs include the University of York (United Kingdom) and the University of Copenhagen.[17]

Just as importantly, having the proven ability to improve the environmental profile of chemical processes and syntheses is a valuable commodity on the job market.[17] "We need green chemists in at the start, designing processes from first principles," says Jeff Hardy of the United Kingdom's Royal Society of Chemistry.[13]

IV. GREEN CHEMISTRY APPLICATIONS

The wide range of applications of green chemistry includes uses in the pharmaceutical industry, as well as new approaches that reduce or eliminate the use of solvents, or render them safer and more efficient. Green chemistry has also inspired a growing number of ways to synthesize traditionally petroleum-based chemicals from biological materials instead, often plant matter or waste. Green chemistry also plays a key role in alternative energy science, and the production of new ways to make solar cells, fuel cells, and batteries for storing energy. When self-assembling molecules use bio-based plant materials, it is considered green chemistry. Because a primary goal of green chemistry is to minimize or eliminate waste in the manufacture of chemicals and allied products, it has inspired the creation of many green "next generation" catalysts. Another important development in green chemistry is the trend toward redesigning chemical products to reduce their hazard.

GREENER PHARMACEUTICALS

The pharmaceutical industry was among the first to recognize the value of green chemistry.[18] Since 1996, processes developed by or for the pharmaceutical industry have been recognized by 11 Presidential Green Chemistry Awards.

By 2005, all the main drug companies had joined a round table with the American Chemical Society's Green Chemistry Institute aimed at developing more efficient, less polluting processes. Between 2004 and 2013, the U.S. drug industry's use of chemicals dropped by nearly half.[9] The drug industry's reductions are largely the result of using less organic solvent, according to an analysis by the EPA. Methanol, dichloromethane, toluene, dimethylform¬amide, and acetonitrile account for 75% of the industry's reductions. Pharmaceutical companies are also selecting less hazardous reagents, reducing reaction steps, and developing better catalysts.[9]

Viagra, known generically as sildenafil citrate, is a blockbuster drug that has long been a "poster child" for the green credentials of its manufacturer, Pfizer.[20] When gearing up for commercial production of Viagra, Pfizer's chemists designed a new reaction strategy that radically reduced the amount of solvent required, cut out the reagents tin chloride (an environmental pollutant) and hydrogen peroxide (a fire and transportation hazard), and produced just a quarter of the waste of the original process.[21] Pfizer has also improved the process to make its well-known Lipitor (atorvastatin), a drug for reducing blood cholesterol, so that it uses an enzyme that catalyzes chemical reactions in water, minimizing the need for potentially polluting organic solvents.[22]

Other well-known drugs have been recognized by the EPA's green chemistry awards for waste-reducing improvements to how they are manufactured. The chemical company BASF now makes its annual output of the painkiller ibuprofen—some 2 billion tablets—in a three-step rather than a six-step process.[23] Of the atoms used in the synthesis, which are mostly derived from hydrocarbons, 77% make it into the final product compared with 40% before.

Another leading drug for treating high cholesterol, Zocor (simvastatin), traditionally used a multistep method involving large amounts of hazardous reagents that produced a large amount of toxic waste. A new method for synthesizing the drug uses an engineered enzyme and a low-cost feedstock that was optimized by Codexis, a biocatalysis company.[24,25] Additionally, Codexis worked with Merck to develop a greener route for synthesizing sitagliptin, the active ingredient in Januvia™, a treatment for type 2 diabetes. This collaboration led to an enzymatic process that reduces waste, improves yield and safety, and eliminates the need for a metal catalyst.[26]

Another notable drug that now requires less waste to produce is the chemotherapy drug paclitaxel (marketed as Taxol). It was originally made by extracting chemicals from yew tree bark, a process that used a lot of solvent in addition to killing the tree. The drug is now made by growing tree cells in a fermentation vat.[27]

GREEN SOLVENTS

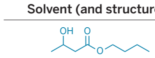
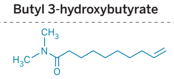
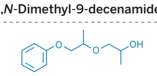
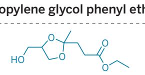
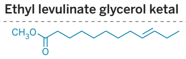
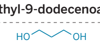
The fifth principle of green chemistry holds that the use of auxiliary substances such as solvents "should be made unnecessary wherever possible and innocuous when used."[28] Solvents are a key priority when greening chemistry, because they are used in high volumes and are typically volatile organic compounds (VOCs), leading to high risk for large amounts of waste, air pollution, and other health concerns. Finding safer, more efficient alternatives or removing solvents altogether is one of the most effective ways to impact the safety and efficiency of a process or product.[29] Between 1996 and 2014, 22 Presidential Green Chemistry Awards have recognized approaches that reduce the use of conventional solvents, including alternative, greener solvents, and processes that use carbon dioxide or water or avoid the use of solvents completely.[30]

A recent example of a green solvent that is now in commercial use is in fabric dyeing. Traditional dyeing also requires a lot of water—about 7 gallons to dye a T-shirt—and is energy intensive because the dyed material must be dried. Dutch start-up firm DyeCoo Textile Systems recently invented an industrial-scale, water-free dyeing process and equipment that uses supercritical carbon dioxide, which functions like a liquid when under pressure and at slightly elevated temperature.[18]

In recent years, manufacturers of laundry detergents, spray cleaners, and other cleaning products for home and industry have been adding greener solvents to improve their performance, for both environmental and human health reasons. Procter & Gamble and DuPont have announced plans to use cellulosic ethanol derived from corncobs and stalks in TideColdwater Clean. The cellulosic ethanol produced by a plant that DuPont is building in Iowa will replace ethanol derived from corn kernels. Blending this cellulosic ethanol into Tide Coldwater will repurpose more than 7,000 tons of agricultural waste a year, the partners say, and in the process will save the amount of energy needed to wash all the clothes in California homes for a month.[31] DuPont also sells another bio-based chemical, 1,3-propanediol, as a solvent, stabilizer, and enzyme carrier. Propanediol is found in environmentally friendly Method brand cleaning products, including a spray cleaner and a concentrated laundry detergent.[31]

Method products, as well as Seventh Generation brand products, also include another green solvent aimed at a similar niche, ethyl levulinate glycerol ketal. That solvent is manufactured by the bio-based chemicals start-up Segetis; its main role is to help solubilize fragrance oils and keep the overall cleaning formula stable, rather than to dissolve soil or grease. Other green solvents used in Method products include, propanediol, ethyl levulinate glycerol ketal, glycerin and methyl esters.[31]

Another green cleaning solvent is butyl 3-hydroxybutyrate, trade-named Omnia, which was developed by Eastman Chemical. Eastman created the new solvent by methodically going through a database of some 3,000 molecules with potential as cleaning solvents and whittling it down to one through a combination of computer simulations and wet-lab testing.[31]

Solvent (and structure)	Trade name	Supplier	Select applications
 Butyl 3-hydroxybutyrate	Omnia	Eastman	Industrial cleaners and degreasers
 *N,N*-Dimethyl-9-decenamide[a]	Steposol MET-10U	Stepan	Household cleaners, adhesive removal, paint strippers
 Dipropylene glycol phenyl ether	Dowanol DiPPh	Dow	Household cleaners
 Ethyl levulinate glycerol ketal	None	Segetis	Detergents, hard-surface cleaners, graffiti removal
 Methyl-9-dodecenoate	Clean 1200	Elevance	Heavy manufacturing, food processing
 1,3-Propanediol	Zemea	DuPont	Laundry detergents, hard-surface cleaners, glass cleaners

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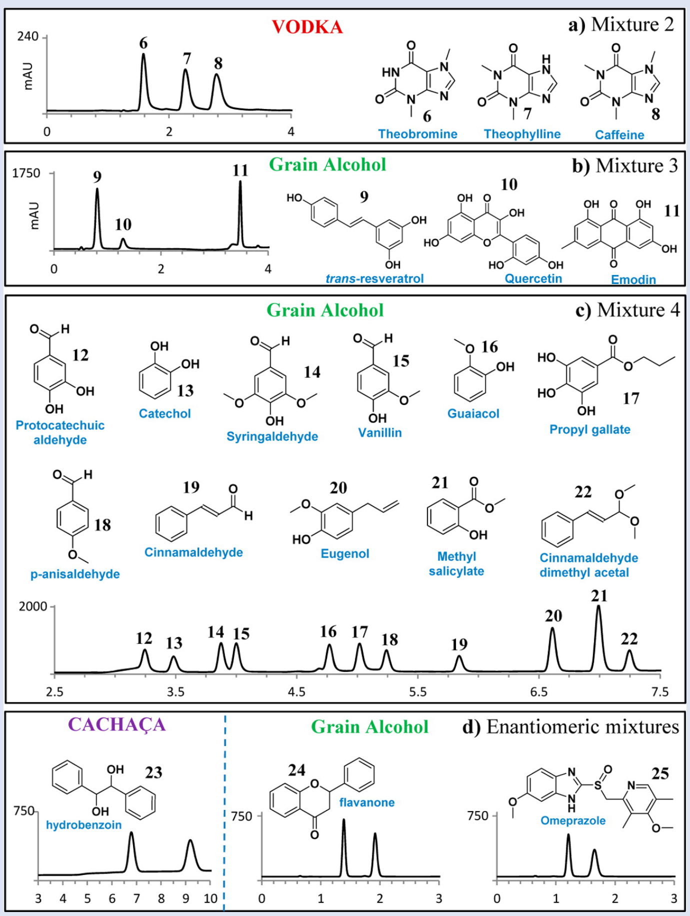
Elevance Renewable Sciences, Inc., a small company that converts vegetable oils into specialty chemicals with olefin metathesis technology invented by Nobel laureate Robert H. Grubbs, has been involved with the production of two green solvents. In collaboration with the surfactants manufacturer Stepan, the company produced a surfactant called Steposol MET-10U, which Stepan launched early last year as a replacement for solvents such as *n*-methylpyrrolidone and methylene chloride in adhesive removers and paint strippers. The surfactant also can be used in household and industrial cleaners in place of glycol ethers.[31]

Elevance has also formulated a heavy-duty degreasing solvent aimed at manufacturing, food processing, and transportation maintenance customers, called Elevance Clean 1200. It is meant to appeal to companies looking for ingredients that are considered low vapor pressure by California and have a low enough vapor pressure or enough carbon atoms to be exempt from EPA's VOC designation. Clean 1200 is being marketed as a replacement for aromatic hydrocarbons and d-limonene, a citrus-derived VOC.[31]

A team at the University of Wisconsin at Madison recently described a promising bio-based green solvent.[32] They used mineral acid catalysts as a solvent in the conversion of hemicellulose and cellulose biomass into high value platform chemicals and transportation fuels. The use of lignin-derived alkylphenols as solvents in this process (carried out in a biphasic reactor) minimized side-reactions in the aqueous phase and enabled recycling of the mineral acid catalysts.[33]



Reversed phase HPLC-UV analysis of several pharmaceutical and food-relevant compound mixtures using conventional HPLC instrumentation with different spirit alcohol-based mobile phases.

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For analytical chemists, a new way to avoid solvents such as acetonitrile in high-performance liquid chromatography (HPLC) may be to replace them with distilled alcohols, such as rum or vodka, combined with household products.[34] New work by a team of scientists from Merck Research Laboratories suggests that this combination can serve as low-cost and sustainable alternative eluents for HPLC, and in many cases produce excellent analytical results.[35] Other green solvents seeing increasing use are water, supercritical carbon dioxide, and ionic liquids.[36]

BIO-BASED TRANSFORMATIONS AND MATERIALS

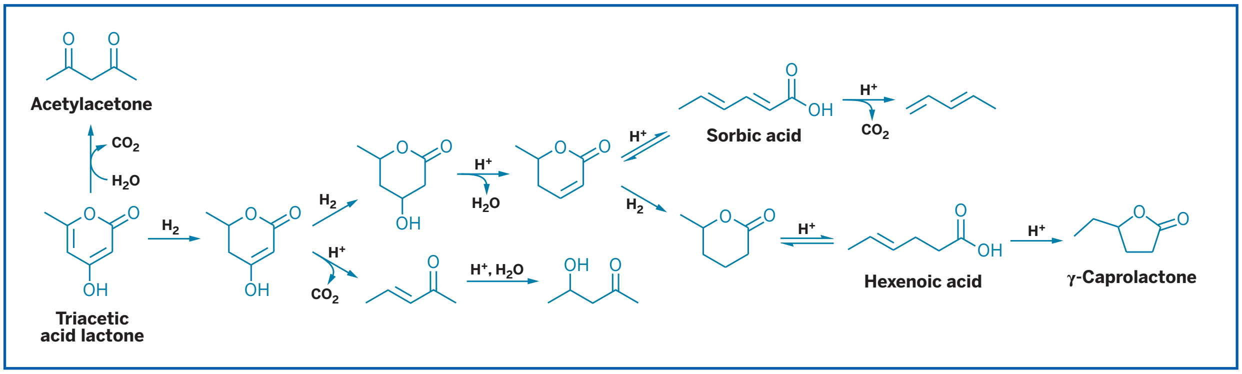
Green chemistry has played a key role in the development of a growing number of alternative ways to synthesize chemicals traditionally made from petroleum or other non-renewable resources. Advances in genetics, biotechnology, process chemistry, and engineering are leading to a new manufacturing concept for converting renewable biomass to valuable fuels and products, generally known as the biorefinery concept.[37]

Between 1996 and 2014, 34 Presidential Green Chemistry Award-winning technologies involved using a renewable resource in place of a petroleum-based or depleting resource.[38] The winning technologies have involved a wide array of biological materials, including algae, bacteria and other microorganisms, biomass, cellulose, oils from crops and other plants, sugars, starch, and yeast. These technologies have been developed by some well-known companies, including Archer Daniels Midland, Cargill, DuPont, Eastman Chemical, Dow, Procter and Gamble, Sherwin-Williams, as well as academic researchers and smaller companies.

DuPont's Sorona® polymer, which earned a Presidential Green Chemistry award in 2003, is an example of a bio-based process that is now commercially available. DuPont developed the process, which uses a genetically engineered microorganism and renewable cornstarch instead of petroleum to make cost-competitive textiles.[39] The Sorona® polymer can be used in apparel, carpeting, and packaging. This bio-based method uses less energy, reduces emissions, and employs renewable resources compared to traditional petrochemical processes.[40]

Using a process developed by Genomatica that earned the EPA's 2011 Presidential Green Chemistry Challenge Award for "Greener Synthetic Pathways," BASF is commercially producing renewable 1,4-butanediol (1,4-BDO).[41] This bio-based material is used to produce BASF's Ecoflex compostable polyester film, which is in turn used together with cassava starch and calcium carbonate to create fully biodegradable Ecovio® bags. These bags, which are certified by the Biodegradable Products Institute, disintegrate into water, CO_2, and biomass in industrial composting systems.[25]

Some recent innovations in producing bio-based chemicals have been the result of coupling chemical and biological processes.[42] In a recent study, a team of academic researchers demonstrated that a variety of high-value products can be produced from a previously unexplored platform chemical—triacetic acid lactone, which is a 2-pyrone compound.[43] The pyrone was synthesized from glucose by a genetically modified *Escherichia coli* and a yeast species, *Saccharomyces cerevisiae*. The researchers were able to produce 2,4-pentanedione (also known as acetylacetone), which has several commercial applications, including in metal extraction, in metal plating, and as a fuel additive. They also converted it to dienoic acid, which is usually produced from petrochemical sources and can be useful as a food and feed additive due to its ability to inhibit the growth of various mold and bacteria. Two other compounds the team reported producing are hexenoic acid, which can be used as a flavoring agent, and γ-caprolactone, a fragrance and cosmetics ingredient.[42]



Reprinted in part from: *C&EN,* **2012**, 90 (32) 37-38.

Another example is the process used by Auckland, New Zealand-based LanzaTech to convert carbon monoxide-containing gases to ethanol and other chemicals via microbial fermentation. Because steel mills produce CO-rich gas streams, LanzaTech recently constructed a 100,000-gallon-per-year ethanol production demonstration plant in Shanghai at Baosteel, China's largest steel producer. LanzaTech's microbes can also produce 2,3-butanediol, which can be converted to other compounds such as 1,3-butadiene, a monomer used to make synthetic rubber.[42] U.S.-based Coskata is another company that is commercializing hybrid chemical processing technology. Coskata produces syngas, a mixture of mainly CO and hydrogen, via thermochemical gasification of biomass or other solids or via catalytic reforming of natural gas. Selective microbial fermentation of syngas yields low-molecular-weight alcohols. Coskata operates a plant that can produce tens of thousands of gallons of ethanol per year from wood chips.[42]

Levulinic acid is a chemical that may be able to be used more widely as the result of new processes for synthesizing from biomass. U.S.-based Segetis sells ingredients for personal care and cleaning products based on levulinic ketals and operates a bio-based levulinic acid pilot plant in Minnesota. In Italy, two chemical firms recently launched projects to produce levulinic acid from biomass. The companies say their technologies will lower costs and turn a niche chemical into an attractive new building block for products used in crop protection, coatings, solvents, and fuels. When conventionally synthesized from maleic anhydride, levulinic acid is rather expensive to produce, limiting its use to low-volume applications such as fragrances and food additives.[44]

Solazyme is a California-based biotech company that engineers microalgae to produce much higher amounts of oil than the 5-10% oil content in wild algae. The company won a Presidential Green Chemistry Challenge Award in 2014.[45] Its products include the commercial production of algal oils that are engineered to be chemically similar to palm oil products, such as the C_{10} and C_{12} fatty acids found in palm kernel oil. The company's oils are found in products such as a laundry detergent from the Belgian firm Ecover.[46] Other notable firms that produce bio-based chemicals are Solazyme and Myriant. Myriant is based in Massachusetts and manufactures bio-based drop-in replacements and substitutes for a wide variety of petroleum-based chemicals including acrylic acid, which has a multi-billion-dollar global market, and succinic acid, which is used in pigments, pharmaceuticals, and metal plating.[47,48]

ALTERNATIVE ENERGY SCIENCE

Solar Photovoltaics

According to a recent analysis, solar photovoltaic technology is "one of the few renewable, low-carbon resources with both the scalability and the technological maturity to meet ever-growing global demand for electricity."[49] The use of solar photovoltaics has been growing at an average of 43% per year since 2000. In recent years, clean energy experts have been very excited about the emergence of two new chemistry-driven solar technologies, perovskite solar cells and quantum dots.

Perovskite solar cells compare well to most older photovoltaic technologies because they offer good power outputs from low-cost materials that are relatively simple to process into working devices.[50,51] The perovskite appellation is a nod to a long-ago-discovered mineral composed mainly of calcium titanate ($CaTiO_3$). Scientists use the term loosely today to refer to a large class of materials that, like $CaTiO_3$, exhibit ABX_3 stoichiometry and adopt the perovskite crystal structure. The perovskites that are getting so much attention in the photovoltaics world these days are organometal trihalides, the most commonly studied of which is $CH_3NH_3PbI_3$. (CH_3NH_3 is the *A* group in ABX_3.) The main reason for the excitement is the recent steep rate of improvement in Perovskite solar-cell performance.[52]

In just a few years, the conversion efficiency of perovskite cells leaped from just a few percent in a forerunner version to more than 20% in 2015.[50] This is a milestone that took other solar cells decades to reach.[53] Most of the advances were reported in 2012 and 2013. The fast-paced improvement, which hasn't shown signs of slowing, coupled with inexpensive materials and preparation methods, prompts some experts to declare that perovskite solar cells are poised "to break the prevailing paradigm" by combining low cost and excellent performance.[52]

Perovskite solar cells can be fashioned using common wet-chemistry techniques. The simplicity of making solar-cell components via liquid-phase chemical reactions and depositing the materials by methods such as spraying and spin coating may make it possible for solar-cell manufacturers to eventually replace clean rooms and sophisticated manufacturing equipment currently used to produce photovoltaics with simple benchtop processes.[52]

Some of the key features of perovskite solar cells were uncovered in a 2009 Japanese study which involved treating a film of TiO_2 with a solution containing CH_3NH_3I and PbI_2. The researchers triggered a self-assembly process that coated the oxide with a layer of $CH_3NH_3PbI_3$ nanocrystals, one of the perovskite materials at the center of current research efforts. The group fashioned solar cells by sandwiching the perovskite-coated oxide films together with an organic electrolyte solution between conducting glass electrodes. They found that the triiodide cell readily generated electric current with a conversion efficiency of 3.8%.[54] Two years later, a South Korean team reported using a similar cell with optimized parameters to achieve a conversion efficiency of 6.5%.[55] From there, a team discovered the improvements possible when using a polyaromatic ring compound in the spirobifluorene family known as spiro-OMeTAD to achieve 9.7% efficiency.[56] Replacing TiO_2 with alumina (Al_2O_3) resulted in an unexpected 10.9% conversion efficiency.

In quick succession throughout 2013, a series of research papers appeared on a number of journal websites, each describing a slightly different perovskite solar-cell design, and each reporting efficiency improvements. The National Renewable Energy Laboratory, which is regarded internationally as the official verifier of solar-cell performance, has been confirming the performance of each improved version. In March 2015, researchers from the U.K. published information about a new low-temperature method for making perovskite solar cells so they can be used in high-efficiency, colorful, see-through photovoltaic films that could be laminated on windows or plastered on walls.[58,59] At least two companies have pledged to begin producing perovskite cells commercially as early as 2017: Oxford Photovoltaics of the U.K. and the Australian firm Dyesol.

Quantum Dots

What have come to be known as quantum dots are nanocrystals of semiconductor materials that emit a bright glow of a pure color when they're excited by light or an applied voltage.[60] Many alternative-energy experts are excited about quantum dot-based solar cells because they have a theoretical conversion of 45%. This is possible because when a single photon is absorbed by a quantum dot, it produces more than one bound electron-hole pair, or exciton, thereby doubling normal conversion efficiency numbers seen in single-junction silicon cells.[61] To date, no one has yet to come close to achieving that kind of efficiency, but the rates have been improving. For example, in 2014, research teams reported that quantum-dot solar cells using ternary $CuInS_2$ achieved a record of 7.04% (with certified efficiency of 6.66%).[62]

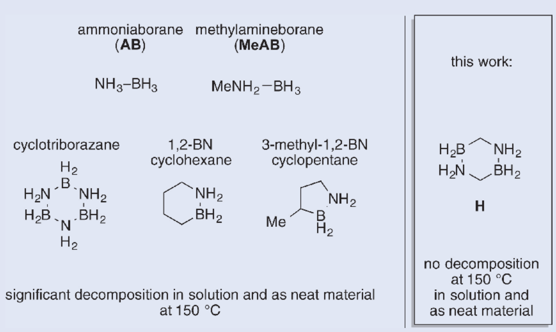
Also in 2014, researchers at the Massachusetts Institute of Technology (MIT) produced a quantum-dot solar cell that changes light to electricity with 9% conversion efficiency.[63] The MIT team says that the technology can be produced using an inexpensive production method that promises to keep manufacturing costs down.[60] And recently, a new class of organometal halide perovskite-based semiconductors has emerged as a viable candidate for quantum-dot solar cells.[64] These cells can use methylammonium lead iodide chloride ($CH_3NH_3PbI_2Cl$) perovskite. Other quantum-dot solar cells use cadmium, prompting some observers to question whether it is correct to call applications of the technology that use such metals "clean" or "green."[62]

Fuel Cells

In the last decade, the cost of fuel cells has dropped, vehicle range has gone up, and engineers have perfected their ability to perform in frigid weather and operate under other challenging conditions.[65] The first fuel-cell cars became available in the U.S. this year, but research by chemists and materials scientists continues to improve the technology the cells use to produce electricity by converting hydrogen and oxygen into water.

For example, over time, normal fuel-cell operation corrodes and oxidizes the carbon materials typically used as catalyst supports, leading to catalyst degradation and poor device performance. Metal nitrides have been studied as replacement supports, but they don't always tolerate the acidic conditions required for some fuels. A Cornell University team recently reported that a titanium chromium nitride material appears to overcome those problems.[66] The researchers used palladium-silver nanoparticles supported on a highly porous $Ti_{0.5}Cr_{0.5}N$ network, and they found it serves as an active and stable catalyst system in acidic and alkaline media across the typical range of fuel-cell voltages. Tests showed the material to be more active and durable than standard carbon materials.

Other important research relates to how to store the hydrogen fuel that fuel cells require. A research team from Boston College recently created an H_2 storage molecule that does not decompose even at extreme temperatures of up to 150 °C.[67] The researchers synthesized a new compound, a bis-BN cyclohexane, which may prove appropriate for applications such as backup generators that would store energy long-term in the event of a natural disaster.



Thermal stability of amine-borane-based chemical hydrogen storage materials.

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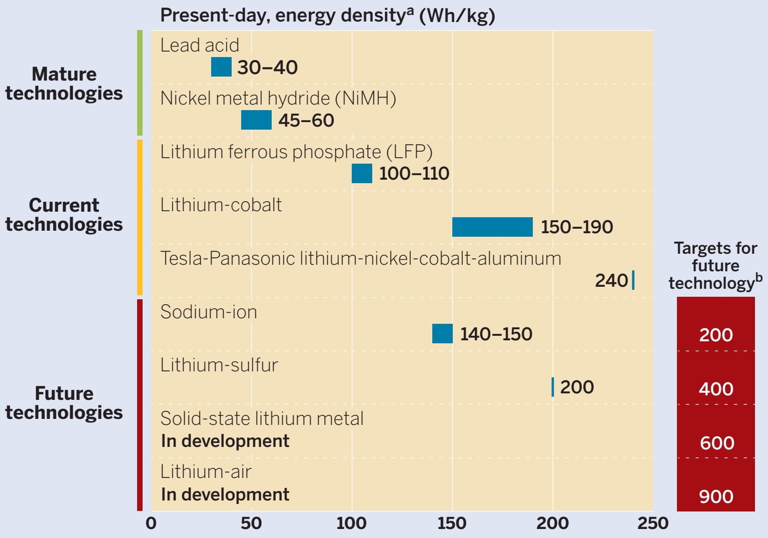
Battery Power

Sustainable energy-storage technologies are important because they can allow the best possible use of energy produced by renewable sources. A growing tendency in both energy storage and conversion systems is to imitate nature and its vast biodiversity.[68] Some researchers are trying to devise new batteries by taking inspiration from life chemistry, which is powered by chemical reactions that are dependent upon ion flux and membrane potential. Researchers recently identified a molecule with the formula $Li_2C_6O_6$ that can be synthesized from a renewable resource, myoinositol, and can reversibly insert and deinsert lithium ions associated with an energy density that is nearly twice what can be achieved with today's lithium methyl carbonate ($LiNi_{1/3},n_{1/3}Co_{1/3}O_2$) electrodes.[69]

A key component of a battery is the electrodes. Batteries with lithium-sulfur electrodes theoretically could store four times more energy than conventional lithium-ion batteries, promising longer play times for electronics and more miles for electric cars between charges. Researchers claim that commercialization of these batteries is within reach. A design using new materials, including graphene oxide with a sulfur coating, shows promise for extending battery life by maintaining a high storage capacity.[70] The battery was successfully charged and discharged, or cycled, 1,500 times, with impressive performance. Its initial energy storage capacity was 500 watt-hours per kilogram (Wh/kg) of battery material. In comparison, conventional lithium-ion batteries store about 200 Wh/kg, and the U.S. Department of Energy's target for electric vehicle batteries is 400 Wh/kg. After 1,000 cycles, the storage capacity dropped to 300 Wh/kg—still beating conventional lithium-ion batteries.[71]

A novel approach described by a team from Stanford University involves a new electrode material that they claim holds promise for grid-storage batteries that can work 30 years without a dramatic decline in performance. The new electrode material described by the Stanford researchers uses smaller hydrated potassium ions to carry charge between the two ends of a battery.[72] In the lab, the copper- and iron-based nano-engineered material was able to take 40,000 charge/discharge cycles while still maintaining an 80% storage capacity. By contrast, the lithium-ion batteries used in consumer electronics degrade noticeably after only a few hundred cycles.[72]

Some researchers are investigating alternatives to lithium because of concerns that the rapid growth in worldwide demand could lead to a shortage of the element. One option under investigation is sodium batteries.[73] U.K.-based Faradion is developing a sodium-ion battery that it says is on track to be one-third cheaper than lithium-ion batteries for the same performance.[74]



Battery developers have set targets to increase the amount of energy in cathode materials via a variety of formulations. a Energy per unit mass. Varies according to electrolyte and anode composition and battery structure. b Set by development efforts currently in progress. Timelines to reach targets vary.

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On a smaller scale, engineers at the University of Illinois, Urbana-Champaign, recently used holograms, which are the 3-D interference patterns of multiple laser beams, to precisely create porous blocks in light-curable polymers.[75] They then used these blocks as scaffolding to build electrodes that could be used for microbatteries to power microelectronic devices, such as sensors, medical implants, and radio frequency transmitters. The hologram process is compatible with conventional 2-D photolithography, which is widely used in the microelectronics industry.[76]

MOLECULAR SELF-ASSEMBLY

Molecular self-assembly is a process in which molecules (or parts of molecules) spontaneously form ordered aggregates without requiring human intervention. The interactions involved usually are noncovalent, and the structures generated are usually in equilibrium states or at least in metastable states. The process of molecular self-assembly is ubiquitous in chemistry, materials science, and biology.[77] An emerging concept in molecular self-assembly involves using previously underutilized bio-based plant materials.[78] For example, glycolipids generated from industrial byproducts such as cashew nut shell liquid can self-assemble to produce soft nanomaterials including lipid nanotubes, twisted/helical nanofibers, low-molecular-weight gels, and liquid crystals.[101]

Scientists are also developing molecules that spontaneously assemble into simpler versions of the extracellular matrix that surrounds many of the body's cells to provide a growth medium for cells, in particular for tissue engineering. The extracellular matrix comprises a complex web of biomolecules including proteins and sugar molecules that provides structure for tissues, facilitates intercellular communication, and traps nutrients. This field has focused mainly on self-assembling peptides.[79]

In a 2014 study, researchers from Brandeis University constructed a sugar-decorated molecule that self-assembles into a hydrogel that mimics the extracellular matrix.[80] Molecules on the surface of stem cells, often sugars, interact with this matrix in ways that are critical to stem cell differentiation and development. The gel encourages mouse embryonic stem cells to grow and zygotes to develop into blastocysts, suggesting that the molecule someday could help grow human tissue in the lab, according to the researchers. A key component of the hydrogel is glycoconjugate, a carbohydrate molecule covalently linked to other molecules that researchers are studying to understand how it may promote stem cell growth and which proteins are involved.[79]

Another team that included researchers from the same Brandeis lab, as well as Tufts University scientists, also designed a peptide that aggregates and engulfs cancer cells only when its phosphate group is removed.[81] The phosphate-free peptides have a hydrophilic end and a hydrophobic one, which allow them to assemble like lipids in a cell membrane. The negative charge on the phosphate groups creates electrostatic repulsion between the molecules and prevents the peptide from engulfing the cancer cells. This phosphate on-off switch is great for targeting cancer because some types of cancer cells overexpress alkaline phosphatase, an enzyme that cleaves phosphates.[79]

Molecular self-assembly is also being used to try to make artificial viruses that could be used as DNA-based drug delivery particles and structural materials. A team led by researchers at Wageningen University, in the Netherlands, has made progress toward that goal with a viral coat protein that self-assembles with DNA in a way that mimics the tobacco mosaic virus.[82] The researchers have shown that these virus-like particles can enter cells and protect the DNA from degradation.[83]

At the 2015 ACS National Meeting in Denver, researchers reported creating a collection of light-emitting platinum-organic metallacycles and metallacages.[84] Chemists at the University of Utah described how, by selecting combinations of linear and angular metal complexes and organic linking groups, they were able to build two- and three-dimensional molecules with fantastic geometries and versatile properties. The molecules may prove valuable for optoelectronic chemical sensors, as building blocks for polymeric hydrogels and fibers, as bioprobes for visualizing and monitoring physiological processes, and as therapeutics.

Other green chemistry approaches involving self-assembly include an approach developed by researchers from the University of Nottingham, in the U.K., involving self-assembly for fabricating trimesic acid monolayer structures on highly oriented pyrolytic graphite.[85] Another recently developed self-assembly technique allows chemists to build polymeric structures on the micrometer length scale. The resulting structures could ultimately be used for molecular electronics and drug delivery applications.[86]

NEXT-GENERATION CATALYST DESIGN

Twenty Presidential Green Chemistry Challenge Awards have recognized green catalysts.[87] A recent example is the technologies developed by Elevance, which uses a Nobel-prize-winning catalysis approach to produce high-performing, green specialty chemicals at advantageous costs. The catalyst technology breaks down natural oils and recombines the fragments into novel, high-performance green chemicals. These chemicals combine the benefits of both petrochemicals and bio-based chemicals. The technology consumes significantly less energy and reduces greenhouse gas emissions by 50% compared to petrochemical technologies. Elevance is producing specialty chemicals for many uses, including in personal care products, cleaning products, lubricants, and in candle waxes.[88] Some of these chemicals are commercially available.[89]

One of Dow Chemical's awards is for a green catalyst that reduces the environmental footprint associated with producing propylene oxide, one of the biggest volume industrial chemicals in the world.[90] The Hydrogen Peroxide to Propylene Oxide (HPPO) process, which was developed jointly with BASF, serves as a chemical building block for a vast array of products including detergents, polyurethanes, de-icers, food additives, and personal care items. The new process reduces the production of wastewater by as much as 70–80 percent and the use of energy by 35 percent over traditional technologies.

Another recently developed catalyst promises to be a less expensive and more efficient catalyst for cleansing diesel engine exhaust.[91] Developed by a team of scientists from the U.S., China, and South Korea, the catalyst uses Mn-mullite(Sm, Gd)Mn_2O_5—manganese-mullite materials containing either samarium or gadolinium to convert the toxic diesel-engine-exhaust product nitric oxide to the more benign nitrous oxide.[92]

A new catalyst developed by pharmaceutical companies Merck and Codexis for the green synthesis of sitagliptin, the active ingredient in the type 2 diabetes treatment Januvia™ may also be useful in the manufacturing of other drugs.[25] For example, a recent clinical trial showed that it may help patients with acute coronary syndrome.[93]

An example of green catalysts with the potential to reduce the pharmaceutical industry's environmental impact is the powerful series of tetra-amido macrocyclic ligand (TAML) catalysts modelled on natural peroxidase enzymes developed by Terry Collins of Carnegie Mellon University.[94] Collins thinks that using the catalysts at a late stage in the sewage treatment process would allow them to break down a wide variety of chemical residues, including those from Lipitor, Prozac, Zoloft, the contraceptive pill, and more, before they enter the environment.[95, 20, 96]

MOLECULAR DESIGN FOR REDUCED HAZARD

Dozens of Presidential Green Chemistry Awards recognize safer chemical products designed for use in a wide variety of industries.[97] In 2014, the Solberg Company earned an award for its halogen-free RE-HEALING Foams for use in fighting fires. Traditionally, firefighting foams used fluorinated surfactants, persistent chemicals that have the potential for environmental impacts. The RE-HEALING firefighting foam concentrates use a blend of non-fluorinated surfactants and sugars, and they work well with far less environmental impact. Control, extinguishing time, and burnback resistance are paramount to the safety of firefighters everywhere, and the new foams have excellent performance in each. The foams also achieve full regulatory compliance with existing fire protection standards.[98]

In 2013, Cargill, Inc. was honored for its Envirotemp™ FR3™ vegetable oil-based insulating fluid for high-voltage transformers. Until they were banned in the 1970s, polychlorinated biphenyls (PCBs) were used in the insulating fluid needed to prevent short circuiting and provide cooling for high-voltage electric transformers. After the PCB ban mineral oil became the primary replacement. Unfortunately, mineral oil is flammable and may be toxic to fish. Cargill's vegetable-oil-based transformer fluid is much less flammable, provides superior performance, is less toxic, and has a substantially lower carbon footprint.[99] According to a life-cycle assessment, a transformer using FR3™ fluid has a lower carbon footprint across the entire life-cycle of a transformer, with the largest reductions occurring in the raw materials, manufacturing, and transportation phases. The total carbon footprint of an electric transformer is about 55-times lower when using FR3™ fluid compared to mineral oil. This is all in addition to high biodegradability and the fact that FR3™ fluids are based on a renewable resource. Furthermore, there have been no known explosions or fires in the hundreds of thousands of transformers filled with FR3™ fluid since the product launched. FR3™ fluid has achieved numerous industry validations including EPA's Environmental Technology Verification and certification as a less flammable fluid by both Underwriters Laboratory (UL) and Factory Mutual Research Corporation.[99]

Faraday Technology, Inc. earned a Presidential Green Chemistry Award for a chrome plating technology that uses trivalent chromium, which is less toxic than hexavalent chromium, a known carcinogen. Applications for Faraday's plating process include as a high-performance chrome plating for many uses in military and commercial markets. This nearly drop-in replacement can reduce millions of pounds of hexavalent chromium without compromising performance.[100] Chrome coatings provide resistance to abrasives and sliding wear in heavy-duty machinery, especially pneumatic tubing. The FARADAYIC® TriChrome Plating process approach maintains the advantages of a functional chrome coating but vastly reduces the hazards associated with the plating process by using Cr(III). The new technology is easy to install in chrome plating facilities because only new plating bath electrodes are required. Use of Faraday's technology could eliminate about 13 million pounds of hexavalent chromium waste each year in the U.S. and as much as 300 million pounds worldwide.[100]

In 2012, Buckman International, Inc. earned a green chemistry award for enzymes that reduce the energy and wood fiber required to manufacture high-quality paper and paperboard. Traditionally, making strong paper required costly wood pulp, energy-intensive treatment, or chemical additives. Buckman's Maximyze® enzymes can achieve the same goal by modifying the cellulose in wood to increase the number of "fibrils" that bind the wood fibers to each other, thus making paper with improved strength and quality—without additional chemicals or energy. Buckman's process also allows papermaking with less wood fiber and higher percentages of recycled paper, enabling a single plant to save $1 million per year.[101]

Maximyze® improves strength so the weight of the paper product can be reduced or some of the wood fiber can be replaced with a mineral filler such as calcium carbonate. Maximyze® treatment also uses less steam because the paper drains faster (increasing the production rate) and uses less electricity for refining. The treatment is less toxic than current alternatives and is safer to handle, manufacture, transport, and use than current chemical treatments used in paper production.[101]

V. OCCUPATIONAL OUTLOOK

The global market for green chemistry is predicted to grow exponentially until the end of this decade. Experts project that the industry's annual growth rate will be 48.5% during this period, transforming what was a $2.8 billion industry in 2011 to $98.5 billion by 2020.[102] The three main themes driving green chemistry and engineering are waste minimization in chemical production processes; replacement of existing products with less toxic alternatives; and a shift toward renewable feedstocks.[103] The key industries where green chemistry applications are expected to take hold or grow in the next decade are pharmaceuticals, fine chemicals, plastics, textiles, paints and coatings, paper and pulp, agrochemicals, adhesives, nanotechnologies, and fuel and renewable energy technologies.

Green chemistry includes opportunities in the four main career pathways available to chemical professionals: higher education, industry, government, and entrepreneurial careers.[104] As interest in green chemistry accelerates, academic courses specifically tailored to sustainable chemistry are increasing in number, which is good for both chemists who are interested in specialized green chemistry training and those who aim to teach green chemistry eventually.[105]

A major requirement for many careers in sustainable chemistry is to be a good chemist, and on-the-job training may be available for those who lack green chemistry education. Biology knowledge also can be important for green chemists, particularly those who work on biologically derived materials.[105] It can require broad thinking because green chemists can be called on to look at all aspects of production processes, including energy inputs, side-products, solvent use, engineering, and transportation.[13]

Green chemistry can be a major component in many careers:

- **Academic Chemists** work in the growing number of universities that offer green chemistry coursework or programs. There are more opportunities for curriculum development in green chemistry programs than with conventional academic chemistry positions.[106] A growing number of businesses are collaborating with academic programs, creating more opportunities for green chemists.[105]

- **Biofuels Plant Engineers** are involved in the large-scale production of alternative, bio-based fuels, such as ethanol-added gasolines, biodiesel, and other new biofuels at biofuel production facilities.[107]

- **Biomolecular Engineers** can be an important part of any green research team. Although the traditional role of chemical and biomolecular engineers has been to develop processes to efficiently produce chemical products on an industrial scale, modern biomolecular engineers tend to be much more involved in all phases of research and development. Green chemistry engineers work on projects such as cleaner smelting and refining processes, and how to turn crops or trees into sustainable fuels as well as biodegradable plastics and fabrics.[107]

- **Pharmaceutical Chemists** aid the drug industry in its ongoing efforts to develop medicines with less harmful side-effects, using processes that produce less toxic waste.[25] The chemical production of drug molecules for commercial use is vastly different from conventional bulk manufacture of, for instance, commodity chemicals. More than half the mass constituting a process stream in the chemical manufacture of active pharmaceutical ingredients generally stems from the solvent(s) utilized; 80–90% if water is included. This means that the potential for production improvements is huge.[108] At some companies, environmental specialists, pharmaceutical development chemists, chemical engineers and medicinal chemists all work together to improve drug manufacturing.[105]

- **Recycling Specialists** work with businesses and municipalities to aid in reusing and recycling chemicals and other wastes produced by industrial processes and by everyday household activities. These specialists develop and run their recycling programs.[107]

- **Regulatory Specialists** work with governmental organizations and policymakers to implement and maintain mechanisms in place to foster green chemistry research and education. At the local, state, and federal levels, these programs can play a key role in prioritizing and promoting green chemistry and sustainable technologies.[109]

- **Research Chemists** undertake research to discover more benign alternatives to the many thousands of hazardous chemicals used in modern refining and manufacturing processes. Hundreds of research chemists are employed in green chemistry. They conduct research in many areas, including safer and less-polluting industrial solvents and plant-based substitutes for petrochemical products.[107]

VI. LOOKING FORWARD

Green chemistry is here to stay, and the discipline is likely to have an even greater impact in the coming decades. The rapid rate of its acceptance as a scientific discipline and the ever-expanding rate of green chemistry's influence suggest that the vast majority of chemicals used in commerce may be benign by design within your lifetime. Furthermore, you may become a significant contributor to the positive changes that industrial green chemistry is creating and will continue to catalyze in our world.

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