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Presidential Green Chemistry Challenge Awards Program:

Summary of 2015 Award Entries and Recipients

GREEN CHEMISTRY CHALLENGE

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Presidential Green Chemistry Challenge Awards Program: Summary of 2015 Award Entries and Recipients

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Introduction

Each year chemists, engineers, and other scientists from across the United States nominate their technologies for a Presidential Green Chemistry Challenge Award. This prestigious award highlights and honors innovative green chemistry technologies, including cleaner processes; safer raw materials; and safer, better products. These awards recognize and promote the environmental and economic benefits of developing and using novel green chemistry.

The U.S. Environmental Protection Agency (EPA) celebrates this year's innovative, award-winning technologies selected from among scores of high-quality nominations. Each nomination must represent one or more recently developed chemistry technologies that prevent pollution through source reduction. Nominated technologies are also meant to succeed in the marketplace: each is expected to illustrate the technical feasibility, marketability, and profitability of green chemistry.

Throughout the 20 years of the awards program, EPA has received 1,653 nominations and presented awards to 104 winners. By recognizing groundbreaking scientific solutions to real-world environmental problems, the Presidential Green Chemistry Challenge has significantly reduced the hazards associated with designing, manufacturing, and using chemicals.

Each year our 104 winning technologies are together responsible for:

- Reducing the use or generation of 826 million pounds of hazardous chemicals
- Saving 21 billion gallons of water
- Eliminating 7.8 billion pounds of carbon dioxide releases to air

And adding the benefits from the nominated technologies would greatly increase the program's total benefits.

This booklet summarizes entries submitted for the 2015 awards that fell within the scope of the program. An independent panel of technical experts convened by the American Chemical Society Green Chemistry Institute® judged the entries for the 2015 awards. Judging criteria included health and environmental benefits, scientific innovation, and industrial applicability. Six of the nominated technologies were selected as winners and were nationally recognized on July 13, 2015, at an awards ceremony in Washington, D.C.

Further information about the Presidential Green Chemistry Challenge Awards and EPA's Green Chemistry Program is available at www.epa.gov/greenchemistry.

Note: The abstracts in this document were submitted in nominations for the 2015 Presidential Green Chemistry Challenge Awards. They were copied directly from the nominations and have only been edited for stylistic consistency. They are not written or officially endorsed by the Agency. These abstracts represent only a fraction of the information provided in the nominations from which they were copied; judging was conducted on all information in the nominations. Claims made in these abstracts have not been verified by EPA. Mention of trade names, products, or services does not convey official EPA approval, endorsement, or recommendation.

Academic Award

Professor Eugene Y.-X. Chen, Department of Chemistry, Colorado State University

Greener Condensation Reactions for Renewable Chemicals, Liquid Fuels, and Biodegradable Polymers

> **Innovation and Benefits**
>
> Condensation reactions are necessary for the production of chemicals, pharmaceuticals, fuels, and materials. However, they generate a large amount of waste and are commonly metal-mediated. To address these problems, Professor Chen developed a condensation reaction using a biomass platform chemical (5-hydroxymethylfurfural) for the production of renewable chemicals, fuels, and polymeric materials. Additionally, he developed a polycondensation using acrylic monomers to create biodegradable unsaturated polyesters. This new technology offers two novel synthetic pathways that are catalytic, waste-free and metal-free.

In condensation reactions, as two molecules combine to form a larger molecule, small molecules split off. Because of the loss of this small molecule, such as water, hydrogen chloride, ethylene, methanol, or acetic acid, these reactions are intrinsically waste-generating. Additionally, condensation reactions are often mediated by metals. For the production of jet or other transportation fuels, fine chemicals, and bioplastics, biomass platform chemicals, such as 5-hydroxymethylfurfural (HMF), need to be upgraded through the C–C bond forming, condensation reaction into chain-extended, higher energy-density substances, such as 5,5'-dihydroxymethylfuroin (DHMF). The twelve-carbon DHMF is a new bio-derived building block that can be catalytically transformed into renewable fire chemicals, polymeric materials, and oxygenated biodiesel or premium alkane jet fuels.

Direct HMF coupling is not possible through aldol self-condensation of HMF because it lacks a necessary hydrogen atom in the α-position to the carbonyl group. Existing alternative methods, such as metal-mediated cross-aldol condensation, have to use other enolizable petrochemicals. These methods also suffer from the unavoidable waste inherent in conventional condensation reactions. Professor Chen and his graduate student Dajiang (DJ) Liu developed a new condensation technology that uses an organic catalyst, such as an *N*-heterocyclic carbene (NHC), to reverse the polarity of the HMF carbonyl (umpolung), to enabling a solvent-free direct condensation coupling of HMF into DHMF with quantitative yield and 100% atom-economy.

Professor Chen and his postdoctoral fellow Dr. Miao Hong also developed a polycondensation method, called "Proton-Transfer Polymerization" (HTP), which uses an NHC catalyst to polymerize dimethacrylates uniquely into biodegradable polyesters with 100% atom-economy. The resulting unsaturated polyesters are of interest for producing tailor-made biodegradable polyester materials through post-functionalization and cross-linking. The synthesis of such polyesters from dimethacrylates is not possible by a metal-based process, such as the Ru or Momediated acyclic diene metathesis, because such methods are ineffective for polymerization of electron-deficient, conjugated or sterically demanding diolefins such as dimethacrylates. In contrast, existing methods polymerize dimethacrylates through non-condensation, polyaddition pathways into non-biodegradable polymethacrylates.

The new condensation technology not only offers two novel condensation synthetic pathways towards the HMF upgrading and polyester production from acrylic monomers, both processes of which are not possible by any existing technologies, it also exhibits important hallmarks of a green technology by being catalytic, metal-free and 100% atom-economical as well as solvent-free (for the HMF upgrading) or biodegradable (for the polyester production).

Small Business Award

Renmatix

The Plantrose® Process: Supercritical Water as the Economic Enabler of Biobased Industry

Innovation and Benefits

The biobased industry requires access to high volume, low cost sugars from a wide variety of biomass. Technologies that extract these second generation sugars from cellulose are typically more expensive than first generation sugars, like corn and cane. Renmatix developed the Plantrose® process, a technology that uses supercritical water to deconstruct biomass and produce cost-advantaged cellulosic sugars. Plantrose® technology enables affordable renewable materials as alternatives to petroleum-derived chemicals and fuels.

Traditional sugar sources, like corn and cane, are expensive feedstocks for producing relatively low value, highvolume products like fuels and chemicals. Unfortunately, the traditional second generation technologies (acid, enzymes, and solvents) that were designed to extract these low value cellulosic sugars lack the practical economics to even compete with first generation sugars, let alone traditional petrochemical sources. In part, this is due to the capital expense of historical technologies like mineral acids and enzymatic processes that hydrolyze cellulosic feedstocks. This reality has severely limited the market adoption and broad integration of cellulosics.

Renmatix's Plantrose® process, which uses supercritical water to deconstruct biomass, provides cost-advantaged cellulosic sugars by using primarily water for conversion reactions. The two-step continuous process deconstructs a range of plant material into renewable feedstocks to produce separate streams of xylose and glucose. After sugar extraction, remaining lignin solids can be burned to supply the bulk of the heat energy required for the process (or utilized in higher value applications like adhesives or thermoplastics).

In the first step, biomass and water are pumped together, heated, and fed into a fractionation reactor, where the hemicellulose is solubilized into a five-carbon sugar stream. In the second step, the cellulose and lignin that were filtered away from the initial sugar steam are pumped into the supercritical hydrolysis reactor. In the reactor, water acts as both a solvent and catalyst, decrystalizing and dissolving the cellulose and hydrolyzing the cellulose polymers. The temperature and pressure of the supercritical water system can be adjusted for very specific reaction condition control, enabling the use of smaller continuous reactors for large-scale commercial production.

Renmatix's technological innovation, the use of water-based chemistry instead of enzymes, and/or acids, provides a cleaner, faster, and lower-cost method for deconstructing biomass into cellulosic sugars. Those sugars become the building blocks for a multitude of renewable downstream technologies to serve significant biochemical market demand – and begin providing meaningful volumes of plantrochemicals, in lieu of the conventional petroleum-derived equivalents. Renmatix partners and customers will build their own biorefineries by licensing the Plantrose® process to convert locally available biomass into cellulosic sugars, enabling profitable scale-up of biochemical, cellulosic ethanol, and advanced biofuels markets worldwide.

LanzaTech Gas Fermentation Process

LanzaTech Inc.

Innovation and Benefits

Waste gas is an attractive resource for fuel and chemicals production due to its low value and high production. LanzaTech microbes utilize waste gas streams with a range of compositions to produce fuels such as ethanol and chemicals such as 2,3-butanediol at high selectivities and yields. Combining robust microbes, innovative bioreactor design, and process development has enabled rapid scale-up to take place, with two 100,000 gallon/year demonstration scale facilities in China using steel mill off gases for ethanol production.

Carbon gas streams are often byproducts of established processes. When they cannot be utilized efficiently they are wasted, normally through venting or flaring. The conversion of carbon monoxide-rich gases through synthetic chemical pathways, for example Fischer-Tropsch or methanol synthesis, requires that H_2 be available in the synthesis gas. Waste industrial gases often do not contain H_2 and therefore cannot be converted using conventional synthetic pathways. Gas fermentation technologies have also stalled because gas toxicity requires expensive microbe conditioning and leads to gas solubility limitations.

LanzaTech developed a method to utilize gas streams with a range of CO and H_2 compositions to produce fuels such as ethanol and chemicals such as 2,3-butanediol at high selectivities and yields. While both CO/CO_2 and H_2 are utilized in the process, LanzaTech's proprietary microbes are also able to consume H_2-free CO-only gas streams, due to the operation of a highly efficient biological water-gas shift reaction occurring within the microbe. The process is facilitated by the enzyme-catalyzed chemistry of the Wood-Ljungdahl pathway whereby CO_2 and CO can be converted in a water-gas shift reaction catalyzed by carbon monoxide dehydrogenase (CODH). Through a series of intermediates, CO and CO_2 are ultimately fixed as acetyl-CoA by the CODH/ACS complex.

The process is a highly efficient conversion of acetyl-CoA to ethanol, as this is actually linked to growth of the organism. LanzaTech has also manipulated the organism for high yields of specific products (e.g. the microbes can make a single enantiomer of 2,3-butanediol), eliminating the need to separate and find markets for co-products. These microbes operate close to ambient temperature and atmospheric pressure and are tolerant to high levels of toxicity. LanzaTech has overcome the gas solubility limitations through proprietary bioreactors that increase volumetric mass transfer by creating more interfacial area per volume bubble size. This results in higher product yield and productivity.

Life cycle analysis studies performed in partnership with MTU, E4Tech, and Tsinghua University have shown that the LanzaTech gas fermentation process can produce fuels from steel mill off-gases with GHG emissions that are 50-70% lower than those of fossil fuels. Particulate matter and NO_x emissions are also reduced. LanzaTech's gas fermentation simultaneously makes valuable fuels and/or chemicals while mitigating the environmental effects of waste and residual industrial emissions. LanzaTech has partnered with over 10 global Fortune 500 Companies across a variety of sectors, including chemicals companies, INVISTA and EVONIK.

Greener Reaction Conditions Award

Soltex (Synthetic Oils and Lubricants of Texas)

A Novel High Efficiency Process for the Manufacture of Highly Reactive Polyisobutylene Using a Fixed Bed Solid State Catalyst Reactor System

Innovation and Benefits

Polyisobutylene (PIB), an intermediate used to produce additives for lubricants and gasoline, is made using a liquid polymerization catalyst. This catalyst is hazardous and must be separated and washed after use which generates substantial amounts of wastewater. Soltex has developed a new process that is based on a solid catalyst in a fixed bed reactor. Soltex produces a high purity product with significantly reduced catalyst usage and no water wash, which reduces capital investment.

Polyisobutylene (PIB) is used in the production of dispersants and detergents for lubricants and gasolines. PIB is an isobutylene polymer containing one double bond per polymer molecule. In high-reactive PIB, the double bond is at or near the end of the polymer chain in a branched position making the product more reactive. When the double bond is located at internal positions in the backbone of the polymer, PIB is less reactive, creating low-reactive PIB.

Traditional processes to make high-reactive PIB use a liquid polymerization catalyst. The catalyst is continually fed to the reactor and mixed with isobutylene monomer. The liquid catalyst is toxic and corrosive and requires special handling systems and procedures to avoid exposure and vapor release. As the reaction mixture leaves the reactor, the catalyst must be immediately neutralized to stop the reaction and separated. The separation process involves washing the neutralized catalyst complex from the reaction mixture with copious amounts of water to remove all catalyst residues. Trace amounts are corrosive to subsequent processing steps and detrimental to product quality and stability. Neutralized catalyst cannot be recycled. This process substantially increases plant capital investment, increases operating costs, and generates approximately as much wastewater as product.

Soltex's new process is based on a novel solid catalyst composition using a fixed bed reactor system. A solid catalyst, in the form of a bead or other convenient geometrical shapes and sizes, is packed into a vessel to form a stationary, completely contained bed. Isobutylene monomer is fed to the reactor at a controlled rate and passes over the solid catalyst allowing the polymerization to occur. The polymer mixture exits the reactor at the same controlled rate. This reactor effluent contains minimal catalyst residues, therefore no subsequent catalyst separation or water wash is required.

The Soltex process, using this solid catalyst composition, produces high yields of high purity product with significantly lower catalyst usage. It is a simplified, highly efficient operation with substantially reduced capital investment, low operating and catalyst costs, and no water wash generation.

Designing Greener Chemicals Award

Hybrid Coating Technologies/ Nanotech Industries

Hybrid Non-Isocyanate Polyurethane/Green Polyurethane™

Innovation and Benefits

Green Polyurethane™ is a hybrid non-isocyanate polyurethane (HNIPU) manufactured by Hybrid Coating Technologies that does not use isocyanates at any point in the production process. Isocyanates irritate the eyes, lungs, skin and throat, are a potential carcinogen, and can cause occupationally-induced asthma. Green Polyurethane™ applications provide a reduction in health and environmental hazards with simultaneous improvements in mechanical and chemical resistance properties. Green Polyurethane™ is also cost competitive compared to conventional polyurethane coatings and foam.

Isocyanates are critical components used in conventional polyurethane products such as coatings and foam. However, exposure to isocyanates is known to cause skin and respiratory problems and prolonged exposure has been known to cause severe asthma and even death. Isocyanates are also toxic to wildlife. When burnt, isocyanates form toxic and corrosive fumes including nitrogen oxides and hydrogen cyanide. Due to these hazards, isocyanates are regulated by the EPA and other government agencies.

To address the health and environmental hazards associated with conventional polyurethanes, Hybrid Coating Technologies (HCT) has developed a hybrid non-isocyanate polyurethane (HNIPU), also called "Green Polyurethane™." HNIPU is formed from a reaction between mixture of mono/polycyclic carbonate and epoxy oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. The result is a crosslinked polymer with β-hydroxyurethane groups of different structure.

HCT developed a novel concept for generating new multifunctional modifiers for "cold" cure epoxy-amine compositions, namely hydroxyalkyl urethane modifiers (HUM), and subsequently developed HUMs based on renewable raw materials (vegetable oils), which are now used for SPF and UV-cured acrylic polymer based coatings. Utilizing HUM provides the cured composition with superior coating performance characteristics including pot life/drying times, strength-stress properties, bonding to a variety of substrates and appearance. Other characteristics, such as weathering and chemical resistance, are also strengthened while HNIPU is not sensitive to moisture in the surrounding environment. HCT also developed a version of its epoxyamine hydroxyurethane grafted polymer that replaces corrosive low molecular weight amines with less hazardous high molecular weight amines.

HNIPU is a safer chemical formulation for use in polyurethane and epoxy applications such as coatings and foam. It also has improved mechanical and chemical resistance properties, replaces up to 50% of its epoxy base with renewable resources (vegetable derived) and is cost competitive compared to other conventional polyurethane and epoxy products.

HCT is currently manufacturing coatings in California with a production capacity of 100,000 tons. Applicators using HNIPU coatings report cost savings between 30-60% due to the product's improved safety profile and excellent properties. HCT expects to see similar benefits for applicators using its spray polyurethane foam once it becomes commercially available in the next 1-2 years.

Specific Environmental Benefit: Climate Change Award

Algenol

The Algenol Biofuel Process: Sustainable Production of Ethanol and Green Crude

Innovation and Benefits

Algenol has developed genetically enhanced strains of cyanobacteria for production of ethanol and "green crude" that can then be converted into replacements for petroleum-derived chemicals and fuels. Algenol's cyanobacteria (blue-green algae) are able to divert over 80% of the carbon that they capture through photosynthesis into the ethanol production pathway. The Algenol technology utilizes waste CO2 from industrial emitters and relies on patented photobioreactors and proprietary separation techniques for low-cost and low-carbon footprint fuel production.

Ethanol can be used as a transportation fuel directly or blended with gasoline. Algenol has developed technologies for the recombinant and classical genetic improvement of cyanobacteria (blue-green algae), leading to strains that divert more than 80% of the photosynthetically fixed carbon into ethanol without a decrease in overall photosynthetic yield. This has led to improved biofuel productivity, higher economic returns, minimal waste production, and a lower carbon footprint.

Algenol's hybrid algae are grown in saltwater in proprietary photobioreactors (PBRs) which minimize heterotrophic contamination and reduce water use. Photosaturation is a common limiting feature in aquatic photosynthesis and occurs when the rate of photon absorption exceeds the rate that the algae can use the energy for product formation (i.e., carbon fixation), such that the energy of the excess photons is wasted through non-photosynthetic processes. Algenol's vertical PBR system offers a productivity advantage over horizontal systems by delivering a more dilute irradiance over a greater surface area of the PBR, thereby limiting photosaturation.

Algenol has also developed proprietary downstream processes for energy-efficient recovery of fuel-grade ethanol. In collaboration with Pacific Northwest National Laboratory (PNNL), Algenol has applied hydrothermal liquefaction technology to convert the spent biomass into green crude. Algenol is also working with PNNL, National Renewable Energy Laboratory, and Georgia Tech on development of higher-value green chemical production concepts.

Algenol has demonstrated about 15–20 times the productivity of corn-based ethanol on a per acre basis. In the past five years, Algenol moved this technology from laboratory scale to pilot scale and is currently completing the construction and commissioning of a 2-acre facility as part of the IBR Project ($52 million project with a $25 million grant from the U.S. Department of Energy). The overall process reduces the carbon footprint relative to gasoline by 60–80% according to peer-reviewed published work from Georgia Tech. A single 2,000 acre commercial Algenol module is the equivalent of planting 40,000,000 trees or removing 36,000 cars from the road. Broad deployment of this technology, with its low carbon footprint, can contribute to CO_2 emission reduction targets and lower dependence on fossil fuel resources.

Entries from Academia

Photocatylic Oxidations of Ethers with Visible/Near UV Light and the Development of a Continuous Flow Photoreactor

Professor Reynaldo D. Barreto, Department of Biology and Chemistry, Purdue University North Central

Water soluble ethers such as methyl *t*-butyl ether (MTBE) and 1,4-dioxane (DIOX) are common solvents and gasoline additives and have found their way into public water systems. Other compounds such as ethyl *t*-butyl ether (ETBE), *t*-amyl methyl ether (TAME) and diisopropyl ether (DIPE) are also water soluble ethers and potential sources of water contamination. This work shows that MTBE, ETBE, and TAME along with 1,4-dioxane and DIPE are actually undergoing a degradation process involving near UV light of 320-375 nm. Using the a batch slurry process incorporating a borosilicate filter that eliminated short wavelength UV light, rate constant for degradation for MTBE, 4.2×10^{-4} s^{-1}, ETBE, 4.63×10^{-4} s^{-1} and TAME, $7.72 \times 10^{-4} s^{-1}$ were observed, comparable with those seen previously, while 1,4-dioxane and DIPE showed rates of 1.1×10^{-3} s^{-1}, and 6.3×10^{-4} s^{-1}, respectively. In all cases, over 80% of the initial substrate was destroyed in less than 150 minutes.

Using these results, a series of continuous flow photoreactors were designed using conventional fluorescent light source. An in-series design, using TiO_2-coated glass tubing, produced 10-15% substrate conversion. A larger in-parallel design using a purgeless oxygenation system and TiO_2-coated glass beads, also yielded a 10-15% conversion rate even at higher flow rates. These reactors clearly demonstrated that water soluble ethers can be degraded using simple fluorescent lighting. While results are preliminary, substrate degradation of up to 15% or 2.0-3.0 mg/L was observed in less than 1 meter of reaction flow distance.

Catalytic Cross-Couplings Using a Sustainable Metal and Green Solvents

Professor Neil Garg, Department of Chemistry and Biochemistry, University of California, Los Angeles

The nominated technology involves one of the most important classes of organic reactions used in modern research: namely, transition metal-catalyzed cross-coupling reactions. These reactions are amongst the most effective and widely used means of constructing carbon–carbon (C–C) and carbon–heteroatom (C–X) bonds. The importance of cross-coupling methodology is underscored by the 2010 Nobel Prize given “for palladium-catalyzed cross-couplings in organic synthesis.” Arguably, the most widely used and reliable coupling methodology is the Suzuki-Miyaura coupling to forge C–C bonds. These couplings have transformed the landscape of drug discovery and development.

Given the importance of the Suzuki-Miyaura coupling, the development of “greener” variants has been a topic of great interest. The American Chemical Society’s Green Chemistry Institute’s Pharmaceutical Roundtable has highlighted the limitations associated with these couplings and, more recently, has incentivized academic research in this area by making it the focus of their 2012 grant cycle. Since 2008, the Garg laboratory at the University of California, Los Angeles has pursued the development of “greener” and more sustainable Suzuki-Miyaura couplings for use in academic and industrial applications. The key green chemistry principles targeted include: (a) developing Suzuki-Miyaura couplings that do not require the use of the precious metal palladium, (b) discovering conditions that proceed in green solvents, rather than less attractive solvents (source reduction), and (c) uncovering a unified set of reaction conditions to enable the Suzuki-Miyaura coupling of an unprecedented range of substrates.

By targeting the aforementioned challenges systematically, the Garg laboratory has developed Suzuki-Miyaura couplings that use inexpensive nickel-catalysis, proceed in “greener” solvents such as alcohols, and are tolerant of a vast range of substrates, including heterocycles, in addition to a variety of electrophiles (e.g., halides and pseudohalides). These studies have led to discoveries in fundamental chemical reactivity and new tools for cross-coupling chemistry. Finally, these efforts have fueled educational initiatives in green chemistry where undergraduate students have performed "green" Suzuki-Miyaura couplings in an instructional laboratory.

Professor Stuart Licht, Department of Chemistry, George Washington University

A Solar Chemical Process to End Anthropogenic Global Warming: STEP Generation of Energetic Molecules

Anthropogenic levels of atmospheric carbon dioxide (CO_2) have reached record levels. The global warming consequences of increasing atmospheric CO_2 concentrations encompass species extinction, population displacement, glacier and ice cap loss, sea level rise, droughts, hurricanes and flooding, and economic loss. One path towards CO_2 reduction is to utilize renewable energy to produce electricity. Another, less explored, path is instead to utilize renewable energy to directly produce societal staples such as metals, fuels, bleach, fertilizer, and cement. STEP is a green chemical process that reduces carbon pollution at its source.

STEP – Professor Stuart Licht's Solar Thermal Electrochemical Process – uses the full sunlight spectrum to produce essentials in excess of 50% solar efficiency in unusual green chemical processes without carbon pollution. The processes for making iron, cement, and ammonia for fertilizer have emitted massive amounts of CO_2 to the atmosphere for centuries. Instead, new molten salt chemistry allows solar thermal energy to drive production without any CO_2 emission. STEP distinguishes radiation that is sufficient to drive photovoltaic charge transfer from solar thermal energy that decreases the chemical splitting energy. The STEP process provides a new pathway to use renewable energy by tuning the chemical reaction energy, rather than the semiconductor bandgap energy, to match and efficiently capture sunlight. As a result, electrosynthesis occurs at solar energy efficiency greater than any photovoltaic conversion efficiency, and the converted solar energy is stored in the products. STEP has been experimentally demonstrated with the efficient, CO_2-free formation of (a) ammonia, (b) fuels, (c) organics, (d) iron, (e) direct atmospheric carbon capture, (f) cement, (g) water treatment, (h) chlorine, and (i) desalinization.

Professor Kent Voorhees, Department of Chemistry, Colorado School of Mines

Rapid Bacteriophage-Based Bacterial Identification and Antibiotic Resistance Test

Antibiotic-resistant bacterial infections are a serious and growing global health problem. Conventional antibiotic resistance determination techniques typically require laborious and time-intensive culture-based assays, which take up to 72 hours and expend an inordinate amount of disposable plastics and bacterial growth media. In contrast, the Colorado School of Mines (CSM) bacteriophage amplification platform allows for a greener alternative by (a) enabling rapid simultaneous identification and antibiotic resistance determination without the need for extensive culturing, (b) minimizing the use of disposable plastics, and (c) reducing overall environmental impact. More importantly, with respect to its impact on human diagnostics, these attributes result in more user-friendly tests with significantly reduced testing times of less than five hours. First described, developed, and patented by the Advanced Biodetection Technologies Laboratory at CSM, it has advanced the technology through several key breakthroughs that have applied the technology as a greener alternative for sensitive and rapid identification and detection of *Burkholderia*, *Listeria*, and *Enterococcus* while maintaining the technology's minimal environmental footprint.

High-Yield and High-Purity Hydrogen Production from Carbohydrates via Synthetic Enzymatic Pathways

Professor Yi-Heng Percival Zhang, Department of Biological Systems Engineering, Virginia Tech

Hydrogen is one of the most important chemical intermediates (i.e., $~100 billion) and will become the best future transportation fuel and energy storage compound. The production of carbon-neutral hydrogen from renewable resources, the storage of high-density hydrogen and costly infrastructure are the three greatest challenges for the hydrogen economy. Carbohydrates, including cellulose, hemicellulose, starch, and sucrose, are the most abundant renewable bioresource. Professor Zhang has designed *in vitro* non-natural synthetic enzymatic pathways that can release all of the hydrogen from a variety of carbohydrates and water under mild reaction conditions (e.g., 30-60°C, atmospheric pressure, and aqueous solution), that is, the production of two H_2 per carbon of carbohydrates. These synthetic enzymatic pathways are comprised of more than 10 enzymes from different sources as well as coenzymes. Also, these biochemical conversions have energy conversion efficiencies more than 100%, meaning that room-temperature thermal energy can be converted to hydrogen energy for the first time. Also, Professor Zhang suggested the use of carbohydrates as a high-density hydrogen carrier with a gravimetric density of up to 14.8 H_2 mass%, far higher than the Department of Energy's hydrogen storage goals. To decrease its production costs, Professor Zhang has developed a number of ultra-stable enzymes with total turn-over numbers of up to 10^9 mole of product per mole of enzyme and changed the coenzyme preference of redox enzymes to low-cost and ultra-stable biomimetic coenzymes. To meet industrial needs, his team has increased its production rates to 150 mmole H_2/L/h by 800 times, suitable for small-size distributed hydrogen generator systems that utilize local biomass resources to produce hydrogen for fuel cell vehicles. This work was done in collaboration with Professor Mike Adams of the University of Georgia, Drs. Jonathan Mielenz and Barbara Evans at the Oak Ridge National Laboratory, and Dr. Joseph Rollin at Cell Free Bioinnovations Inc.

Pathex®/PathShield™ Antimicrobial Filter Media for the Control of Bacteria in Stormwater and Industrial Process Waters

A S Filtration™, LLC

Pathex® antimicrobial filter media (PathShield™ is alternate brand name) reduces and controls coliform bacteria in industrial wastewater, recirculating cooling towers, heat transfer systems, industrial fresh water systems, stormwater, service water and auxiliary systems, and municipal wastewater treatment.

The unique surface bond of this organosilicon quaternary ammonium chloride compound to siliceous materials, without release of chemicals, offers a new approach to water treatment. Pathex®/PathShield™ kills bacteria as it moves over the filter media granules. The media is effective, even at loading rates up to 20 gpm/ft^2, without releasing, discharging, or leaching antimicrobial agents, chemicals, harmful disinfection byproducts, or heavy metals. When used within side-stream filters for industrial cooling towers, the filter media achieves 20% water savings. The filter media can also achieve up to 40% energy savings due to enhanced temperature exchange capacity from biofilm reduction and at least a 90% decrease in the use of traditional chemical biocides.

It is projected that Pathex®/PathShield™ antimicrobial filter media annually can eliminate the use of 486 million pounds (243,000 tons) of chemical biocides, repurpose 280 billion gallons of makeup water for potable water, and eliminate the need for biocide chemical removal from the same 280 billion gallons of water at local waste treatment facilities. The filter media is stable, non-toxic, not consumed, non-corrosive, requires no power source to kill bacteria, and is not affected by temperature changes.

Using Bioethanol as a Raw Material, to Produce: 1. SAFEN: A Low Cost Nematicide and Fungicide, Based on Ethyl Formate, which is Generally Regarded as Safe by the FDA, and Which Biodegrades Into Two Naturally Occurring Substances, with No Lasting Detrimental Effects to Air, Soil and Water; and 2. Ethyl Formate in a Second Development as a Suitable Raw Material for Propionic Acid and Acrylate Production

Acid-Amine Technologies, Inc. (AAT)

SAFEN is a green chemical nematicide and fungicide that is environmentally friendly to air, soil, and water. The Montreal Protocol emphasized the need for pesticides that were environmentally friendly and eliminated the use of methyl bromide, an ozone depleting agent commonly used worldwide. SAFEN represents a green alternative to methyl bromide. SAFEN's components are made from low cost raw materials and its primary component ethyl formate is made from ethanol, a renewable resource. SAFEN's simple molecules biodegrade into naturally-occurring substances after use.

Aequor, Inc.

New Chemical Impedes Biofilm Formation and the Adhesion of Foulers

Aequor has developed novel, non-toxic chemical compounds that inhibit the attachment of bacteria, microfoulers (corroders, contaminants, fungi), and macrofoulers (algae, mussels, barnacles) to living and inert surfaces. Of its portfolio of novel chemicals, Aequor has purified one with broad efficacy and a simple structure that enables scaling-up commercial production and easy incorporation in multiple delivery systems (sprays, washes, pastes, paints, coatings, etc.). Aequor's proprietary chemical can be used alone to replace biocides (antimicrobials, antifouling agents, antiseptics, antibiotics) that are toxic to the environment or health, or as a "biobooster" to enhance the performance of these biocides and reduce their overuse. The price point of Aequor's leading chemical is competitive at lab scale, with the promise of price leadership at commercial scale-up. On the healthcare side, Lonza validated that Aequor's lead compound combats bacterial contamination and infection in a new way. It removes existing biofilm, which "no other known chemical can do at non-lethal doses," and inhibits the ability of Gram-negative and Gram-positive medically-relevant bacteria to colonize without triggering bacterial resistance. On the industrial side, the novel compound inhibits the attachment of microfoulers to industrial surfaces, equipment, and materials. This improves operational efficiencies of, for example, condensers, forward and reverse osmosis filters and membranes, heat exchangers, recirculating cooling systems, solar panels, wind turbines, etc., and reduces fuel consumption and noxious emissions. Aequor's proprietary chemical also inhibits the attachment of macrofoulers to surfaces in contact with water, which reduces fuel consumption and emissions by up to 50% in the transportation, energy, and water sectors, while boosting yields in emerging cleantech industries (aquaculture) and renewable energy industries (algae, tidal). Aequor validated market demand by signing pilot testing agreements with 14 market leaders interested in licenses to develop new, sustainable end-use products for rapid market penetration.

Amyris, Inc.

Myralene™: A Renewable, Pure Hydrocarbon Non-VOC Solvent Produced from Plant Sugars

Amyris has developed, industrialized and applied a combination of 21st century advances in biology, chemistry, and engineering to meet green chemistry principles. Using a state-of-the-art organism engineering platform, Amyris has re-engineered ethanol-producing baker's yeast to consume sugars and convert them into a hydrocarbon rather than an alcohol. Amyris has also demonstrated industrial-scale production of this hydrocarbon using its proprietary yeast strains in a fermentation process, converting any fermentable sugar, including those derived from cellulosic biomass, into *E*-7,11-dimethyl-3-methylene-1,6,10-dodecatriene (β-farnesene, Biofene®). This technology platform can be used to not only produce the 2014 Presidential Green Chemistry Challenge Award winning drop-in diesel and jet fuel blendstock 2,6,10-trimethyldodecane, but it also provides an innovative renewable building block molecule applicable in numerous industrial areas, ranging from novel polymers with unique properties to value-added cosmetic and fragrance ingredients. In keeping with the Amyris mission to address daunting global challenges, the company has now used β-farnesene to manufacture partially hydrogenated farnesene (PHF, Myralene) on an industrial scale by a simple, efficient and economical catalytic hydrogenation, thus bringing to market a unique organic solvent that addresses the environmental, health and performance issues of existing solvents, both renewable and petroleum-based. With regulatory approval in the United States and abroad anticipated in 2015, the commercial launch of this newly designed chemical is expected to have a significant impact in the solvent marketplace, where human exposure, health and environmental impacts, and biodegradability continue to be significant concerns.

Estolides: A Low-Cost, High-Performance Renewable Fluid Certified for Motor Oil

Biosynthetic Technologies

Estolides, environmentally acceptable lubricant base oils, are synthesized from fatty acids found in soybeans and other crop sources through a unique catalytic reaction and esterification process. As a vegetable-based specialty fluid replacing petrochemical lubricating oil, estolides reduce negative impacts on the environment. Over 40% of the pollution in United States waterways comes from motor oil. Multi-pronged pollution from industrial lubricants – primarily motor oil – represents a staggering environmental problem to which no viable solution has emerged. With the introduction of the highly stable estolide compound, makers of industrial lubricants finally have a base oil option that functions impressively across the many severe applications in which lubricants are used. Estolides conquered the most daunting of these – motor oil – in 2014.

Significant displacement of toxic petrochemicals will occur as estolides are adopted in the industrial lubricant industry. Biosynthetic Technologies has entered into commercialization partnerships with Valvoline, Infineum (a joint venture between ExxonMobil and Shell), Castrol, and other major industrial lubricant brands to help bring the technology to market. These companies have formulated, and intend to launch, finished products blended with a significant concentration of Biosynthetic Technologies' renewable estolide base oil.

In addition to reduced water pollution, estolides are biodegradable and emit less greenhouse gases (GHG) across their lifecycle. A third-party life cycle analysis has confirmed that the GHG emissions lifecycle associated with estolides is significantly lower than that of comparably performing, petrochemical based lubricating base oils. Biosynthetic Technologies' estolide base oil has earned American Petroleum Institute motor oil certification. The base oil is currently produced in an operating demonstration plant with a commercial plant nearing construction.

Ultra-High Energy Density Metal-Free Sugar Biobattery

Cell Free Bioinnovations Inc.; Professor Yi-Heng Percival Zhang, Department of Biological Systems Engineering, Virginia Tech

Building high-energy density, green, and safe batteries is highly desirable for meeting rapidly-increasing needs of portable electronics. Enzymatic fuel cells (EFCs)/biobatteries are appealing metal-free bioinspired batteries, where low-cost enzymes are used to convert chemical energy stored in a few chemicals to electricity. Sugars, the most abundant renewable bioresource, are natural high-energy storage compounds. A sugar biobattery is a type of enzymatic fuel cell that converts sugars to electricity in a closed system. Incomplete oxidation of complex sugars mediated by few enzymes in EFCs suffers from low energy densities and slow reaction rate. Cell Free Bioinnovations Inc. designed a synthetic ATP-free and CoA-free catabolic pathway comprised of 13 enzymes for producing 24 electrons per glucose unit of maltodextrin through in an air-breathing EFC without mobile parts. Also, the biobattery exhibited the maximum power output of 1.2 mW cm^{-2} and current density of 8.6 mA/cm^2, far higher than microbial fuel cells. A sugar-powered biobattery with a characteristic of complete oxidation of 15% maltodextrin had an energy storage density of 596 Ah kg^{-1}, one order of magnitude higher than those of lithium batteries. These metal-free biobatteries featuring 100% biodegradability, absolute safety, and fast refillability would be next-generation green power sources, especially for portable electronics.

Green Biologics, Inc. (GBI)

The Reinvention of Biomass Based n-Butanol for the Renewable Chemicals Industry

Through application of modern biology, combined with the engineering of advanced solvent recovery systems, GBI has developed an integrated, patent-pending process ready to be installed for commercial deployment in Little Falls, Minnesota. As a result of scale-up success, GBI is leading the industry race in bringing renewable acetone and n-butanol to the chemical ingredient marketplace.

Chemical grade n-butanol is currently produced through petrochemical processes, but can also be produced through fermentation of sugars derived from biomass. Until the mid-1940s, n-butanol was produced largely through fermentation of molasses using Clostridia bacteria. The petro-industry captured the market by offering cheaper sources. With scientific advances in microbiology and synthetic biology, as well as dramatic improvements in process technology, GBI's process has achieved economics that can again compete with the much larger carbon-intensive petrochemical processes. Process outputs offer higher purity n-butanol with a carbon footprint approximately 40% better than petroleum-based butanol.

n-Butanol is used in derivatives that are key raw materials in paints, coatings, adhesives, and inks, as well as cosmetics, cleaners, food ingredients, and specialty products. In addition to a drastic source reduction of carbon, renewable n-butanol offers consumer goods manufacturers the opportunity to "green" their products without facing cost disadvantage.

The primary source reduction is derived through replacing petro-derived chemicals with chemicals produced through renewable biomass feedstocks. GBI's Clostridia micro-organisms have high C-5 (cellulosic sourced sugars) productivity and business development plans seek low-value biomass or waste resources. With the commercial launch project in Minnesota, source reductions are similar to ethanol production and equate to approximately 31,000 metric tons per year. Forward projects will incorporate C-5 sugars and be much less carbon intensive. Once GBI business model volumes have been reached, it is expected that total source reductions will exceed 314,000 metric tons per year.

H-O-H Water Technology, Inc.

Cooling Tower Water Conservation & Chemical Treatment Elimination

Properly engineered electrolytic extraction of calcium carbonate from recirculating cooling water has successfully controlled deposit formation on heat exchange and other surfaces in practical systems such as industrial and HVAC cooling tower systems. Electrolysis of ionic-rich water produces exploitable *in situ* chemistry requiring no external chemical reagent other than electricity. A *Green Machine* consists of a series of steel tubes that are made the cathodic element of an electrolytic cell where water is reduced to form molecular hydrogen and hydroxide ion, and calcium carbonate is subsequently made to accumulate. Centered in each tube typically is a titanium rod coated with a mixture of ruthenium and iridium oxides, and serves as the anode of the electrolytic cell. The common name for an anode of this type is "dimensionally stable anode," or DSA. It is the coating of the anode that is critical in driving the oxidation of water to produce molecular oxygen, hydrogen ion, and higher oxygen species such as hydroxyl free radical and ozone. DSA technology allows for the efficient splitting of water at a low practical voltage potential above that theoretically required, the difference being termed overpotential. DSAs have been responsible for past Green Machine success. Supplementing DSAs with anodes coated with boron-doped, ultrananocrystalline diamond now allows not only control over troublesome calcium carbonate deposition, but more efficient *in situ* chlorine formation and degradation of organic contaminants. Microbiological control in cooling water is significantly more efficient.

High Performance Solvent-Free Coating Technology

Light Curable Coatings

Corrosion is a tremendous problem and cost to society, with a staggering annual cost of $400 billion in the United States. Many primers and paints used to coat metal surfaces for corrosion resistance and decoration pose environmental hazards from cradle to grave. Conventional epoxy-based coatings commonly contain corrosive components, hazardous air pollutants (HAPs), volatile organic compounds (VOCs), and other solvents, and often contain chromium compounds. Urethane-based paints contain isocyanates and often contain other HAPs, VOCs, and other solvents. Because isocyanates are strong irritants to mucous membranes, they can sensitize exposed individuals, in some cases causing severe asthma attacks. The hexavalent form of chromium is carcinogenic, particularly for lung cancer.

Light Curable Coatings has developed pollution-free coating technology for high performance protection of industrial and aerospace surfaces, including corrosion resistance, solvent resistance, and weathering resistance. Light Curable Coatings technology also provides the advantages of efficiency and economy, with fast cure under an ultraviolet (UV) light and with improved properties with much less material usage than conventional materials. The green chemistry of Light Curable Coatings does away with chromium compounds, isocyanates and other HAPs, solvents, and VOCs completely, producing high-performance, corrosion-resistant solvent-free technology without using any toxic chemicals. Field application and fast UV cure of Light Curable Coatings technology has been demonstrated with good performance on large structures at temperatures as low as 34°F. Customer studies show savings of over 90% in the time required for painting operations for maintenance activities and factory processes.

Light Curable Coatings technology is a green alternative to current systems that contain toxic components, and provides a significant positive societal impact in terms of a better quality of life for industrial workers and for citizens through safer workplaces and a cleaner environment.

The Recovery of Organic Halides from Waste Streams by the Chemical Reaction of Hydrogen and Carbon Dioxide

Midwest Refrigerants, LLC – a Missouri Limited Liability Company

Fluorocarbon compounds, including chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, perfluorocarbons, and halons, are used in a wide variety of applications including air-conditioning, refrigeration, medical, fire protection, and solvent uses. They are also widely recognized as ozone depleting substances (ODSs) and/or greenhouse gases (GHGs). At the end of the life of such applications, the chemical is either destroyed, or worse, vented into the atmosphere. This venting, now prohibited in many countries, has been recognized to contribute to the depletion of the stratospheric ozone layer and is considered a cause of global warming and climate change.

The most common methods of ODS and GHG destruction are incineration by thermal oxidizer, rotary kiln, and plasma arc. These methods are costly, create their own waste streams and stack emissions, and yield outputs with little or no economic value. Destruction capacity around the world is limited or in some countries, non-existent. With increased regulation of older fluorocarbon products with high global warming potential and with the economic and environmental challenges of existing destruction technologies, there is great need for an alternative approach.

The Midwest Conversion Technology not only deals with unwanted ODSs and GHGs, but also can be applied to the waste streams at fluorocarbon manufacturing plants. The outputs are the manufacturing source chemicals, i.e., 99.999% anhydrous hydrogen fluoride, 99.98% anhydrous hydrogen chloride, 99.98% anhydrous hydrogen bromide, and carbon dioxide, all ready for new use. The technology is original and the process is safe, clean, inexpensive, energy-efficient, waste-free, and meets many sustainability targets. It creates useable outputs and it is an economically advantageous process compared to existing alternative destruction technologies.

Pilot plant data and computer model testing has shown that this technology can reduce the direct cost of destruction by current methods by 60-70%.

Modular Genetics, Inc.

Greener Synthesis of Surfactants

Surfactants are used broadly as foaming agents, emulsifiers, and dispersants. Today, surfactants are manufactured from petroleum, or from seed oils. For example, 250,000 metric tons of acyl amino acids are manufactured annually by combining palm-oil-derived fatty acids with amino acids using the Schotten-Baumann reaction. This reaction requires use of chlorinated fatty acids, which are produced industrially using either phosgene or thionyl chloride. Phosgene is highly toxic, while thionyl chloride is on the Hazardous Substances List, and reacts explosively with water, releasing toxic gas. About 100,000 metric tons of phosgene or thionyl chloride are used annually to manufacture acyl amino acid surfactants. The need for a greener method of production can be met with the use of engineered *Bacillus subtilis* strains for the production of acyl amino acid surfactants. The surfactants have been validated by key customers, with commercial launch anticipated in 2015. No synthetic chemistry steps are used to produce these surfactants, as they are generated enzymatically by a microorganism and secreted into the fermentation broth. The surfactants are purified to a high level using green methods involving only low energy and water. An additional positive feature is that no oil is used to manufacture these surfactants. The bacterium converts cellulosic carbohydrate, which cannot be used as food, into a microbial oil (a fatty acid) and an amino acid, and links them together to create the surfactant. It has been estimated that a complete switch to microbial production of surfactants will eliminate annual emissions of atmospheric carbon dioxide equivalent to the combustion of 3.6 billion gallons of gasoline, while also reducing the rainforest destruction associated with palm plantation expansion.

Newlight Technologies, LLC

AirCarbon: Carbon-Negative Plastic Made from Carbon Sequestration

Newlight Technologies has developed a microorganism-based biotechnology process to convert air and methane-based greenhouse gas (GHG) emissions into carbon-negative thermoplastics that can replace oil-based plastics at commodity scale. The resulting product – AirCarbon® – is a material made from methane-based GHG emissions that can match the performance of a range of oil-based plastics, such as polypropylene and polyethylene, while out-competing on price, representing a market-driven solution to carbon capture. Following critical breakthroughs on process yield and product performance, and overcoming classical and longstanding challenges to the microorganism-based conversion of GHGs into thermoplastic materials, AirCarbon has patented and commercialized, and is currently being used to manufacture furniture, bags, caps, and a variety of other products. Partners include Fortune 500 companies and brand-name market leaders such as Dell, Sprint, and KI.

Phyllom BioProducts Corp.

grubGONE!®, beetleGONE!® and boreGONE!®, Biological Insecticides with Low Impact on Humans and the Environment Yet Effective Against Destructive Beetle Pests

Phyllom BioProducts Corp. (Phyllom) biological insecticides grubGONE!® beetleGONE!® and boreGONE!® are derived from microbes naturally found in soils and on plants, *Bacillus thuringiensis* (BT). While other forms of BT insecticides have been used by organic gardeners, farmers and foresters for decades, Phyllom licensed a novel strain called BT *serovar galleriae* SDS-502 strain with a patented natural Cry8Da protein. This protein is uniquely effective against certain beetles, weevils, and borers including the difficult to control adult stage. Phyllom's bio-insecticides are produced via a bio fermentation process utilizing plant carbohydrates and proteins. The process uses no solvents and generates no hazardous wastes. Food grade inerts are used in the formulas and most formulas are compliant with the USDA National Organic Program.

Phyllom's bio-insecticides demonstrate advantages such as improved plant/poultry health and control of invasive and/or insect pests resistant to traditional chemistries. Phyllom's bio-insecticides demonstrated virtually no adverse effect on non-targets tested, including honey bees, wasps, lady bird beetles, mammals, birds, plants, fish, and aquatic invertebrates.

Wood boring invasives such as the Emerald Ash Borer are anticipated to cause nearly $1.7 billion in annual government expenditures and $830 million in lost residential property values. An Integrated Pest Management program including Phyllom's bioinsecticides could economically slow the spread of invasives by providing the option to suppress adult beetle reproduction.

EPA Office of Pesticide Programs reports 93 million pounds of insecticides were applied within the United States in 2006. Phyllom's bio-insecticides will replace a portion of this volume with effective yet more human health and environmentally benign alternatives.

PROSOCO R-Guard: High-Performance Phthalate-Free Air and Water Resistive Barrier Sealant and Sealant Coating System

PROSOCO, Inc.

In 2011, BEI and PROSOCO were working with Miller Hull architects to provide a high-performance vapor barrier sealant and coating system for the Bullitt Center, a Living Building Challenge (LBC) project in Seattle, Washington developed in partnership with Point32. Spearheaded by Denis Hayes of the Bullitt Foundation, the project demonstrates the ability to create a minimal impact commercial building using available technologies.

To meet air tightness requirements driven by net zero energy (NZE) goals and overall biomimicry in design principles, it was necessary to use a high-performance membrane that allowed wall assembly materials to flex and breathe, expelling water vapor, while keeping out external moisture. Miller Hull selected the PROSOCO/BEI "Cat 5" coating and related sealants based on previous successful use of the system designed for wet weather application typical in Pacific Northwest construction.

After further research, Point32 informed PROSOCO the system could not be used due to presence of dibutyl phthalate (CAS 84-74-2), a chemical restricted by LBC materials criteria. Phthalates are widely used as plasticizers and are a nearly ubiquitous environmental contaminant. Phthalates have been shown to have effects on the reproductive systems of lab animals and on human health.

In response, PROSOCO and BEI co-developed alternative formulations that substituted polypropylene glycol for dibutyl phthalate while preserving application characteristics and meeting International Code Council Evaluation Service (ICC-ES) air leakage and durability performance standards.

Initially, the formulations were specific to the Bullitt Center project. However, PROSOCO and BEI evaluated cost and performance and opted to switch the entire product line to the polypropylene glycol chemistry. This milestone was reached by the end of 2012 with subsequent commercial, residential, LBC, LEED, EnergyStar, and Passive House high-performance and NZE applications across North America. This project demonstrated that phthalate-free and commercially viable sealant systems can be manufactured using current technologies.

Resinate Materials Group, Inc.

Creating Multi-Functional Polyols Using Recycled Raw Material Streams

Environmental, health, and safety concerns continue to drive rapid growth for chemistry solutions with lower environmental and human health impacts. This growth, further compounded by increased social awareness of depleting finite resources, the growing world population, and constrained food resource, has companies seeking highly sustainable feedstock solutions. Although bio-based materials have provided feedstock options that are more sustainable than fossil petroleum alternatives, use of recycled content has remained relatively unexplored. With this in mind, Resinate Materials Group (Resinate) has developed proprietary technology through which it creates multi-functional polyols using recycled raw material streams, including recycled poly(ethylene terephthalate) (PET). The technology extends the lifecycle of valuable, finite resources by harvesting spent materials otherwise destined for landfills. Furthermore, studies have shown recycled PET (rPET) to have more favorable life cycle assessment scores than comparable fossil petroleum-based or bio-based PET materials, including lower human health impacts and lower carbon footprint. By harnessing the inherent properties of rPET, Resinate is able to impart a unique balance of properties into coatings, adhesives, sealants, elastomers and foams, making recycled content an attractive and viable option, all while developing a highly sustainable feedstock option.

Sagamore-Adams Laboratories, LLC

PLATech, Green Chemistry Universal Adhesive-Sealing Technology

With 2013 estimated sales and production in the adhesive and sealants market of over $42.4B/year and 28.3B pounds/year, respectively, the applications of these products are broad-based and include areas such as automotive, general wood products, and consumer products. Virtually all adhesives/sealants used worldwide are volatile organic compound (VOC)-based and not environmentally preferable. Addressing this market challenge, PLATech comprises a class of VOC-free adhesives/sealants in tandem with tailored application methods for enabling adhesion to most substrates. PLATech adhesives/sealants are based on polylactic acid (PLA) – a renewable corn/soy-based derivative – and offer high performance capabilities while remaining bio-renewable and selectively biodegradable. PLATech also provides enhanced functionality including versatility to adhere to a vast class of materials, including challenging materials such as aluminum to steel, and even Teflon. PLATech provides a sustainable alternative combined with the ability for tailored strength, flexibility, ease of application and removal, and set times. Indeed, the burgeoning use of adhesives in the auto industry is stymied by the inability of most adhesives to join aluminum to steel – something PLATech achieves readily, while remaining biodegrable and sustainable. PLATech can be tailored to meet or exceed the performance of commercially available polyurethane, cyanoacrylate, EVA, and formaldehyde-based adhesives by over 100%, reaching bond strengths of over 45 MPa (6,200 psi) with low cost applicators. No pressurization or substrate surface preparation is required for use on a wide range of substrates, eliminating the need for chemical and physical treatment. Furthermore, the ability to selectively tailor PLATech adhesives via radiation-based crosslinking has been demonstrated, allowing for enhanced formulation of application-specified bond strength and functionality even in elevated temperature environments over 200°C. PLATech adhesives/sealants provide sustainable alternatives for the marketplace while meeting the cost and performance requirements of the industry including strength, flexibility, and adhesion to even the most difficult substrates.

Cleaner Transportation Fuels and Commodity Chemicals from Methane

Siluria Technologies, Inc.

The abundance of methane supplies from shale gas and renewable sources has created a profound and global opportunity. However, difficulty in transportation and technical constraints of using methane has relegated it to a low-value commodity fuel, or worse, a wasted and unused resource. Today, methane is mostly burned to produce heat and/or power. As much as half of the world's methane supply is logistically challenged or stranded in hard to reach geographies or is being flared with no economic value and negative environmental impact to the tune of 5,000 billion cubic feet per year. Globally abundant supplies of methane, the continuing need for transportation fuels and chemical and sustainability concerns are a combination for which the world needs a solution through new innovation.

Siluria Technologies has developed a novel catalytic process that transforms methane into transportation fuels and petrochemical building blocks in an efficient, cost-effective, scalable manner. Siluria's breakthrough Oxidative Coupling of Methane (OCM) process technology is believed to be the first commercially viable and economically competitive process to directly convert methane to ethylene. Siluria's second process technology can convert ethylene to liquid fuels such as gasoline, diesel, or jet fuel, enabling methane to potentially supplement petroleum as the worldwide basis for transportation fuels and commodity chemicals.

Siluria operates three pilot facilities and recently completed construction and startup of the world's first OCM demonstration plant. Siluria is actively commercializing the technology in partnership with leading engineering and operating companies for a broad range of applications in the upstream, midstream gas processing, downstream chemicals production, and refining operations.

1,1-Disubstituted Alkenes

Sirrus, Inc.

Sirrus advances manufacturing technology through chemistry relating to the synthesis, stabilization, activation, and formulation of a unique and reactive class of 1,1-dicarbonyl substituted alkenes. These monomers, their derivatives, and resulting polymers provide the foundation for enabling Sirrus' partners and customers to meet their customer's desire to reduce manufacturing costs, improve quality, and improve their environmental footprint. These monomers, their derivatives, and resulting polymers provide fast cure speeds at ambient temperatures to significantly reduce cycle times, increase throughput, reduce energy requirements, and enable new material selection in a broad range of customer and consumer applications, including automotive, electronics, packaging, and hygiene.

An Application of Hybrid Multispectral Analysis; Real-Time Wastewater Process Control

ZAPS Technologies, Inc.

Hybrid Multispectral Analysis (HMA) is a unique combination of advanced optical, photonic, and statistical technologies applied to the challenge of providing synchronized high frequency data for complex water components. Such information is required to control treatment processes in real time. HMA allows plants to continuously adjust treatment recipes based on current and on-line historical data to eliminate over and under treatment, provide real time water security, and enable closer compliance with and more effective enforcement of environmental laws.

HMA utilizes a single optical probe to conduct over 3.3 million *in situ* measurements per day, collecting direct molecular data on absorption, reflectance, and fluorescence. Molecular data is used to rapidly quantify critical water quality parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total free chlorine (HOCl+OCl-), total suspended solids (TSS), and ultraviolet A (UVA) over the concentration range spanning from wastewater influent to effluent. Parameter values and/or control signals are broadcast about every two minutes for real time process control which can be used to determine the chemical load or energy consumption of a plant and quality of water it discharges. This technology can help guide chlorine injection or UV lamp settings, as well as aeration blower speeds, nutrient injectors, or to stop pumps when water security parameters are violated.

HMA incorporates several green chemistry principles including elimination of reagents and standards for sampling, elimination of sample preparation and storage, elimination of treatment guard bands used to compensate for delays in conventional data, and the need for only 72 watts to operate. HMA is sold under the trade name LiquID™. To date, over 85 LiquID™ Stations shipped have proven useful in the fields of municipal water, wastewater treatment, water reuse, and industrial process control. The HMA methodology was developed through support in part by the EPA, Office of Naval Research, Oregon State University, and Oregon Nanoscience and Microtechnologies Institute.

Entries from Industry and Government

Dow Polymeric Flame Retardant

The Dow Chemical Company

Polystyrene (PS) foam is widely used as insulation in the building and construction market, thus it must meet rigorous building code and fire safety performance standards. The Dow Polymeric flame retardant (FR) is an innovative technology that is essential for the preservation of the PS foam insulation industry, which annually produces foam insulation that avoids service lifetime totals of 1.7 giga tons of CO_2 equivalent greenhouse gases. With impending global regulation and restriction of hexabromocyclododecane (HBCD), the incumbent FR, the PS foam industry needed an alternative FR that could provide a significantly improved Environmental, Health, and Safety (EH&S) profile while cost-effectively matching HBCD's fire safety performance and foam properties and processing performance. The Dow Polymeric FR was scientifically engineered to achieve this set of requirements by using a combination of chemistry, polymer science, process technology, application know-how, and EH&S expertise. Success was achieved by designing a FR polymer, which is inherently more sustainable than small molecule FRs, with a controlled stability to survive foam manufacturing and processing conditions while still delivering the release of the active FR agent under fire conditions. The Dow Polymeric FR has met the challenge, leading the global PS foam industry to select it as the new standard FR. This breakthrough technology is enabling the industry to meet increasingly stringent building and construction energy efficiency codes while continuing to meet fire safety performance standards.

Development and Commercialization of an Integrated Cellulosic Ethanol Production Platform

DuPont Company

This nomination describes the integration of chemistry, biology, and process engineering to develop a commercially viable, scalable technology platform for the production of cellulosic sugar and its conversion to ethanol. The work required the integration of a novel pretreatment process, the development of improved enzymes for hydrolysis, and the genetic engineering of a novel, highly efficient fermentation host. The resultant DuPont integrated process is a novel integrated production platform, with three major technology components, for the production of ethanol at sufficiently high yields and titers to achieve commercially viable economics. To optimize the process it was necessary to consider and innovate all three conversion steps holistically. First, a novel dilute ammonia biomass pretreatment process decouples the carbohydrate polymers from the lignin matrix with minimal formation of compounds which inhibit subsequent fermentation, thus eliminating the need for costly "detoxification" steps which are common in other cellulosic ethanol technologies. Next, an enzymatic hydrolysis step uses a novel suite of high performance enzymes specifically engineered by DuPont to depolymerize and hydrolyze both cellulose and hemicellulose to high titers of fermentable sugars in a single sugar stream. Thirdly, DuPont integrated and optimized the metabolic pathways of a recombinant bacterium, *Zymomonas mobilis*, to simultaneously metabolize both 6-carbon (glucose) and 5-carbon (xylose) sugars to efficiently produce ethanol at high yields and titers from the hydrolysate. This unique integration of three technology components enables a very efficient, "clean" flowsheet with minimal steps, a reduced environmental footprint, and reduced cost and capital versus other known cellulosic ethanol processes. DuPont has achieved commercially viable ethanol yields consistently in its 250,000 gallon per year demonstration facility in Vonore, Tennessee. Yields of >70 gallons/ton of biomass and ethanol titers in excess of 70 g/L have been demonstrated. Comprehensive "Well-to-Wheel" Life Cycle Analyses show that DuPont's combined process has the potential to achieve more than a 100% reduction in greenhouse gas (GHG) emissions compared to gasoline, which is substantially better than current grain-based ethanol GHG performance. The DuPont technology has been demonstrated successfully and the first commercial plant for conversion of corn stover to ethanol is under construction in Nevada, Iowa.

Eastman Chemical Company

Eastman Omnia™ Solvent – Changing the Chemistry of Clean. New, Safe, Highly Effective Solvent for Cleaning Applications

To enable development of cleaners that are safer for humans and the environment, formulators need safer ingredients. It is rare, however, for a solvent used in cleaning products to be safe for people, the environment, and surfaces being cleaned – and still enable efficient cleaning and compliance with air quality requirements. With this unmet need in mind, Eastman developed a solvent offering exceptional safety, performance, and value throughout the industry – from formulators to cleaning staff to customers.

With thousands of molecules to consider, Eastman narrowed the solvent universe using computer modeling based on human health and environmental safety criteria and specific physical/chemical properties to predict good performance. Minimum safety criteria for candidates were based on Design for the Environment (DfE)'s Solvent Screen.

The final candidate, Eastman Omnia™ solvent, has an excellent safety profile, as evidenced by meeting DfE's Solvent Screen criteria, listing in GreenBlue's CleanGredients® database with no restrictions, and listing in DfE's Safer Chemical Ingredients List with highest rating. Performance testing demonstrates Omnia™'s excellent cleaning ability: neutral-pH formulations with Omnia™ were highly effective and outperformed alternatives.

Eastman satisfied requirements for Toxic Substances Control Act (TSCA) Inventory listing and began manufacture of Omnia™ in October 2013. Since then, Omnia™ has been commercialized by multiple customers in a wide range of applications, with over 75 additional customers currently evaluating it in a variety of applications. Based on Eastman's volume projections and the fact that a typical janitorial cleaning formulation contains around 2% solvent, the use of Omnia™ could represent a safe, effective alternative in over 60 million gallons of cleaning products per year in the United States.

The combination of powerful cleaning and excellent safety profile makes Omnia™ an excellent choice for formulators challenged to comply with increasingly stringent safety, regulatory, and market demands. Eastman Omnia™ solvent is changing the chemistry of clean.

Ecolab

Environmentally Preferable Biocide for Water Treatment in Hydraulic Fracturing

In the past years, unconventional oil and natural gas production has steadily increased in the United States. Driven by the development of new technologies such as horizontal drilling and hydraulic fracturing, shale gas has led to major increases in reserves of oil and natural gas. During hydraulic fracturing, water and chemicals are injected, at high pressure, into the geologic formation to increase the fractures in the rock layers and allow hydrocarbons to flow. Because large quantities of water are used during this process, the need for water treatment and reuse has become critical. Water treatment prevents the introduction of microorganisms in the formation, which can result in problems such as reservoir souring, biofouling, and microbiologically-induced corrosion. Additionally, facilitating the reuse of produced water through cleaning reduces the constant demand for fresh water. Based upon these concerns, Ecolab developed an improved formulation of the oxidizing biocide peracetic acid (PAA). This chemistry shows superior results when compared to other conventional biocides (e.g., glutaraldehyde, chlorine dioxide), including faster and longer duration microbial efficacy, water cleanup properties, solids dropout, and less corrosion. Importantly, PAA had no adverse effects on other chemistries present in the hydraulic fracturing fluids, such as friction reducers and scale inhibitors. Ecolab's PAA biocide is an environmentally preferable chemistry as it breaks down into innocuous components – water and acetic acid (e.g., vinegar). A concern associated with hydraulic fracturing is impacts on surface water quality. Ecolab's EC6734A PAA biocide enables the reuse of produced water brine, reducing fresh water draw. Use of this biocide facilitates safe, cost-effective onsite water disposal by minimizing emissions, and reduces plugging by controlling biological growth and thus maintaining hydraulic conductivity. These benefits contribute significantly to better quality and management of surface waters.

OxyCide™ Daily Disinfectant Cleaner

Ecolab

OxyCide™ Daily Disinfectant Cleaner (OxyCide) is a broad spectrum, EPA-registered hospital grade disinfectant developed by Ecolab. OxyCide was the first non-bleach concentrate sporicidal disinfectant sold to the acute care market. It is a multi-faceted solution for improving hospital performance in the areas of infection prevention, efficiency, source reduction, and impact to the environment.

Healthcare-associated infections (HAIs) are a persistent issue in hospitals, affecting one in every 25 hospital patients. In 2011 there were an estimated 722,000 HAIs in United States acute care hospitals, and about 10% of these patients died during their hospitalizations. One of the most prevalent HAI causing organisms is *Clostridium difficile* (*C. difficile*), which causes 17.1% of all HAIs and is linked to 14,000 deaths annually. OxyCide provides hospitals with a powerful tool in the fight to prevent HAIs. In only five minutes, OxyCide kills 33 microorganisms commonly found in healthcare settings, including *C. difficile* spores.

OxyCide's active ingredients hydrogen peroxide and peracetic acid replace environmentally persistent ingredients found in other concentrated hospital disinfectants with similar efficacy profiles. The concentrated format of OxyCide reduces the number of containers by 40 times for an equivalent amount of ready-to-use disinfectants. Its innovative closed loop packaging and dispensing system work together to properly dilute the product, ensuring disinfectant efficacy while reducing product waste from over-dilution. Additionally, the diluted product, when applied according to label instructions, requires no personal protective equipment.

Low Global Warming, Non-VOC, Zero-ODP Molecule for Energy Efficient Polyurethane Foam Insulation Blowing Agent, Solvents, and Heat Transfer

Honeywell International

Honeywell has risen to and is delivering on the EPA plans to tackle the super-potent heat-trapping pollutants called hydrofluorocarbons (HFCs), an important step forward in carrying out President Obama's Climate Action Plan with the development and commercialization of a greener chemical 1-chloro-3,3,3-trifluoropropene, or HFO-1233zd(E).

The 100-year global warming potential (GWP) for HFO-1233zd(E) is equivalent to that of CO_2 (GWP=1), which is 1,000 times lower than the hydrofluorocarbons (HFCs) it is designed to replace. It is non-flammable, non-toxic, non-ozone depleting, and classified by the EPA as VOC exempt. In May 2014, VOC exempt status was also granted by per the highly stringent California Southcoast Air Quality Management District (SCAQMD). Honeywell's extensive testing proves that HFO-1233zd(E) offers lower GWP, is safer, more energy efficient, and more cost-effective to implement compared to existing blowing agents such as cyclopentane and HFCs.

HFO-1233zd(E) is being adopted globally in a wide variety of industries such as appliances, transport, construction, refrigerants, and precision cleaning for metals and electronics. Widespread use of HFO-1233zd(E) to replace HFCs in these industries in the United States alone will result in a reduction of more than 25M tonnes per year of CO_2-equivalent; globally this number would exceed 90M tonnes based on Honeywell's internal analysis. This new product will not only help reduce global warming, but it will spur economic growth and job creation in the United States.

Linde North America

Development of Vapormate as a Replacement for Methyl Bromide Fumigants

For decades, global trade in fresh fruits and vegetables has been dependent on the use of methyl bromide as a fumigant to kill indigenous insect pests. However, methyl bromide has been found to deplete the stratospheric ozone layer, and is being rapidly phased out under the Montreal Protocol. Without a viable replacement, global trade in fresh foods would be severely curtailed due to concerns about the spread of indigenous pests.

Linde North America has developed Vapormate – a combination of ethyl formate and carbon dioxide – as an effective and environmentally friendly replacement for methyl bromide. Vapormate's active ingredient, ethyl formate, has no known ozone depletion or global warming potential. It eradicates pests efficiently, and quickly breaks down into metabolites that occur naturally in the environment. In addition to its important role as a replacement for a known contributor to ozone depletion, Vapormate has other environmental benefits. First, it is less toxic than methyl bromide and most commodity fumigants in current use and therefore safer for human exposure. Second, Vapormate fumigates and dissipates more rapidly than methyl bromide, allowing fresh foods to be shipped more expeditiously. This reduces spoilage and allows for more sustainable farming practices.

Vapormate is currently approved for use in select countries, including South Korea, Indonesia, the Philippines, New Zealand, and Australia. It was submitted to the EPA for registration in February 2012, and is currently undergoing the established review process. As Vapormate wins approval in additional markets and achieves broader use, it will have two important benefits. It will reduce depletion of the ozone layer by eliminating current usage of methyl bromide. It will also enable more efficient global commerce in fresh foods by reducing spoilage.

The Procter & Gamble Company; DuPont Company

Cold-Water Enzyme: Reducing the Environmental Footprint of Residential Laundry through Low Temperature Cleaning

Each day, Americans do 123 million loads of laundry. They have become accustomed to a certain level of cleaning and ease in performing this essential activity of modern living. And when it comes to stain removal, most choose to set their dials to warm or hot to ensure a quality clean. The research teams at DuPont and its strategic partner Proctor & Gamble have invented an entirely new enzyme that allows consumers to wash their clothes at significantly lower temperatures with dramatically improved performance. The enzyme helps reduce energy use by 50% with each load.

This superior enzyme technology, cold-water protease, is available now in Tide Coldwater Clean. Both companies felt passionate about pursuing the development of this enzyme because success meant significant environmental benefits due to the sheer scale of use. Current laundry washing creates 40 million metric tons of emissions of carbon dioxide. If the loads were cleaned instead in cold water, the energy savings would reduce those emissions by 80%. In other words, that is the equivalent of taking 6.3 million cars from the road, based on annual United States emissions. Use of this cold-water protease has equivalent performance and stability compared to the traditional technology used. DuPont's Genencor scientists applied novel protein engineering methods to invent an optimal protease enzyme that at 60°F matches the cleaning performance of the previous incumbent generation product at 90°F. Joint commercialization of this breakthrough technology means it has the potential to become the largest manufacture of an engineered enzyme in the world – greening one of the most common household chores on a macro scale. Consumer habit surveys indicate that low temperature cleaning is on the rise in both North America and Europe, and that the potential benefits enabled by this technology are becoming a reality.

S.C. Johnson's Greenlist™ Process Drives Continuous & Measurable Improvements in Windex® Brand

S. C. Johnson & Son, Inc.

The S.C. Johnson Greenlist™ process is setting a new standard for environmental responsibility employing a rigorous, scientific approach to impact better material (Raw Material and Packaging Components) choices. This patented process includes ratings for all of the materials S.C. Johnson uses in manufacturing its products, other than those in newly-acquired products that are still being evaluated.

The Greenlist™ process uses a four-point scale for rating ingredients: 3 "Best," 2 "Better," 1 "Good" and 0-rated materials (which are used only on a limited basis). In 2001, S.C. Johnson started with 18% "Better/Best" ingredients; in 2014, the company was at 47%. S.C. Johnson was a 2005 Presidential Green Chemistry Challenge Award winner for its Greenlist™ process. However, the measurements submitted in 2005 tracked the average Environmental Classifications (EC) score and now track "Better/Best" ingredients. The Better/Best score puts more of a focus on using the "Better" and "Best" materials. To compare how S.C. Johnson is tracking since 2005, 47% Better/Best equates to an average EC score of 1.65, up from 1.41 in 2005. The company currently rates greater than 98% of its Raw Materials exceeding the 90% rated in 2005.

As it relates to Windex®, the formula has had significant improvement in its environmental profile, as described back in the 2005 Presidential Green Chemistry Challenge Award submission, but the improvements did not stop there. S.C. Johnson has continuously improved its profile, both from a formula and packaging standpoint, and this process is being used to benefit all of its product lines.

VF Corporation: CHEM-IQ℠

VF Corporation

Chemical management in the apparel and footwear industries is complex. VF Corporation produces close to 500 million units of product at more than 2,000 facilities annually, operating one of the largest and most sophisticated supply chains in the world. VF recognized the need for simplified solutions in chemical management and saw an opportunity to use its size and scale to improve workplace safety, environmental protection, and product quality by creating an innovative chemical program.

VF challenged itself to take an entirely different approach to existing chemical management programs which evaluate products for chemical composition after they are produced. Instead, VF focused on testing and eliminating potentially harmful chemicals before they enter manufacturing processes. CHEM-IQ℠ is a first-of-its kind, cost-effective, simple process for factory suppliers to submit chemicals to be screened of over 400 potentially harmful substances. Each test costs approximately $50 compared to $1,000 for other methods – a 95% cost reduction.

Chemical identification prior to manufacturing provides suppliers with clear instructions on which chemicals are preferred and non-preferred. CHEM-IQ℠, developed in collaboration with an advisory council from Natural Resources Defense Council, University of Massachusetts-Lowell, Modern Testing Services, and the University of Leeds, scans chemical samples and delivers an easy-to-understand, color-coded rating to the supplier indicating whether or not the formulation is permitted for use.

CHEM-IQ℠ is currently used at VF-owned facilities and supplier factories in the United States, China, Turkey, Taiwan, and Mexico. To date, CHEM-IQ℠ has removed more than 250 tons of non-preferred textile auxiliaries from VF's supply chain before they entered the factory. Thus, CHEM-IQ℠ has already had a positive impact on VF's ability to prevent potential worker and customer exposure, as well as the discharge of non-preferred chemicals to air, water, or land.

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Award winners are indicated with asterisks.

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