Process intensification

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Conservation of materials and energy is a major objective to the philosophy of sustainability. Wherever production processes can be intensified to assist these objectives, significant advances have been developed to assist conservation as well as cost. Process intensification (PI) has four goals: “to maximize the effectiveness of intra- and inter-molecular effects, to optimize the driving forces/maximize specific interfacial areas, and to maximize the synergistic effects of partial processes”. The development of intensified processes provides engineering potential to the chemical industry. Process intensification can be conveniently analyzed on several levels: spatial, thermodynamic, functional and temporal domains. Spatial considerations include molecular-scale structures, structured reactors, and structured internals for mass transfer operations. The thermodynamic considerations involve energy in chemical reactors, and energy in separation systems. The functional considerations were identified as combining nanoscale functions in catalysis, and reactive and hybrid separations. Temporal considerations included changing the characteristic times of events, introducing dynamics (pulsing) in reactors, and periodicity in separations. Some of the domain aspects of PI are in their infancy and the authors offer considerations for each as to underscore future issues. Clearly, PI can be a major contributor to achieving green chemistry objectives.

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Stereoselective enzyme evolution

Carbon having four attached substituents can exist as an optically active center and each isomer will rotate plane-polarized light. At first glance this might appear to be an esoteric consideration important to the organic chemist. In nature, each isomer is related to its enantiomer by changes in the rotation to plane-polarized light in a specific direction. Many pharmaceutical products have therapeutic value related to a specific enantiomer. Chemical synthesis methodology until recently has not been sufficiently specific to enhance the production of one enantiomer exclusively. A product resulting from non-discriminating chemistry is a 50:50 mixture of enantiomers or racemic mixture where the concentration of the desired isomer is diluted by the non-therapeutic isomer. There are some instances where the undesired enantiomer can exhibit toxic effects. The case of thalidomide as a remedy to morning sickness was made problematic by undesired isomer which exhibited teratogenic characteristics leading to birth defects. This striking example shows the importance of optical isomer purity when the product target is a therapeutic agent. The ability to select isomers synthetically becomes very important. There are asymmetric chemical methodologies that can accomplish these ends but the use of enzymes to accomplish this is well known. Biocatalysts have suffered from several limitations involving limited substrate reactivity, poor enantioselectivity, limited stability, and the potential of product inhibition. How can these limitations be ameliorated? One approach is to modify existing enzymes to produce the desired feature. Directed evolution has been employed to this end by striving to emulate nature through repeated cycles of gene mutagenesis, expression, and selection until the desired biocatalytic activity is attained. A new approach, involving a repeated

cycle of mutagenesis, plating, and screening, has been developed which uses a variant of the directed evolution methodology. This methodology requires that the gene of a stereorandom or poor enantioselective enzyme is subjected to mutagenesis which provides a gene library that can be inserted into a bacterial host such as *E. coli*. Plating the inserted host followed by expression permits transformant harvest. Screening evaluates the enantioselectivity of the enzyme mutants and the improved mutant is the starting template for the next cycle which is continued in sequence until the desired enzyme properties are accomplished. A 300-amino acid residue enzyme can lead to 5,700 mutants with the replacement of one amino acid and if two simultaneous substitutions are replaced, the mutant field expands to 16 million. This review shows the use of directed evolution of enantioselective enzymes thereby providing a new asymmetric catalysis methodology. The enhancement of laboratory protocols to enable faster, more efficient processing opens the vast array of enzyme activities as a source of selective and robust catalysts for application to enantioselective needs of science and industry. The use of the lipase for *Pseudomonas aeruginosa* (PAL) in the kinetic resolution of an ester is an early example of enantioselective enzymes derived from directed evolution protocols.

Angew Chem Int Ed 2011, 50, 2–39

Modern flow chemistry

Flow chemistry has been utilized in industry as a process concept for some time. Chemists have found that miniaturized reaction assemblages in laboratories to accomplish synthetic operations in significantly less space than typical laboratory synthetic batch conversions. This feature article offers insight into the use and versatility of small scale reactors. Microfluidic conditions of 10 to 500- μm -internal diameter (id) dimensions are found in academic laboratories and in applications to diagnostic and analytical needs. Mesofluidic conditions of 500 μm to several millimeters of id have become popular in the industrial context but also attract academic interest. Each of these operating regimes offers advantages and disadvantages. Supercritical water

hydrolysis of the 6-aminocapronitrile leads to ϵ -caprolactam as follows.

The multistep flow synthesis of ($\pm$)-oxomaritidine was conducted using meso and micro flow reactors in 90% purity. All the steps were found to proceed quantitatively except for an oxidative phenolic coupling step which was limited to 50% conversion. The intricacy and control of this efficient multistep synthesis offer clear evidence of the power of these techniques.

Chem Commun 2011, 47, 4583–4592

Green chemistry awards

The results of the 2011 Presidential Green Chemistry Challenge Awards Program have been made available for inspection on the web. Awards were made in five categories: academic award, small business award, greener synthetic pathways award, greener reaction conditions award, and designing greener chemicals award. The awardees were Bruce Lipshutz for the academic award, BioAmber for the small business award, Geomatica for the greener synthetic pathways award, Kraton for the greener reaction conditions award, and The Sherwin-Williams Company for the designing greener chemicals award.

Academic award

Often organic solvents provide the supporting medium in which chemical synthesis can be conducted. The large percentage of the world's chemical production is composed of organic solvents that can be volatile and present deleterious problems to the environment. These materials are generally used to provide a homogeneous reaction medium to enhance the reactivity of starting materials for a synthetic step due to the hydrophobicity of most organic chemicals. Surfactants can be used to solubilize reactants and catalyst. This award recognizes the discovery and utility of a surfactant TPGS-750-M derived from tocopherol, succinic acid, and methoxypoly(ethylene glycol). The

surfactant forms nanomicelles in water where the outside of the hydrophilic and the inside is lipophilic. Small quantities of TPGS-750-M in water from 50 to 100 nm diameter micelles to serve as potential nanoreactors. These conditions have been shown to facilitate a wide range of organic reactions, such as carbon coupling reactions (Heck, Suzuki–Miyaura, and Sonogashira), unsymmetrical aminations, allylic aminations, silylations, olefin metathesis, and aryl borylations. No frothing or foaming was observed as was the case with other surfactants. Isolation of reaction product was uncomplicated. Surfactant recycling can be conducted efficiently with the aqueous surfactant reused with negligible loss of activity.

J Org Chem 2011, 76, 4379–4391; Angew Chem Internat Ed 2011, 50, 7820–7823

Small business award

The simple four-carbon diacid, succinic acid, is used in products ranging from food and drugs to chemicals and polymers. Succinic acid has been produced from a variety of petroleum feedstocks. This award recognizes the effort to develop an integrated technology that is capable of producing commercial quantities of succinic acid by fermentation technology. A licensed *E. coli* strain, developed by the US Department of Energy produces succinate salts from sugar and carbon dioxide, was based on three gene knock-outs and productivity unencumbered with few by-products. Twenty-five percent of the carbon in the products comes from CO₂ since the biosynthesis consumes CO₂ rather than generating it as a product. Carbon-14 analysis showed that 72% of the carbon incorporated in the succinic acid product was derived from glucose and the remaining 28% from CO₂. Hence, the technology can generate carbon credits for the process operators. Commercial-scale production of succinic acid using the *E. coli* strain began in 2010 at Pomacle, France using wheat-derived glucose in a 350,000 L fermenter at a 3,000 mt/year production capacity. Expansion to North American is envisioned to include in the 2011 timeframe to a 20,000 mt/year production facility. The process designers are confident that this process yields succinic acid that is 40% below the cost

of petroleum-based product and can be competitive at petroleum process below \$40/barrel. Biologically produced succinic acid can be a cost-effective feedstock for the production of tetrahydrofuran and 1,4-butanediol. One promising application is the synthesis of polybutylene succinate which is heralded as a biodegradable and as viable alternatives to phthalates.

Greener synthetic pathways award

The highly useful intermediate, 1,4-butanediol (BDO), has been synthesized from a number of fossil-based starting materials, such as acetylene, allyl alcohol, butadiene, maleic anhydride, etc. Having a current global market of 2.5 million mt/year and a compound annual growth rate of 6%, BDO is exceedingly attractive to new venture developments using renewable feedstocks. This award recognizes the research effort to utilize a strain of *E. coli* that has been altered using metabolic engineering to engage the first biocatalytic route to BDO. An accurate genome-scale metabolic model of *E. coli* and biosynthetic pathway prediction algorithms were used to sort through some 10,000 pathways of 4–6 steps for the synthesis of BDO. Pathway elimination was accomplished through the use of group contribution theory to reject unfavorable thermodynamics or by constraint-based modeling evaluation of theoretical yield. The selected strain was found to produce more BDO than the wild-type host when grown microaerobically rather than anaerobic or near-anaerobic conditions. An increase in the BDO titer of three orders of magnitude fold, to almost 20 g/L was realized through the metabolic engineering. Continued research is required to bring these findings to commercial-scale application.

Nature Chem Biol 2011, 7, 445–452

Greener reaction conditions award

Halogen-free polymers have been developed through the use of less-hydrocarbon solvent and the avoidance of halogenated solvents for the formation of high-flow polymer membranes. Many purification processes depend on polymer membranes to selectively control the passage of certain molecules across the membrane barrier. Application of these membranes includes water ultra-purification, desalination by reverse osmosis, salt and waste acid recovery. A new family of pentablock polymers have been invented and characterized by enhanced performance and environmental benefits for a wide array of applications. The polymers are formed of block segments in the following composition: poly(*t*-butyl styrene-*b*-(ethylene-*r*-propylene)-*b*-styrene-*b*-(ethylene-*r*-propylene)-*b*-(*t*-butyl styrene copolymer (tBS-EP-S-EP-tBS)

A = poly(*t*-butyl styrene) tBS

B = poly(ethylene-co-propylene) EP

C = poly(styrene-co-styrene sulfonate) SPS

In a subsequent synthetic step, the styrene block is selectively sulfonated using acyl sulfate chemistry. The resulting pentablock polymer depicted above gives approximate composition. The ion exchange capacity of the polymer can be adjusted from 0.4 to 2.0 meq/g through selective sulfonation. The tBS block was selected to give the polymer strength. The EP block provides toughness, flexibility, and elasticity and SPS block provides unique performance characteristics, such as water/moisture and ion transport, selectivity and reactivity. The production process for the new polymer calls requires 50% less-hydrocarbon solvent and elimination of halogenated cosolvents. These polymers have been found to exhibit a high water flux (greater than 400 times current RO membranes). Model evaluation of RO application indicates that the membrane costs could be lowered by more than 70% and energy costs by about 50%. Electrodialysis and humidity regulation applications are expected to benefit through the use of these new polymers. The polymer(s) has been produced at a 10 mt scale in 2010.

Designing greener chemicals award

A new coating technology was developed from a hybrid of recycled polyethylene terephthalate (PET) and green feedstocks derived from soybeans. Petroleum-based solvents were replaced by soybean oil which became a reactive diluent and solvent. The soy PET alkyd is made from recycled PET flake and soybean fatty acids with catalysts at 255°C. The next step grafts acrylic functionality into the alkyd to form an acrylic alkyd melt. The melt is dispersed

in water by a homogenizer/mill with the addition of an amine. Products based on the dispersed melt were found to have comparable performance and finish characteristics to traditional oil-based coatings. A semi-gloss product for commercial applicator use was found to have less than 100 g/L VOC for US nationwide compliance. Industrial maintenance coating was successfully formulated from the dispersion. Commercialization of the dispersed melt was conducted at a 500,000 gal capacity which was introduced to the 2007 market. This new technology is expected to use 250 million lbs of recycled PET each year and replace 1 million barrels of petroleum through its reduced demand for petroleum-based solvents and anticipated replacement of oil-based alkyd polymers. Finally, the performance of the new alkyd polymer performed well against current competing VOC compliant technologies.

<http://www.epa.gov/greenchemistry/pubs/pgcc/past.html>

Microchannel reactor applications win award

The research team at Velocys Inc., developing a microchannel reactor to produce synthetic fuels, has received the Kirkpatrick Award for Chemical Engineering Achievement from Chemical Engineering. This award recognizes the most noteworthy chemical engineering technology that was commercialized globally during 2009 and 2010. This new reactor is designed to convert natural gas to synthetic fuels. Other potential applications for the reactor are biomass-to-liquids and coal-to-liquids technology. In the currently designed configuration, the reactor is designed to conduct the stream-methane-reforming (SMR) of natural gas to form synthesis gas with Fischer–Tropsch (F-T) synthesis to form liquid fuels over a bed of catalysts. This reactor consists of parallel arrays of channels ranging in size of 0.1–5.0 mm in width. Smaller dimensions permit processes that are accelerated by factors of 10–1,000 resulting from the reduction of distances required for mass and heat transfer. Hence, transfer resistance between process fluids and reactor walls is significantly reduced. System volumes can be reduced tenfold or greater in contrast to fixed- or slurry-bed reactors. For the natural gas conversion, the microchannel conditions are ideally suited to conducting catalytic reactions as is the case with the highly endothermic SMR, and the highly exothermic F-T synthesis. The catalyst in the natural gas conversion achieved 1,500 kg/m³/h as compared with productivities in the fixed- and slurry-bed reactors of 100 and 200 kg/m³/h. Plugging or fouling can present formidable hurdles for large-scale implementation. High wall shear and good flow distribution can mitigate the plugging risk. The sweep of solid particles enables the microreactor to respond to certain levels of solids in the process stream. A Brazilian plant using

microchannel F-T and microchannel SWR was expected to begin processing natural gas in 2011.

Chem Engin 2011, 118(10), 19–22

Insect resistance to Bt maize

Millions of acres/hectares are planted annually with crops engineered to produce insecticidal toxins derived from the bacterium *Bacillus thuringiensis* (Bt) which is considered by some an environmental asset since the application of broad-spectrum chemical insecticides is reduced or avoided. The pesticidal trait of these Bt crops is a protein that is toxic to the larval form of the targeted pest. The western corn rootworm *Diabrotica virgifera virgifera* (Coleoptera: Chrysomelidae) is the primary pest of corn in the United States targeted by these engineered maize varieties. This insect is a serious pest whose larvae feed on the maize roots and the leading cause of the majority of crop loss for Bt corn varieties. A 2009 study of four production fields and five control fields was conducted in Iowa during the growing season for maize production. Problem sites were associated with grower complaints of severe injury for maize varieties expressing the Cry 3Bb1 western corn rootworm trait. These fields were found to contain goose-necked plants (bent to the soil surface) and lodged plants (tilted, non-erect). Each of the fields had a recorded history of planting operations across the period of 2003–2009. Insects were collected from all field locations and subjected to laboratory bioassays for resistance to the Cry 3Bb1 maize trait. The western corn rootworm larvae used in the bioassays showed higher survival for insects from the problem fields having severe root injury when compared to insects from control fields. This study is the first published report of field-evolved western corn rootworm resistance to a Bt toxin by any species of Coleoptera. Incomplete resistance management practices by growers may have significantly contributed to the observed pest resistance. The potential yield loss from this infestation could be considerable and have a negative impact on the cost and availability of corn. This constraint can translate into associated food availability and energy production process economics.

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Importance of coal fly ash to transportation

The use of coal electrical power for electrical generation has been highly debated for its direct contribution of enormous quantities of green house gas constituents which

are noted for their complicity in the global effects of climate change and atmospheric warming. Despite these roles, coal is considered to be the low-hanging fruit to meet the immediate needs of increasing electrical power generation. A poorly recognized use of coal ash is its role in the construction of roads, runways, and bridges. The importance of this role could increase by an estimated \$104.6 billion over the next 20 years should coal ash be not available as a building material. Eliminating coal ash as a material for road and bridge construction would bump up construction and repair costs by \$5.2 billion annually. A report, *The Economic Impacts of Prohibiting Coal Fly Ash Use in Transportation Infrastructure Construction*, issued by the American Road and Transportation Builders Association's Transportation Development Foundation exposed these consequences. This estimate reflects the annual increase in cost for building materials without the coal ash and repair costs of the different replacement concrete mixtures. Cement blends that use coal ash are found to enhance the lifetime of cement blends and the coal ash-based blends are cheaper than replacement blends. The report was developed as a direct response to the US Environmental Protection Agency's proposed regulation of coal ash, which could limit or eliminate the availability of the material and the potential cost to the transportation construction industry. The average life span of 20–25 years for traditional roads can be compared with new road design incorporating coal ash having a 30- to 60-year life span. In a 20-year span, coal ash concrete materials are expected to save between \$25 billion and \$65 billion in road construction and repair. It is interesting see how differing environmental control objectives can become opposed to each other. The understanding of coal issues and the utilization of waste derived from its use will be very instructive to the regulatory process.

<http://www.artba.org/mediafiles/study2011flyash.pdf>

Measuring environmental change

A report entitled: *Keeping Track of Our Changing Environment: From Rio to Rio + 20 (1992–2012)*, produced as part of the UN Environmental Program's Global Outlook series, is an inviting and well-organized contribution depicting the changes in the environment across the two decade span of 1992–2012. The collection of vignettes on various topics from energy efficiency to population to ocean acidity is quite sobering. Greenhouse gas emissions are found to be increasing with the retreat of glaciers and ocean acidity is increasing from additional amounts of dissolved CO₂. Marine life is significantly affected by the heightened ocean temperatures and increased acidity.

This 111-page report is subdivided into three major sections of population and human development, economy, environmental trends, energy, industry, transport and tourism, and technology. The world population has increased by 45% to 7 billion in the past two decades. Increased urban populations have been recorded and the number of cities having populations of 10 million has increased from 10 in 1992 to 21 in 2010. Efforts across the globe to reduce carbon emissions have not been successful. A string of the hottest 10 years ever measured occurred since 1998. Globally, forested land has decreased by 750 million acres in this time period. A 540% increase in investments was recorded for green energy solutions, such as solar and wind energy during 2004–2010.

http://www.unep.org/GEO/pdfs/Keeping_Track.pdf

Toxic chemicals in baby mattress

Concern with materials of construction for baby mattresses has been detailed in a 27-page report published by Clean and Healthy New York and the American Sustainable Business Council (ASBC). The study asserts that most crib mattresses as made using chemicals that can lead to sickness, allergies, and cancer. The survey involved 28 mattress manufactures that produced 190 models of standard US crib mattresses. The mattress manufacturers were found

to resist disclosure of chemicals used during manufacture. The chemicals of concern are flame retardants and vinyl or polyurethane foam, and undisclosed proprietary chemicals. There is a significant interest in parents with children potentially affected by these chemicals and materials to strongly advocate major changes in composition for the mattress manufactures.

<http://www.womensvoices.org/science/reports/the-mattress-matters/>

Flame retardants: Chemosphere 2002, 46, 583–624; Environ. Int. 2003, 29, 683–689; Environ. Sci. Technol. 2004, 38, 945–956; Env Health Perspect. 2004, 112(1): 9–17

New journal

A new addition to the Elsevier Current Opinion series can be found in the open access inaugural issue of Current Opinion in Chemical Engineering. The new journal will consist of four issues organized in the following subject area: nanotechnology, energy and environmental engineering, biotechnology and bioprocess engineering, separation engineering, materials engineering, process systems engineering, and reaction engineering and catalysis.

Curr Opin Chem Eng 2011,1, 1–88