Appendix C

Opportunities for Further Study: Additional Cases from First International Conference on Green & Sustainable Chemistry, Tokyo, March 2003

Introduction

The First International Conference on Green & Sustainable Chemistry was held March 13–15, 2003, at the Waseda University International Conference Center, Tokyo.[173] During the conference a number of additional developments were discussed that either added information on cases we have studied or pointed to possible additional cases. There were also discussions in measuring the benefits of green and sustainable chemistry.

Information on Cases

Details are given in Table C1.

Measuring Benefits

At the conference there was also considerable discussion on measuring the benefits of green and sustainable chemistry, or the "metrics for green and sustainable chemistry" or metrics for sustainability.

We can measure the benefits of one process or chemistry at a time, as we have done in this report.

The pharmaceutical firm of GlaxoSmithKline (GSK) has identified a set of core "sustainability metrics": mass, energy, toxic dispersion (greenhouse gas, toxicity, eutrophication, Total Organic Carbon, acidification, and ozone precursors), natural resource utilization (oil), solvents, "chemistry greenness," and economics.[174] Evaluation of GSK chemistries and processes using such metrics revealed:

- From an economic standpoint, yield remains a very good metric, especially for high value added materials such as pharmaceuticals, and exerts significantly more influence on cost than poor atom economy, at least in the short term.
- Atom economy may be useful as an organizing concept or in combination with other metrics, but at this time it is not considered to be useful as a standalone metric.
- Reaction mass efficiency combines key elements of chemistry (including atom economy) and process and represents a simple, objective, easily derived and understood metric for use by scientists and focuses attention away from waste toward the use of materials.

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[173] See Abstracts, The First International Conference on Green & Sustainable Chemistry, Green & Sustainable Chemistry Network Secretariat, Japan Chemical Innovation Institute, 1-3-5 Kanda Jinbo-cho, Chiyoda-ku, Tokyo 101-0051, Japan.

[174] Abstracts, pp. 84–85 and Constable, Curzons, and Cunningham "Metrics to 'Green" Chemistry—Which Are Best?" *Green Chemistry* No. 4, 2002, pp. 521–527.

- Mass productivity is a good metric for businesses because it highlights resource utilization.

- It is important that we have “green processes,” not just “green chemistries,” and this will require the integration of technology and chemistry.

GSK has a range of tools on the company intranet to help researchers develop green processes and determine some of these metrics: a green chemistry guide, a fast life-cycle evaluation of synthetic routes, a materials selection guide (especially solvents), and a green packaging guide.

In Japan, the Green and Sustainable Chemistry (GSC) Network, in evaluating nominations for the Japanese GSC award, uses four categories: (1) energy consumption (or carbon dioxide emissions), (2) virgin resource consumption, (3) consumption of landfill sites, and (4) environmental emissions. These are plotted on a radar chart.[175]

In making these measurements, one must consider to what extent are they relative. Do we consider the process the green process is actually replacing, or for a new product do we consider a hypothetical alternative process based on traditional chemistry that would never be commercialized for a variety of reasons?

Eventually one might sum the benefits over all newly installed processes to get the total impact of green chemistry on the environment and society. Alternatively we can measure the decrease in overall emissions, reduction in energy use, waste reduction, reduced hazard chemical storage, and increased use of renewable feedstocks.[176]

Subhas Sikdar, director of the sustainable technology division at National Risk Management Research Laboratory, EPA, discussed the scope and limitation of “sustainability metrics” for products and processes. He pointed for the need to quantify benefits in three areas: economic development, ecological preservation, and social good. In some areas, benefits are more difficult to quantify.[177]

We have not discussed the potential benefits of green chemistry itself—the attraction of more students into the discipline of chemistry, the improvement of the public’s appreciation of

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[175] Abstracts, pp. 87–88.

[176] This problem is somewhat similar to that encountered in modeling the impact of technologies on global climate change. Bottom-up or engineering systems models take one technology at a time (microeconomics); top-down or macroectonomic models look at the overall impact. See http://www.iea.org/pubs/studies/files/mapping/fig4.pdf.

[177] Abstracts, pp. 71–73.

chemistry, seeing chemistry as part of the solution rather than the problem, and the improvement in the image of the chemical industry.

Table C1. Cases from the conference.

Case	Description	Comments	Benefits	Speaker or Reference
1	Supercritical carbon dioxide as solvent	Cleaning semiconductor wafers with supercritical carbon dioxide gives increased penetration as device dimensions approach the nanoscale. Development involving industry, government, and academia is being commercialized.	Eliminate 4 million gallons of waste water that are produced and thousands of gallons of chemicals used on an average day in a single semiconductor manufacturing facility.	Laura.rothman@scfluids.com SC Fluids, Inc. 472 Amherst St. Nashua NH 03063 p. 55 of abstracts
5	Dimethyl carbonate	1. Vapor-phase reaction of methanol and CO with copper chloride catalyst in fluid bed; optimization. 2. National Institute of Advanced Industrial Science and Technology (AIST), Japan, developed a cyclic carbonate process using supercritical carbon dioxide and ionic fluids.	1. Eliminates problems from liquid phase reactions. 2. 100% yield and 100% selectivity "expected to significantly accelerate the development of production methods for environmentally friendly engineering plastics."	1. ito.hirofumi@jgc.co.jp p 127 of abstracts. 2. See www.aist.go.jp/index_en.html for "What's New" 2/26/03 ; good website for a number of green chemistry developments.
17	Room Temperature Ionic Liquids	A representative sample of research studies that were reported: —Application of Ionic Liquids to extractive fermentation of lactic acid (p. 112). —Enzymatic esterification in green solvents: application of ionic liquids in bioconversions (p.115). —Electrochemical fluorination of oxygen-containing heterocycles	None to the point of process development and commercialization.	See abstracts as noted.

		in ionic liquids (p. 119). —The Fischer Indole Synthesis in an ionic liquid (p. 122). —Green carbohydrate chemistry: Environmentally benign chemical glycosidation using ionic liquids (p. 123).		
18	New refrigeration processes	Greenfreeze refrigeration technology based on hydrocarbons; collaborative work involving Greenpeace	Eliminates CFCs; discussed as "controversial."	J. Michael Fitzpatrick, President and Chief Operating Officer, Rohm and Haas; ebush@rohmhaas.com Comments during talk
20	Biodegradable polymers	1. BASF has developed a biodegradable plastic, Ecoflex®, which is enjoying "double-digit growth rates." 2. A series of biodegradable polymers are being developed in China with the Polymer Material Engineering Lab, Changchun Institute of Applied Chemistry; the polymers are manufactured from carbon dioxide and various epoxides.	2. The new biodegradable plastics cost less than $1/lb have mechanical properties comparable to polyethylene, low oxygen and water permeability approaching that of PVDC. BioCO2™ 3000 uses cyclohexene as the epoxide. Another product uses ethylene and propylene oxides with carbon dioxide.	1. Dietmar Nissen, President BASF East Regional Headquarters; nissend@basf-east-asia.com.hk p. 7 of abstracts 2. Xianhong Wang: xhwang@ciac.jl.cn p. 54 of abstracts
26	Thermal green chemistry	Higher temperatures than normal offer opportunities for efficiencies in time and energy, and some batch reactions can be made continuous. At 200 degrees C and pressures of 2–3 MPa reactions in traditional solvents can be carried out in shorter time periods and at higher yields. A microwave batch reactor and continuous microwave reactor were used. Reactions were also carried out in high temperature water.	Additional work will be needed to scale-up for commercial applications.	C. R. Straus, Center for Green Chemistry, Monash University, Australia strauss@sci.monash.edu.au Abstracts pp. 43–46

27	New routes to vinyl acetate and ethyl acetate	Acetic acid, oxygen, and ethylene are reacted in a fixed bed reactor which “fluidizes” the catalyst to produce vinyl acetate; the use of the fluidized bed saved 30% of capital costs and x-ray imaging eliminated the need for a $20–30 million demonstration plant and three to four years in development time. Acetic acid is added to ethylene with a heteropolyacid as catalyst.	Allowed plant consolidation, improved economics, reduced energy in transportation of raw materials, reduced water use, and 35% less raw materials. The two processes received industrial awards, one (ethyl acetate) being the AstraZeneca Award for excellence in Green Chemistry and Engineering.	Ian Dobson, General Manager BP Chemicals, Sunbury on Thames, Middlesex UK. Abstracts pp. 47–51.
28	Recyclable waterborne coating system	Nippon Paint develop a waterborne coating and a system that collects uncoated waste paint for recycle.	Eliminates VOCs and reduces waste in industrial coating operations	Sakuichi Konishi: konishi_NP2060@npc.nipponpaint.co.jp Abstracts pp. 31–33
29	Environmentally safe marine antifoulant	Sea-Nine antifoulant, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one an alternative to organotin compounds.	Eliminates use of organotin, with bioaccumulation essentially zero and no chronic toxicity.	Mentioned by J. Michael Fitzpatrick at the conference. Winner of 1996 Green Chemistry Presidential Challenge Award: see www.epa.gov/greenchemistry/docs/award_recipients_1996_2002.pdf pp. 72–73
30	Safer insecticide	CONFIRM™—selective caterpillar control agent. The product acts by strongly mimicking a natural substance found within the insect’s body that is the natural “trigger” that induces molting and regulates development in insects. CONFIRM™ disrupts the molting process causing insects to stop feeding; they then die. Related Selective Insect control agents were also described.	Inherently safer to non target organisms, lower use rates.	Mentioned by J. Michael Fitzpatrick at the conference. Winner of 1998 Green Chemistry Presidential Challenge Award: see www.epa.gov/greenchemistry/docs/award_recipients_1996_2002.pdf pp. 52–53

31	Use of solid acid catalysts	DuPont has developed a solid acid (poly-perfluorosulfonic acid, or Nafion®) on silica sol-gel network for polymerization of tetrahydrofuran to polytetramethylene ether glycol, which is used to manufacture Lycra® spandex fiber.	Eliminates use of fluosulfonic acid and allows recovery of the acid. Activity increased 1,000x by use of the support; solids reduced 99.5% and biological oxygen demand to almost zero.	Mentioned by Thomas Connelly, Chief Science and Technology Officer at DuPont, abstracts p. 98
32	Supersolids clear coat	DuPont created a very high solids automotive coating—reduced molecular weight that crosslinks when drying.	Won an EPA Clean Air Award; improved properties (scratch resistance, higher gloss) with 25% less solvent emissions.	Mentioned by Thomas Connelly, Chief Science and Technology Officer at DuPont, abstracts p. 99; Note: he also mentioned Tyzor Polyester catalysts, titanium-based catalysts that eliminate the Sb and Ge heavy metal catalysts. Can be used when a light coloring is permitted.
33	New route to caprolactam	Clean production of caprolactam without production of significant quantities of ammonium sulfate is accomplished by combining a process developed by Sumitomo Chemical with one developed by Eni Chem. Cyclohexanone is reacted with ammonia, hydrogen peroxide and TS-1 catalyst; the resulting oxime is converted to caprolactam via the Beckmann rearrangement in the vapor phase.	The only by-product is water; commercial operation begins in 2003.	Akio Kosai, Chairman, Sumitomo Chemical Company 27-1, Shinkawa 2-chome, Chuo-ku, Tokyo 104-8260; abstracts p. 11 Note: He mentioned without details the catalytic oxidation of HCl back to chlorine; a commercial plant to begin operation in "the near future" and a new route to a rubber intermediate ethylidene norbornene.