

The Principles of Green Chemistry

*Canadian Pollution Prevention Roundtable
Halifax, June 14, 2006*

**Prof. C.J. Li
McGill University**



Sustainability-definition

“Sustainable development meets the needs of the present without compromising the ability of future generations to meet their own needs”

(In 1987, the World Commission on Environment and Development developed a definition of sustainability that was included in its findings)

--- Brundtland Report.

Sustainability

- Resource Sustainability
- Economic Sustainability
- Social Sustainability
- Environmental/ecological Sustainability

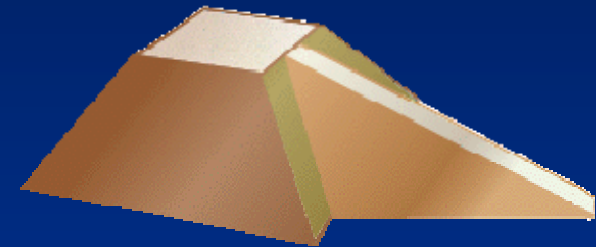
Great Human Achievements

on the Macroscale and Microscale

>2000 years ago, The Great Pyramid

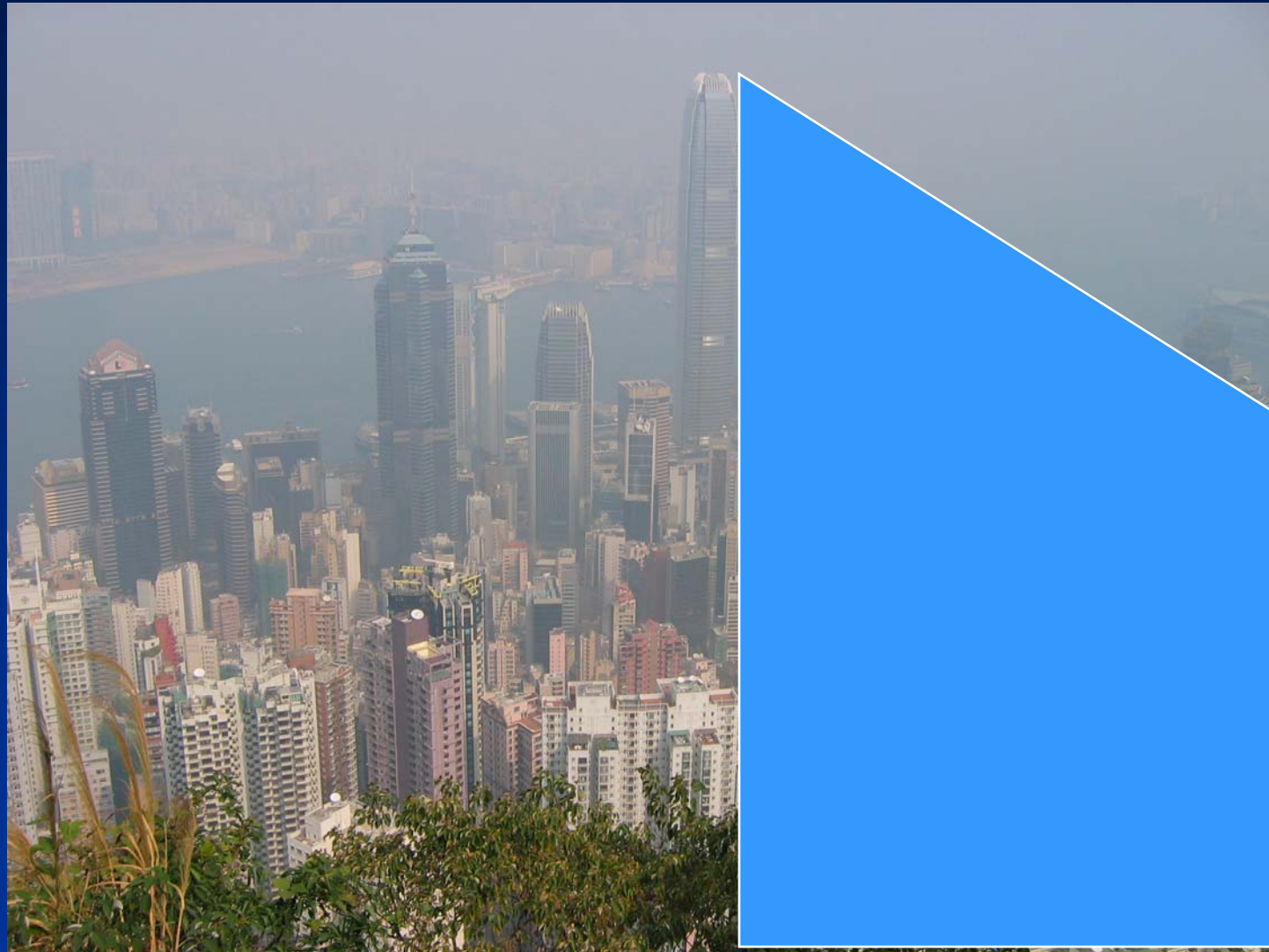


Copyright Lee Krystek, 1999



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Hong Kong, Dec. 2004



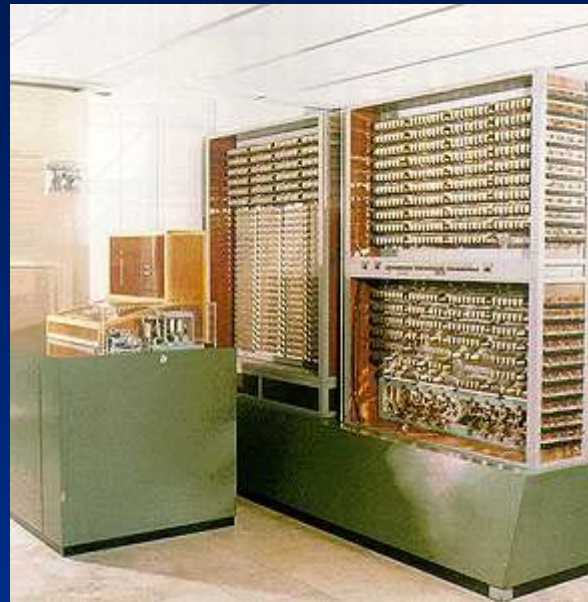
On the nanoscale

Z3 Computer (1941)

22 bites (1961) (**based on vacuum-tubes**)

Weight: 1000 Kg

Length: 5 meter



http://irb.cs.tu-berlin.de/~zuse/Konrad_Zuse/en/Rechner_Z3.html

Samsung Cell Phone

4,000,000,000 bites (2004) (**based on silicon chips**)

Weight: 0.099 Kg

Length: 0.05 meter



power/weight

10^{13}



<http://cellphones.about.com/od/samsungreviews/>

On the molecular scale

-The production and use of chemical products

Chemistry and Sustainability

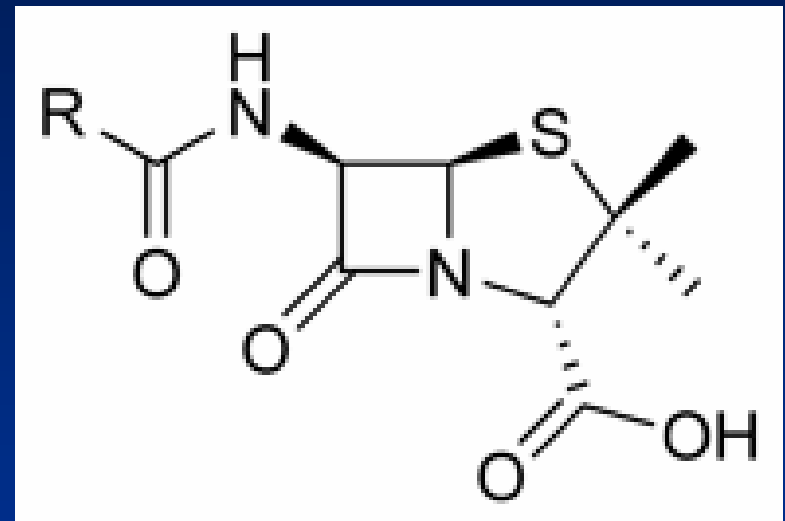
Polyester



www.supermodels.com



www.familycar.com



<http://www.pbs.org/>

The Challenges

A Sustainable Situation?

- Only 10% of the resources removed from the Earth end up in the goods manufactured
- 90% End up as waste
 - Double economic penalty
 - Resource depleting rapidly
 - The waste becomes huge environmental problems
- Source: WRI 2001

(from Buzz Cue)

THE COST OF WASTE

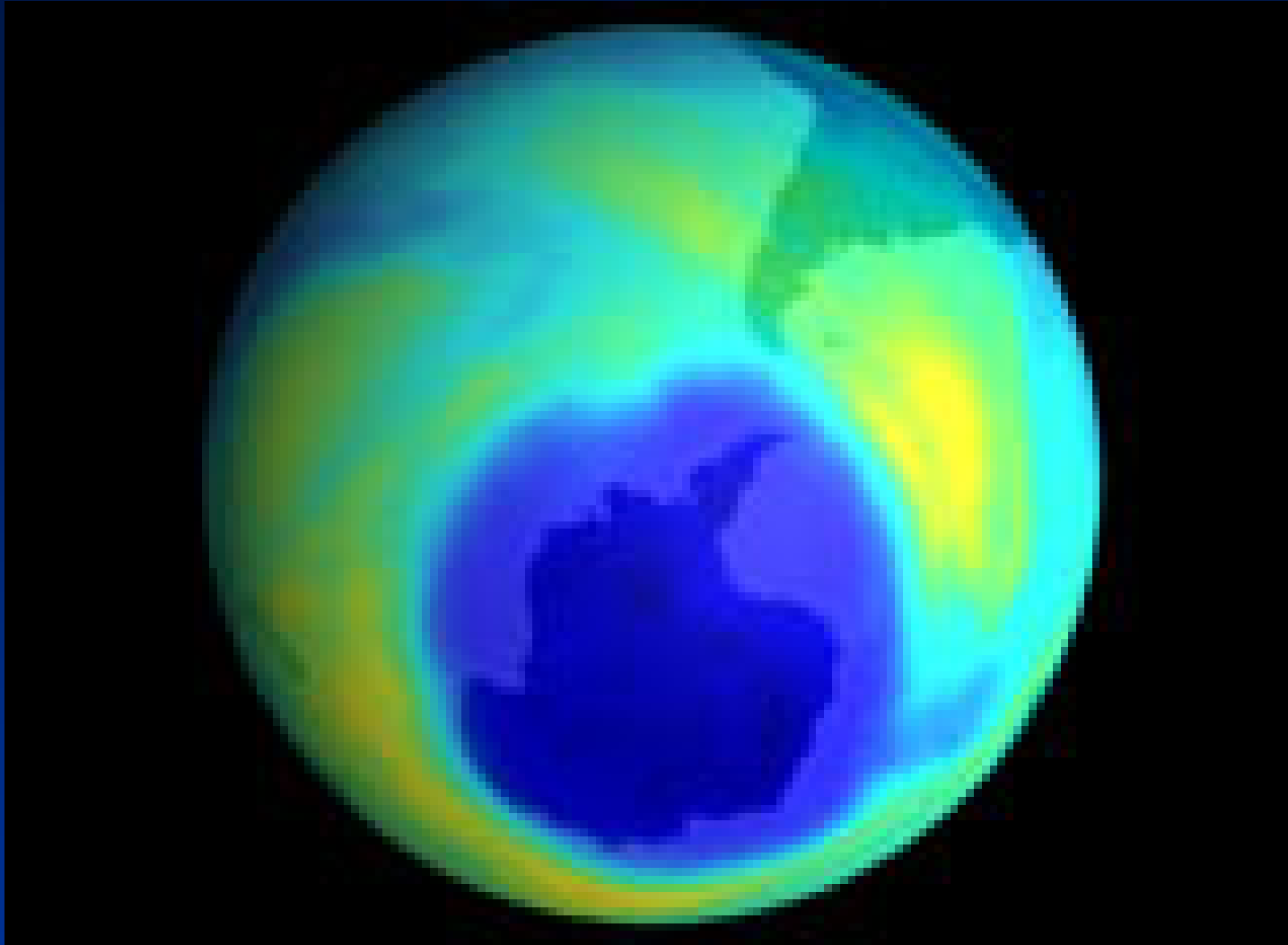
- The cost for its manufacturing: the initial purchasing cost
- The cost for its transportation
- The cost for its storage
- The energy cost for heating and cooling the waste
- The cost for its separation (from products)
- The cost for its disposal (recycling, treatment etc).
- **The cost for meeting regulations**



www.nbmjg.unr.edu/slides/oil/1.htm



Slide provided by Prof. D. N. Harpp of McGill University



<http://www.coolantarctica.com>



http://www.panda.org/news_facts/education

Environment



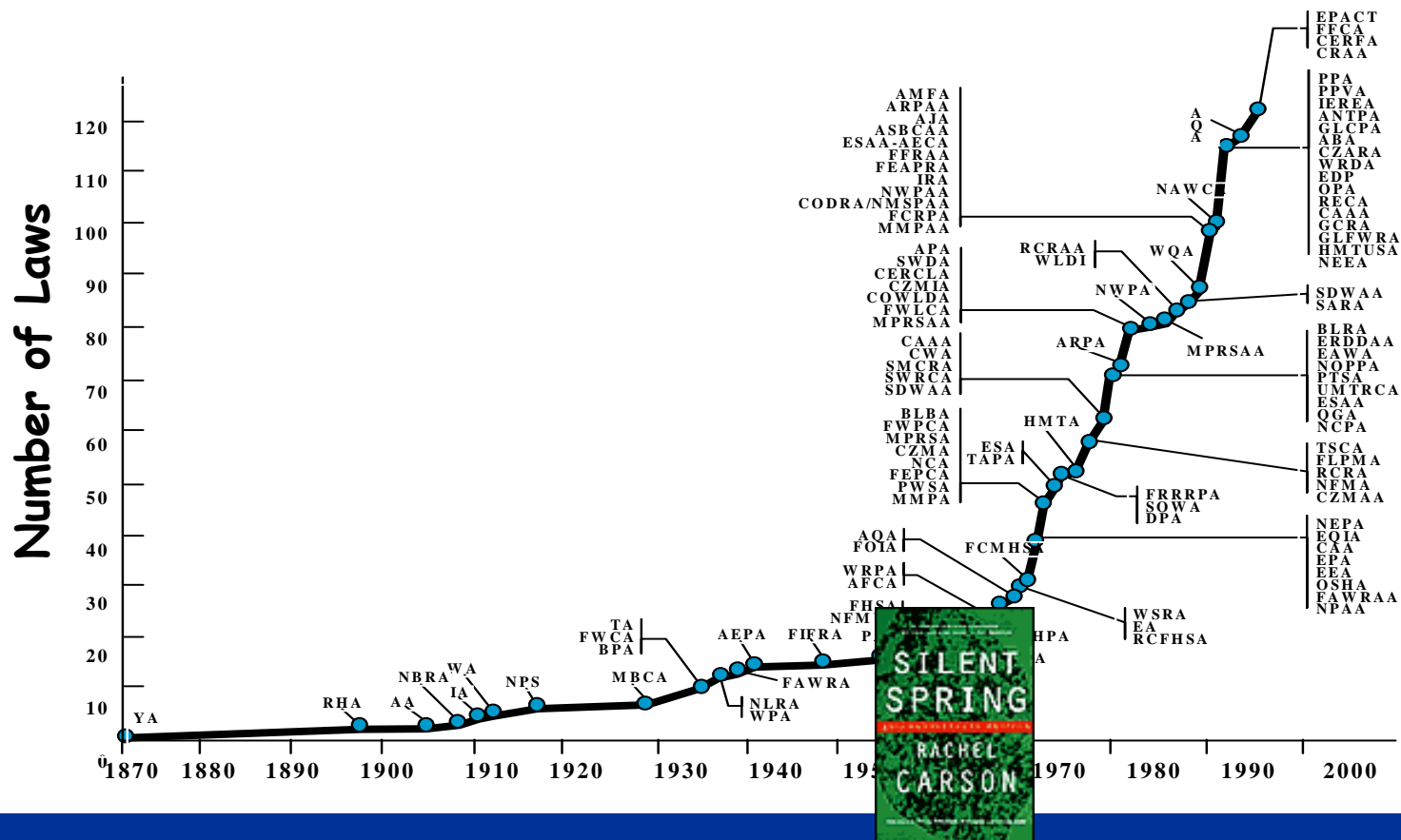
Economy

Conventional Environmental Protection VS Economical Development

All based on “defense” strategies

The Challenge: Regulatory Advance

Environmental Regulations



Source: Green Chemistry Institute

Conventional Environmental Protection VS Economical Development

All based on “defense” strategies

Is there a proactive way to both develop economy and protect the environment?

Green Chemistry!

The Successes

“...the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.”

-Paul Anastas and John Warner, *Green Chemistry: Theory and Practice*,
Oxford University Press, 1998

12 Principles of Green Chemistry

1. Prevention:
2. Atom Economy:
3. Less Hazardous Chemical Syntheses:
4. Designing Safer Chemicals:
5. Safer Solvents and Auxiliaries:
6. Design for Energy Efficiency:
7. Use of Renewable Feedstocks:
8. Reduce Derivatives:
9. Catalysis:
10. Design for Degradation:
11. Real-time analysis for Pollution Prevention:
12. Inherently Safer Chemistry for Accident Prevention:

Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998

Green Chemistry – Cutting-edge research for a greener sustainable future



ISI Impact Factor -- 3.5

www.rsc.org/greenchem

Green Chemistry

Published by the Royal Society of Chemistry, UK

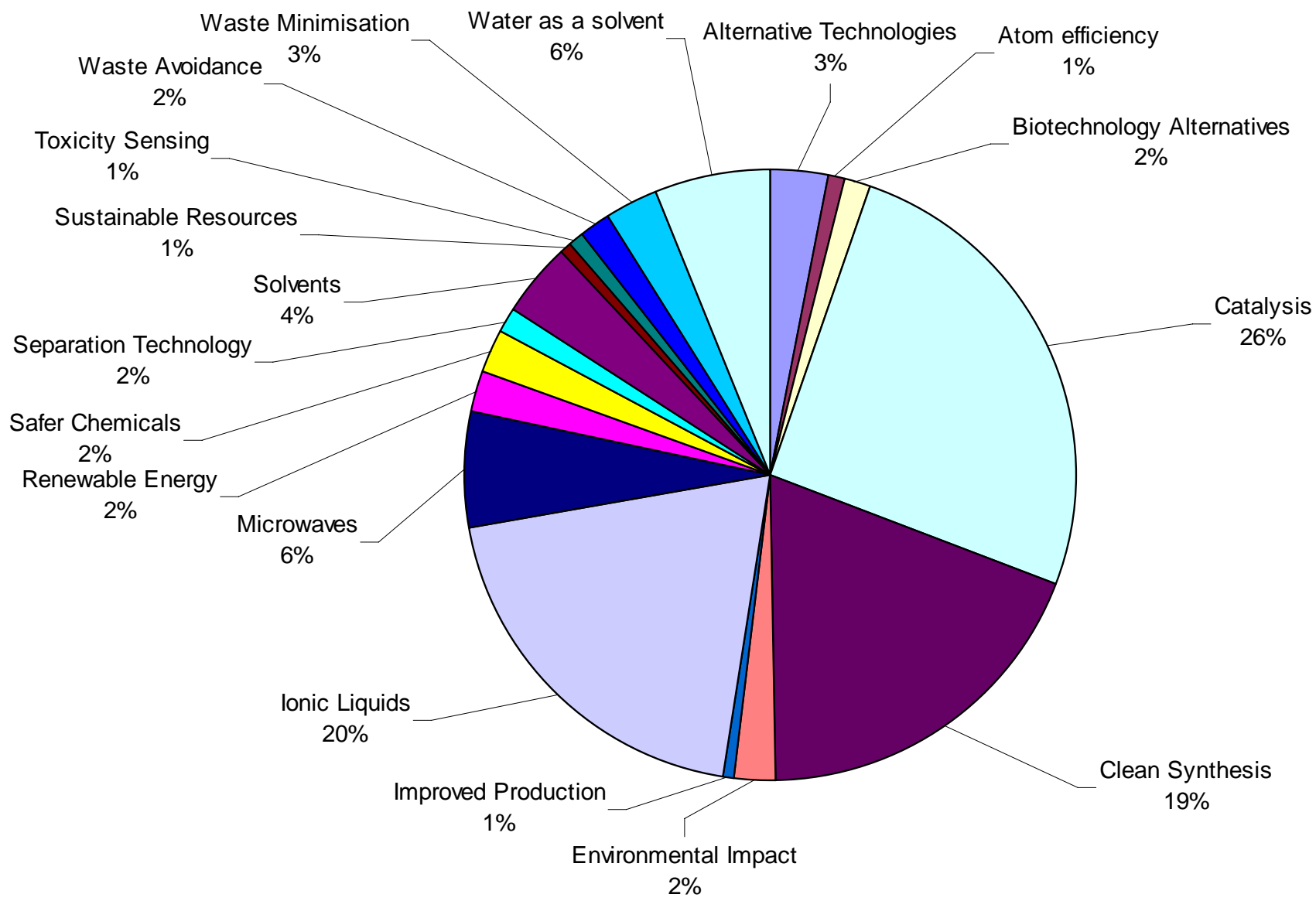
Chairman of Editorial Board: Prof. Colin Raston

Scientific Editor: Prof. Walter Leitner

Associate Editor for Americas: Prof. C. J. Li

Managing Editor: Sarah Ruthven

GC Submissions - Subject Areas



Canadian Green Chemistry Network

2002, Initiated by Prof. T. H. Chan, McGill University

- Initially, over 40 (>100 estimated) academic research scientists from across Canada at universities: UBC, Alberta, Regina, Saskatchewan, Guelph, Toronto, Queens, McGill, Montreal-Ecole- Poly, Laval, Sherbrooke, INRS-UQ, St. Mary's;
- Research scientists from NRC, NRCan and EC;
- Diverse disciplines: chemistry, biochemistry, microbiology, engineering, agriculture, forestry, management, social science;

Canadian Green Chemistry Network (2003)

Coordinator

2003-2005 **T. H. Chan**

2005 **H. Alper**

2005-present **C. J. Li**

Reorganization of the network expected 2006

2003 IUPAC Conference (Ottawa)

Green Chemistry Symposium-

(organized by the Canadian Green Chemistry Network)



Canada—U.S. Joint Workshop on Innovative Chemistry in Clean Media

**Thursday, May 20 and Friday, May 21, 2004
on the campus of McGill University in downtown Montréal, Canada**

You are cordially invited to attend this two-day workshop that will feature lectures and panel discussions by leading academic and industrial scientists from the U.S., Canada, and Europe on the frontiers and issues of using "greener" solvents in science and technologies. It is the hope that through this workshop, leading researchers can exchange innovative ideas on pushing the frontiers in the field and bring academic researchers, industrial scientists, and governmental policy makers together to develop green chemical technology in a constructive manner. The workshop will be excellent for those who want to learn more about this field and for graduate students/postdocs who are exploring career potentials in Green Chemistry. A poster session has also been scheduled. Submissions of abstracts for posters to be presented at the workshop are also being accepted.

Invited Speakers and Panel Discussions

P. Anastas, White House OST, U.S.
R. Breslow, Columbia University, U.S.
W. Turmas, Los Alamos National Laboratory, U.S.
K. Seddon, The Queen's University of Belfast, U.K.
N. Leadbeater, University of Connecticut, U.S.
R. Varma, EPA Clean Processes Laboratory, U.S.
E. Beckman, University of Pittsburgh, U.S.
C. Mehnert, ExxonMobil, U.S.
R. Rogers, University of Alabama, U.S.
W. Leitner, RWTH Aachen, Germany
P. Jessop, Queen's University, Canada
T. H. Chan, McGill University, Canada
R. Singer, St. Mary's University, Canada
P. Percival, Simon Fraser University, Canada
A. C. Weedon, University of Western Ontario, Canada
C. J. Li, McGill University, Canada
R. Tillyer, Merck Co., U.S.
S. Horne, Brantford Chemicals, Canada
B. Cue, Pfizer-VP retired, U.S.
W. Vladuchick, Eli Lilly Co., U.S.
H. Mahabadi, Xerox Research Centre of Canada

Workshop Registration Fee

Regular: CAN\$250.00, Student: CAN\$25.00

The workshop is limited to 100 participants and early registration is strongly advised (by personal cheque or money order). Pre-registration can be made at: Canada—U.S. Workshop Secretary
Department of Chemistry, McGill University
801 Sherbrooke St. West
Montréal, QC, Canada H3A 2K6

For information, please contact C. J. Li at
cj.li@mcgill.ca; tel. 514-398-8457; fax 514-398-3797.

Organizing and Scientific Advisory Committee

P. Anastas, U.S. White House, OST, U.S.
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R. Young, Merck Frost Pharmaceuticals, Montréal, Canada
B. Cue, Pfizer Pharmaceuticals (retired), Connecticut, U.S.
J. Cunningham, Industry Canada, Ottawa, Canada
P. R. Sundararajan, CIC/CSC, Canada

Local Organizing Committee

T. H. Chan, McGill University, Canada
C. J. Li, McGill University/Tulane University, Canada/U.S.
P. Jessop, Queen's University, Canada
J. Lessard, Université de Sherbrooke, Canada

Abstract Submission Procedure

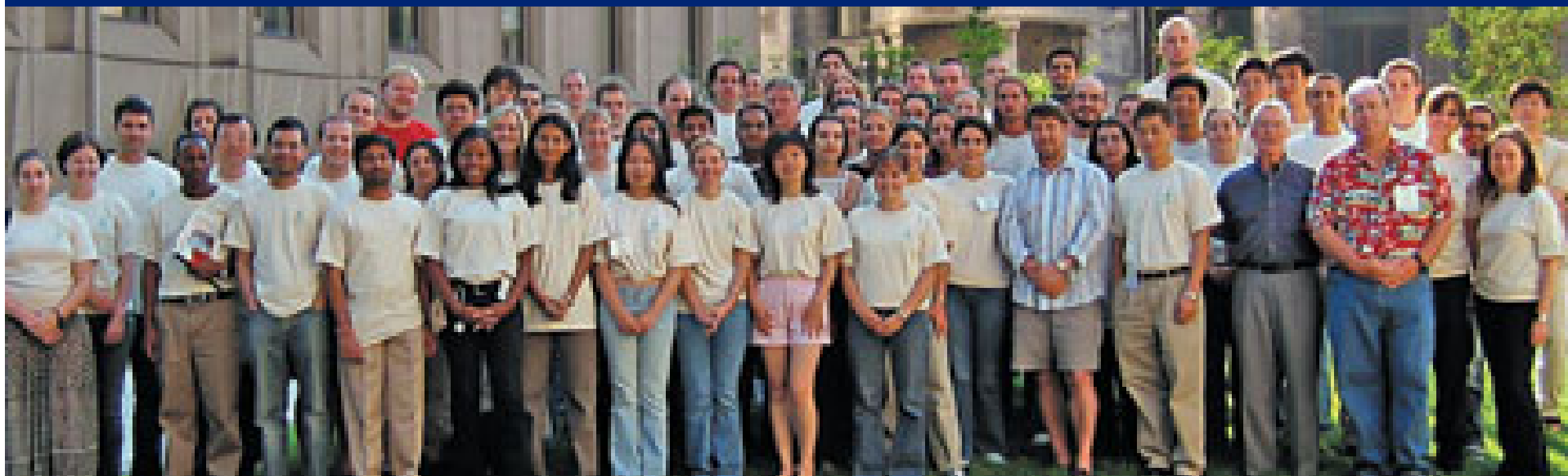
Invited speakers and those who wish to present a poster should submit their abstracts to Philip Jessop at jessop@chem.queensu.ca by April 30, 2004. For form of the abstract and detailed information of the conference, see:

www.greenchemistry.ca

ACS (Pan-America) Green Chemistry Summer School

(2005, McGill University)

Host: C. J. Li



Higher Efficiencies, Faster Discoveries, Quicker Diversities, Cleaner Processes, Cheaper Feedstocks

Symposium on Green Chemical Processes for Pharmaceuticals and Fine Chemicals

Organizers

Prof. C. J. Li
Department of Chemistry
McGill University

Dr. Berkeley Cue
Pfizer (VP retired)

Dr. Paul T. Anastas
Green Chemistry Institute
American Chemical Society

Time: October 6-9 (tentative), 2006

Location: Montreal

International Advisory Board Members:

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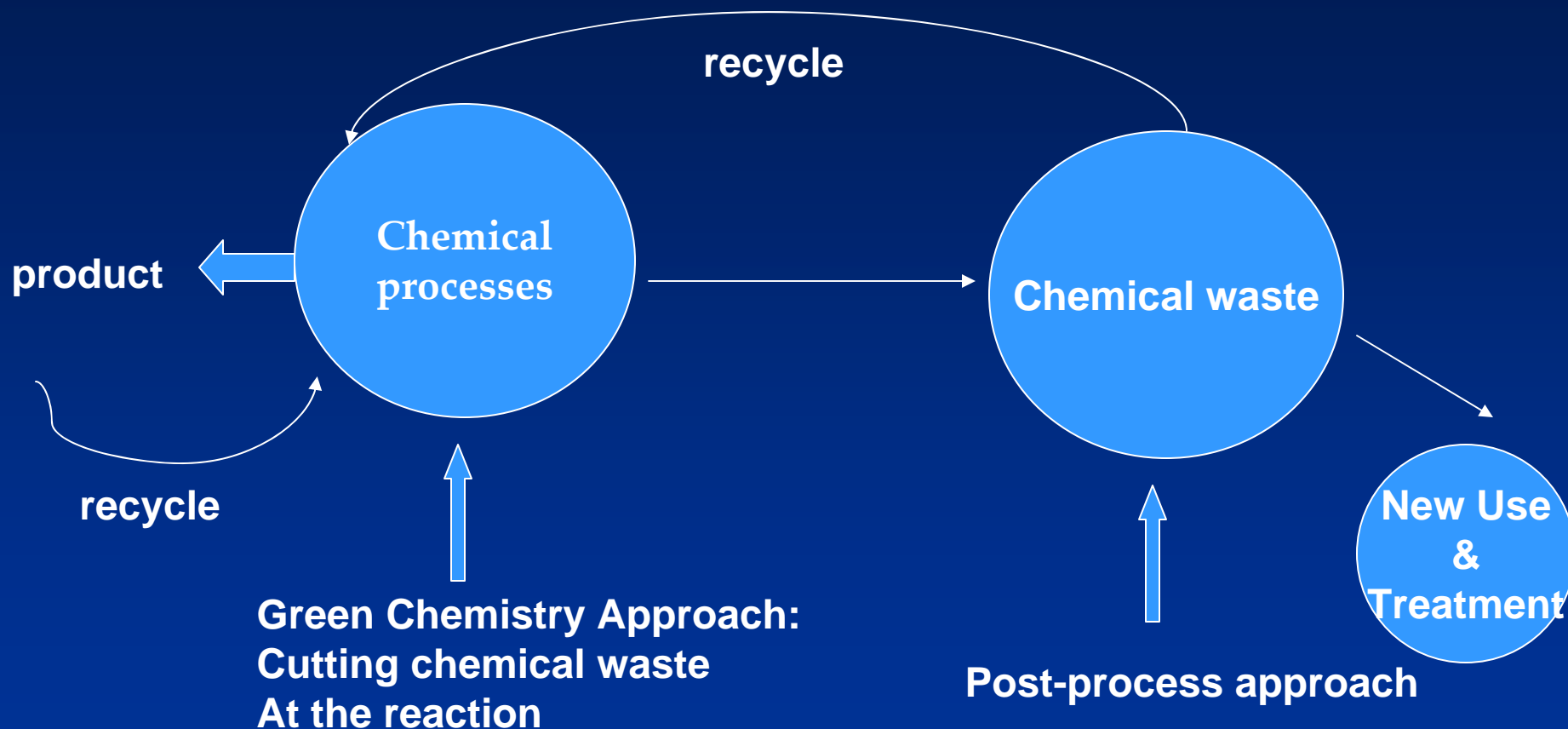
Canadian Green Chemistry Medal

*To recognize annually the outstanding contributions of individual(s) to the promotion and development of green chemistry **internationally as well as in Canada**. The winner will be presented with a citation recognizing the achievements together with a sculpture.*

- 2004 Paul T. Anastas (Director of the Green Chemistry Institute, the American Chemical Society)
(for his leadership in the promotion of green chemistry worldwide and in Canada)
- 2005 Jean M. Belanger (former President of the CCPA)
(for his critical role in the creation of Responsible Care® worldwide and in Canada)

LONG-TERM

Goal of Green Chemical Productions



1. PREVENTION

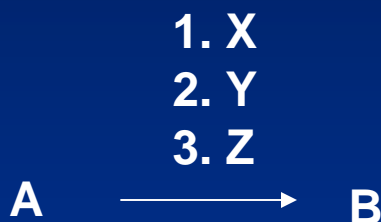
Creat new scientific means to **prevent** waste, hazards, accidents, harms etc.

2. ATOM ECONOMY

(1998 US Presidential Green Chemistry Challenge Awardee)



Barry M. Trost
Stanford University



$$\text{Yield} = \frac{\text{mole of P (obt)}}{\text{mole of P (theor)}} \times 100\%$$

www.stanford/chemistry



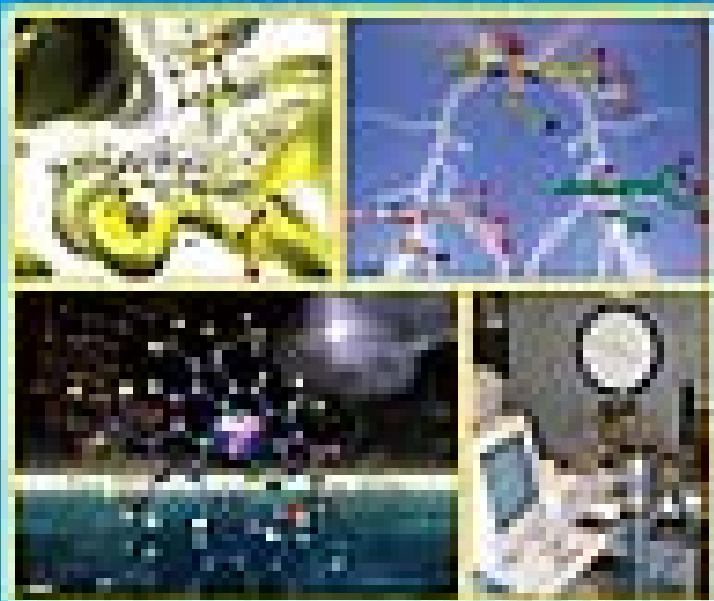
5. SAFER SOLVENTS AND AUXILIARIES

CLEANER REACTION MEDIA

- Solventless
- Supercritical and liquids CO₂
 - Ionic liquids
- Water(including hot water)
- Perfluorated hydrocarbons

CHEMICAL REVIEWS

MONOMETALIC AND BICENTROMETALIC MECHANISMS



www.acs.pub.

Chem. Rev. 1993, 93, 2023-2030

2023

Organic Reactions in Aqueous Media—With a Focus on Carbon–Carbon Bond Formation

1993

Chao-Jun Li

Department of Chemistry, Stanford University, Stanford, California 94305-5080

Received August 26, 1992 (Revised Manuscript Received May 13, 1993)

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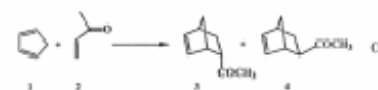


Chao-Jun Li (born in 1963) obtained his B.Sc. in Chemistry from Zhengzhou University, China. After two years of teaching in Henan Medical University, he did his M.Sc. under the supervision of T. H. Chan (McGill University) at the Institute of Chemistry, Academia Sinica, where he received a young Cramer Award. He then completed his Ph.D. study with T. H. Chan and D. N. Harpp at McGill University, where he received a Max Bell Fellowship and a Clifford H. Wong Fellowship. In addition, he was on Dean's Honor List of Ph.D. graduates. Currently, he is a Natural Sciences and Engineering Research Council of Canada Postdoctoral Fellow at Stanford University with Barry M. Trost. His research interests include all areas of synthetic efficiency and special organic reactions.

II. Diels–Alder Reactions and Claisen Rearrangement Reactions

A. Diels–Alder Reactions³

The Diels–Alder reaction is the most important method used to form cyclic structures. Diels–Alder reactions in aqueous media were first carried out back in the 1930s.³ No further study was carried out until recently. In 1980, Breslow⁴ and later Grieco as well as others reported that Diels–Alder reactions were accelerated by using water as solvent. Water as a reaction solvent also strikingly affected the selectivity of some Diels–Alder reactions.⁵ At low concentrations, where both components were completely dissolved, the reaction of cyclopentadiene with butanone gave a 21:4 ratio of endo/exo products when they were stirred at 0.15 M concentration in water, compared to only a 3:85 ratio in excess cyclopentadiene and an 8:5 ratio in ethanol as the solvent (eq 1). Aqueous detergent



I. Introduction

Carbon–carbon bond formation is the essence of organic synthesis. Although the well-known Kolbe synthesis was discovered in 1849⁶ (the first observation was made in 1834 by Faraday),⁶ for more than a century, carbon–carbon bond formation in aqueous media has been limited mainly to electrochemical processes and aldol condensation reactions. This is in contrast to the many enzymatic processes that by necessity must occur in an aqueous environment. In the last decade, there has been increasing recognition that organic reactions carried out in aqueous media may offer advantages over those occurring in organic solvents. For example, protection and deprotection processes in organic synthesis can possibly be simplified. This review will survey this area, concentrating mainly on the last decade.

The review is organized into three main portions: nonorganometallic reactions, organometallic reactions, and transition–metal-catalyzed organic reactions in aqueous media. The conventional aldol-type and related reactions, stabilized carbanion alkylation reactions, electrochemical reactions as well as bioorganic reactions involving aqueous media and leading to carbon–carbon bond formation will not be included.

0009-2665/93/0703-2023\$12.00/0

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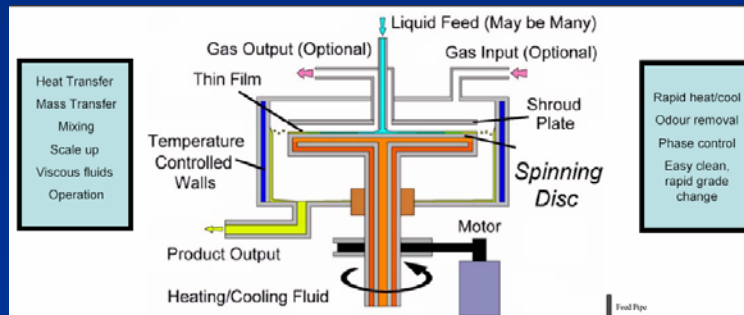
1997



Organic
Reactions
in Aqueous
Media

Chao-Jun Li
Tak-Hang Chan

6. DESIGN FOR ENERGY EFFICIENCY



<http://www.protensive.co.uk/>

7. USE OF RENEWABLE FEEDSTOCKS

10. DESIGN FOR DEGRADATION

Future Challenges

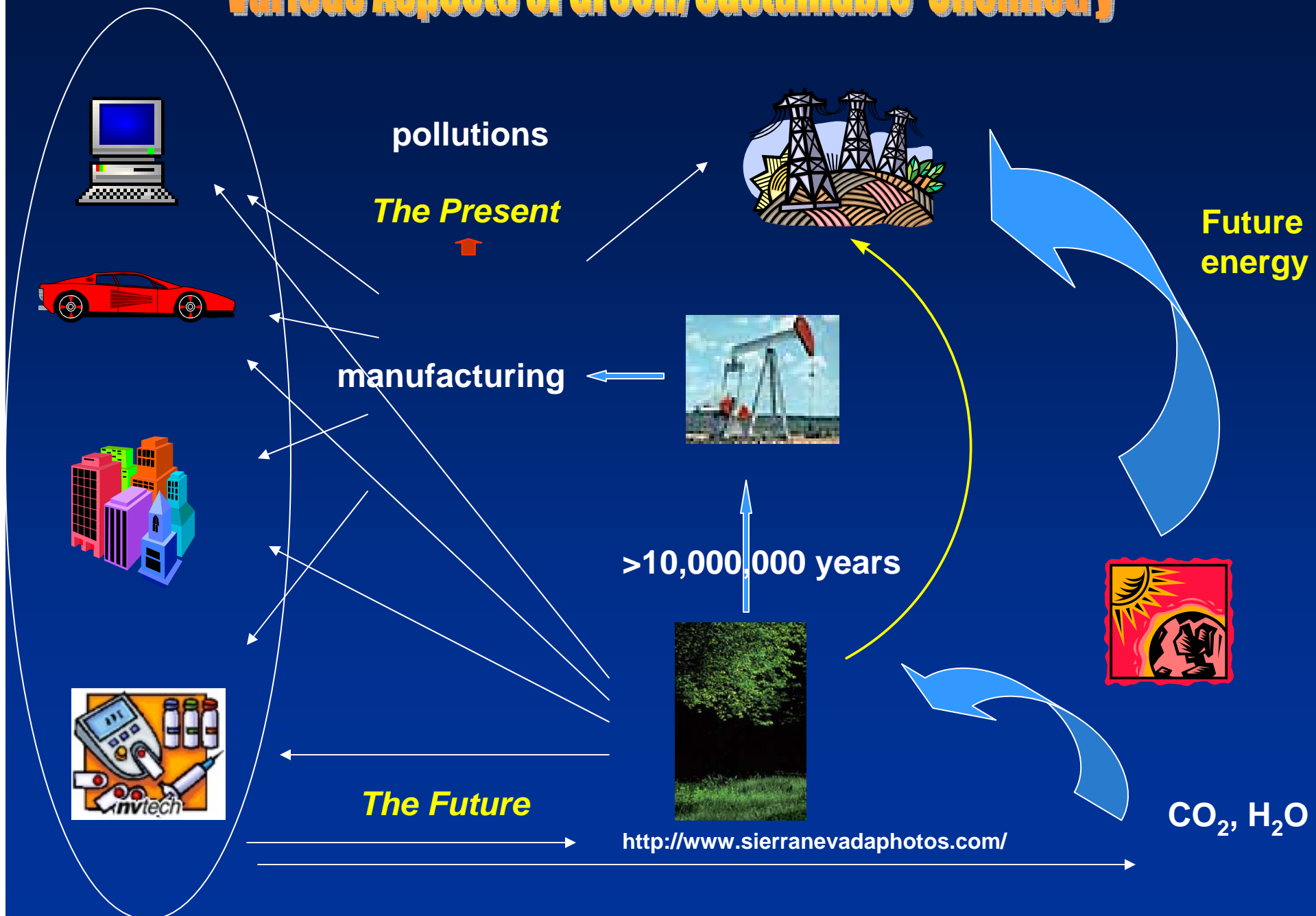
- Plastics and polymers designed for innocuous degradation through the use of additives-free design.



Source: Green Chemistry Institute

The Future

Various Aspects of Green/Sustainable Chemistry



Research Interests of the Li's Group

Hydrocarbons

CO₂, CO

H₂O

N₂, NH₃

Biomass (carbohydrates, lignins)

O₂

Cat.

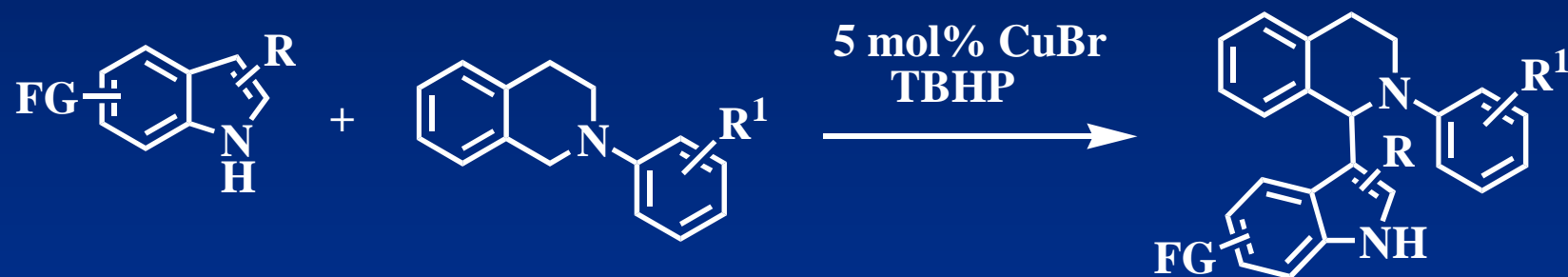


Chemical Products

The environmental, social, economical benefits.

Highly Efficient Way to Make Pharmaceutical Agents

CDC: sp^3 C-H with sp^2 C-H



Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 6968.

Materials

CJ Li et al. NASA Report 2005; The SAMPE Meeting (Nov. 2004)

Polyimides (wide-range of applications):

Conventional method

- Increase cost for the feedstock
- Increase cost for the treating the waste
- Increase cost for meeting regulations
- Increase transportation cost

Our solution by new design:

- No waste. No solvent.
- Properties are better than or similar to the conventional standard method.
- Now, it has been used in some electronics

(Published >200 research papers)

Some News Report of the CJ Li Group

Scientific American, March 2006;

Chem & Engineering News, Aug 22, 2005;

Chem & Engineering News, July 28, 2005;

Chem & Engineering News, May 23, 2005;

Chem & Engineering News, Dec. 6, 2004;

Chem & Engineering News, Oct. 13, 2003;

Chem & Engineering News, May 20, 2002;

Chem & Engineering News, July 2, 2001;

Chem & Engineering News, January 22, 2001;

Science, Editor's Choice, September 29, 2000;

Chem & Engineering News, September, 2000;

Chem & Engineering News, September 20 1999;

Chem & Engineering News, April 7, 1996;

**2001 (US) Presidential Green Chemistry Challenge Award (Academic)
(Washington DC)**





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Scientific American



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“We shall escape the absurdity of growing a whole chicken
in order to eat the breast or wing
[within the next 50 years]
by growing these parts separately
under a suitable medium.”

---- **Winston Churchill** *Fifty Years Hence* (1930)

Maybe we can apply the same statement to
Chemical Synthesis!



[artisticportraits.com/ churchill.jpg](http://artisticportraits.com/churchill.jpg)