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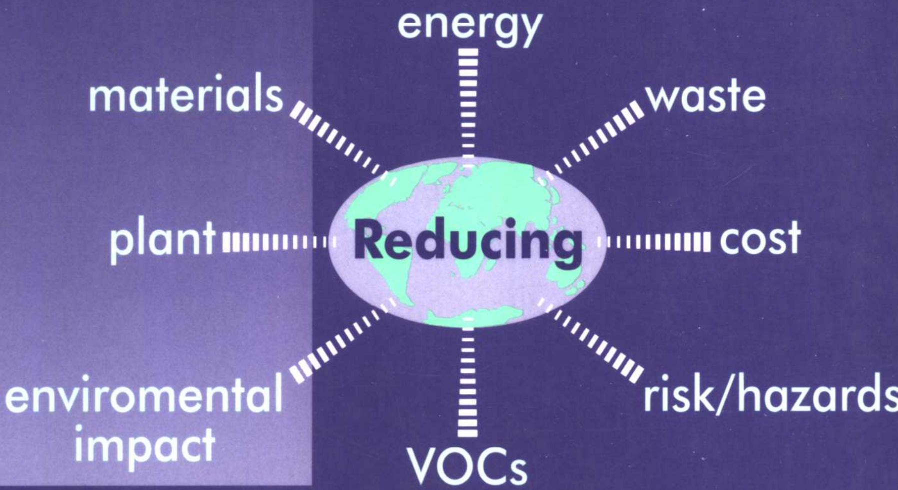

green chemistry

AN INTRODUCTORY TEXT

MIKE LANCASTER

RSC Paperbacks

GREEN CHEMISTRY: An Introductory Text

Mike Lancaster

Green Chemistry Network, University of York

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藏书章

ROYAL SOCIETY OF CHEMISTRY

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In loving memory of Ant, whose love of intelligent technology promised so much, and to Amanda, Neil and Sarah, in the hope that your children inherit a more sustainable world than my generation leaves behind.

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Preface

Many academic texts are available to teach chemists the fundamental tools of their trade, but few books are designed to give future industrial research and development chemists the knowledge they need to contribute, with confidence and relevance, to the development of new environmentally benign chemical technology. This book aims to be a handbook for those chemists attempting to develop new processes and products for the twenty-first century, which meet the evermore stringent demands of a society that wants new products with improved performance, and with a lower financial and environmental price tag.

The concepts discussed in this book, including waste minimization, feedstocks, green metrics and the design of safer, more efficient processes, as well as the role catalysts and solvents can play, are outlined in simple language with the aim being to educate, rather than over complicate. Industrially relevant examples have been included throughout the text and are brought together in Chapter 9 on Industrial Case Studies. Whilst these studies are taken from across various sectors of the chemical industry, wherever possible I have drawn extensively on my own research and process development experiences in various chemical companies, in order to produce a text that will be of real value to the practising chemist.

Green Chemistry means different things to different people: some purists would argue that chemists and the chemical industry have no right appropriating the term at all. At the other end of the spectrum there are individuals and companies that see the 'green' label as a route to product differentiation and higher profits, but wish to do as little as possible in terms of making the step changes needed to achieve sustainability. My own view is somewhere in the middle and can be summarized quite simply. As a society we should be using our skill and ingenuity to develop products and processes that meet our requirements in as sustainable and environmentally benign ways as possible. Green Chemistry should not be about making products with inferior performance or using end-of-pipe solutions to get an Eco-label. It should be about using our resources to produce the materials we need with as minimal negative impact on the world as possible. Sometimes there will be a price to pay, but the ingenious 'Green Chemist' will devise win-win-win products and processes, in line with the Triple Bottom Line benefits now pursued by many industry sectors.

Whilst the content of this book is broadly based around undergraduate modules and a Masters course in Clean Chemical Technology at the University of York, it should also be of interest to industrial chemists, engineers and managers wishing to learn about Green Chemistry. Since Green Chemistry essentially covers most of chemistry and chemical engineering, the in-depth background information cannot be presented in a book of this size (or, indeed, in several books of this size). The book therefore is designed to be read at two levels. First, the principles and concepts behind the subject are simply presented, enabling them to be understood and appreciated by the 'amateur'. Secondly, those with a more thorough understanding of chemistry will be able to use their knowledge to fully understand the in-depth background to the information summarized. In order to keep the book simple, references to the primary literature have only been given in the chapter on Industrial Case Studies. In other chapters, further reading has been suggested, which will give in-depth information on the concepts covered, as well as reviewing particular aspects of Green Chemistry in more detail. These suggestions are given in the same order as the concepts they deal with are introduced in the text. Review questions have been included at the end of each chapter; these have not been especially designed to test knowledge, but are intended to encourage the reader to think about, and apply the concepts covered, to new situations.

There are many people who have contributed to my enthusiasm for, and understanding of, Green Chemistry, not least the active members of the Green Chemistry Network who have been so supportive over the last three years. Special thanks are due to James Clark, who, apart from introducing me to the subject, got the Green Chemistry movement going in the UK, not least by convincing the Royal Society of Chemistry to fund the GCN and the *Journal of Green Chemistry*. Thanks are also due to colleagues from similar organizations to the GCN based outside the UK, in particular in the USA, Japan and Italy, who have contributed so much to the global understanding and development of Green Chemical Technology. Whilst it is somewhat unfair to select one person from the many who have contributed to the pursuance of the principles of Green Chemistry, it would also be unfair not to mention Paul Anastas, who has been such a superb global ambassador. Finally a very special thank-you to my wife Gill, not

only for her understanding during the writing process but also for reviewing much of the text and making constructive suggestions from a critical chemical engineer's viewpoint!

Mike Lancaster
York, February 2002

Abbreviations Used in Text

20-E	20-hydroxyecdysone
AFC	alkaline fuel cell
AMPS	aminopropyl silane
APG	alkyl polyglucoside
BATNEEC	Best Available Technology Not Entailing Excessive Cost
BHT	bis(2-hydroxyethyl) terephthalate
BOD	biological oxygen demand
BSI	British Standards Institution
CNSL	cashew nut shell liquid
COD	chemical oxygen demand
COSHH	Control of Substances Hazardous to Health
CSTR	continuous stirred tank reactor
DALA	5-aminolevulinic acid
DMF	dimethyl formamide
EA	Environment Agency
ee	enantiomeric excess
EMAS	European Eco-management and Audit Scheme
EMS	Environmental Management Systems
EMY	Effective Mass Yield
ENB	5-ethylidene-2-norbornene
EO	ethene oxide (ethylene oxide)
EPA	United States Environmental Protection Agency
EPDM	ethene/propene/diene monomer
FCC	fluid catalytic cracking
GWP	global warming potential
HAZOP	Hazard and Operability
HDPE	high-density polyethene
HLB	hydrophilic lipophilic balance
HMS	hexagonal mesoporous silica
IPC	Integrated Pollution Control

IPCA	Integrated Pollution Control Act
IPPC	Integrated Pollution Prevention and Control
ISD	inherently safer design
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LDPE	linear density polyethene
LLDPE	linear low-density polyethene
MIC	methyl isocyanate
MTBE	methyl *t*-butyl ether
NIR	near-infrared
PAFC	phosphoric acid fuel cell
PEMFC	proton exchange membrane fuel cell
perc	perchloroethene
PET	poly(ethene terephthalate)
PFS	process flow sheet
PHA	polyhydroxyalkanoate
PI	process intensification
PLA	polylactic acid
POP	persistent organic pollutant
ppm	parts per million
PTC	phase transfer catalysis
PTFE	poly(tetrafluoroethene)
PV	photovoltaic
PVC	poly(vinyl chloride)
RESS	rapid expansion of supercritical solution
RMM	relative molecular mass
$scCO_2$	supercritical carbon dioxide
SCF	supercritical fluid
SCWO	supercritical water oxidation
SDR	spinning disc reactor
SHE	Safety, Health and Environmental
SOFC	solid oxide fuel cell
THF	tetrahydrofuran
THOD	theoretical oxygen demand
THP	tetrakis(hydroxymethyl) phosphonium
tpa	tonnes per annum
TS	titanium silicate
TTF	tetrathiafulvalene
VCH	4-vinylcyclohexene
VNB	5-vinyl-2-norbornene
VOCs	volatile organic compounds
XRF	X-ray fluorescence

Contents

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Chapter 1

Principles and Concepts of Green Chemistry

1.1 INTRODUCTION

During the twentieth century chemistry changed for ever the way we live. Perhaps the greatest perceived benefits, to the general public, have come from the pharmaceuticals industry with developments of painkillers, antibiotics, heart drugs and, more recently, Viagra. However, it is difficult to think of an important facet of modern life which has not been transformed by products of the chemical and related industries, for example:

- Transportation – production of gasoline and diesel from petroleum, fuel additives for greater efficiency and reduced emissions, catalytic converters, plastics to reduce vehicle weight and improve energy efficiency.
- Clothing – man-made fibres such as rayon and nylon, dyes, waterproofing and other surface finishing chemicals.
- Sport – advanced composite materials for tennis and squash rackets, all-weather surfaces.
- Safety – lightweight polycarbonate cycle helmets, fire-retardant furniture.
- Food – refrigerants, packaging, containers and wraps, food processing aids, preservatives.
- Medical – artificial joints, 'blood bags', anaesthetics, disinfectants, anti-cancer drugs, vaccines, dental fillings, contact lenses, contraceptives.
- Office – photocopying toner, inks, printed circuit boards, liquid-crystal displays.
- Home – material and dyes for carpets, plastics for TVs and mobile phones, CDs, video and audio tapes, paints, detergents.
- Farming – fertilizers, pesticides.

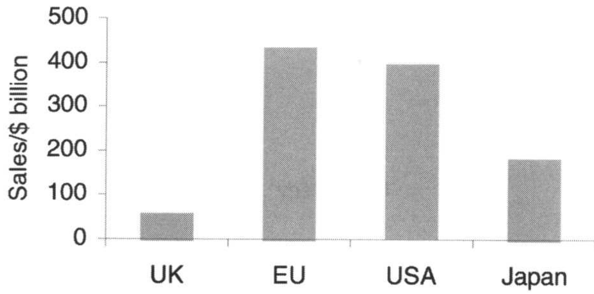

Figure 1.1 *Chemical industry turnover*

The value of the chemical industry is shown in Figure 1.1. In the UK over 450 000 people are employed by the industry (including pharmaceuticals and plastics) and the industry is manufacturing's number one exporter.

In many countries, however, the chemical industry is often viewed, by the general public, as causing more harm than good. There are several reasons for this, including general ignorance of the end use and value of the industry's products; however, a major reason is that the industry is perceived as being polluting and causing significant environmental damage. There is a certain amount of truth in this view with well-publicized disasters such as Bhopal causing both environmental damage and loss of life. As well as specific disasters, general pollution which came to the public's attention in the 1960s and 70s through eutrophication, foaming rivers, the discovery of persistent organic pollutants and the famous 'burning' Cuyahoga river, have all played a part in formulating this view of the chemical industry.

Chemists and engineers engaged in development of chemical products and processes have never set out to cause damage to the environment or human health. These have occurred largely through a lack of knowledge, especially of the longer-term effects of products entering the environment and possibly an over-reliance on procedures to ensure operations are carried out safely. The challenge for the chemical industry in the twenty-first century is to continue to provide the benefits we have come to rely on, in an economically viable manner, but without the adverse environmental side effects.

1.2 SUSTAINABLE DEVELOPMENT AND GREEN CHEMISTRY

Current thinking on sustainable development came out of a United Nations Commission on Environment and Development in 1987 (Bruntland

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