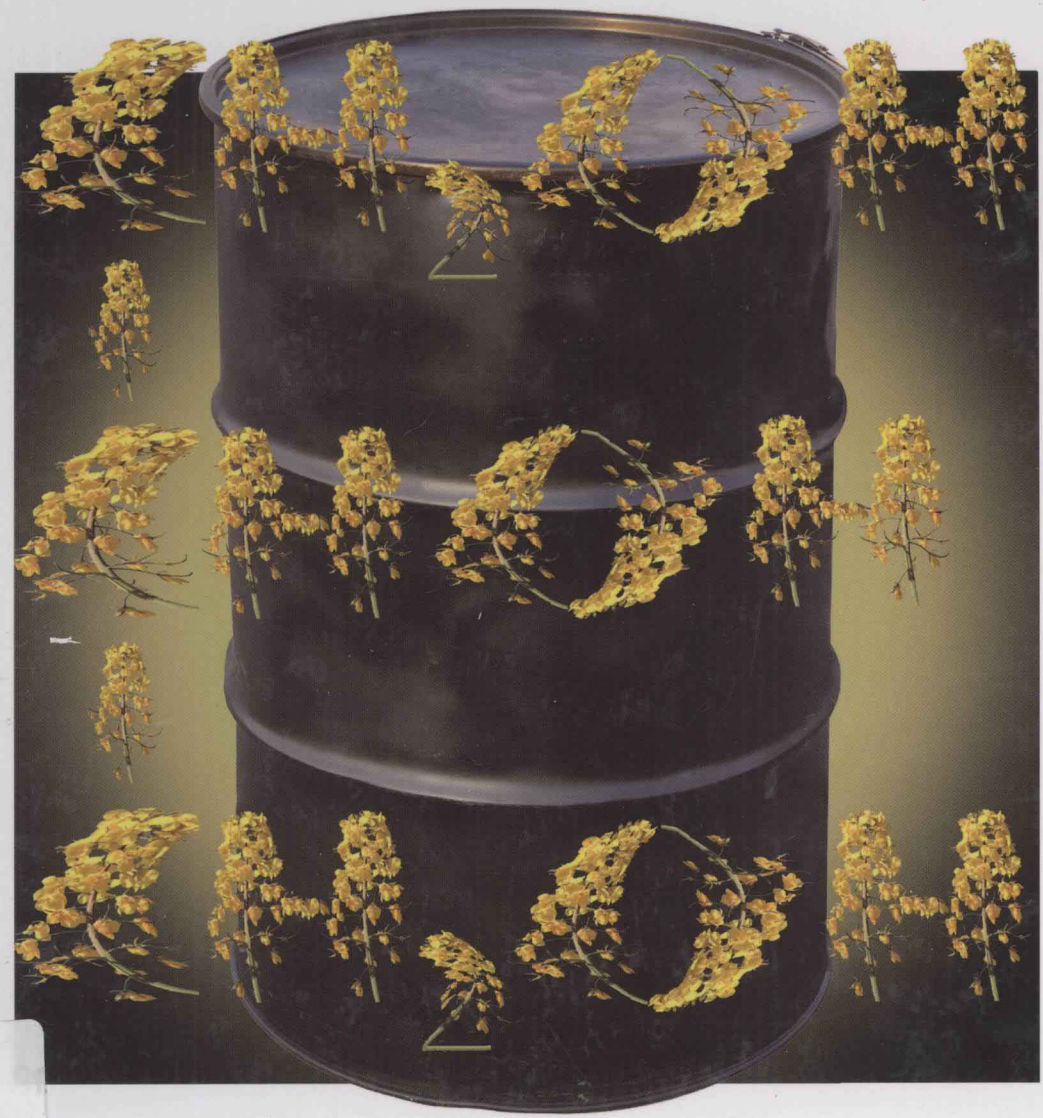
2nd Edition

RSC Green Chemistry Series

Mario Pagliaro and Michele Rossi

The Future of Glycerol



RSC Publishing

The Future of Glycerol
2nd Edition

Mario Pagliaro
CNR, Institute of Nanostructured Materials and Institute for Scientific Methodology, Palermo, Italy

Michele Rossi
Department of Inorganic Chemistry, University of Milan, Milan, Italy

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RSC Green Chemistry

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Preface to the 2nd Edition

Massive production of epichlorohydrin at Solvay in France (10 000 tonnes per year); several thousand tonnes of bioglycerol used as a concrete additive since 2008 by W R Grace; the first thousand tonnes of propylene glycol delivered to customers in the US by Senergy Chemical; a 20 000-tonne production plant for methanol in the Netherlands opened by BioMCN in 2008—these are examples of the first wave of plants employing crude glycerol for large-scale production. This raw material is now available in large quantities as a 10% by-product of biodiesel manufacture.

The preface to the first edition of this book contained this intriguing prophesy:

> *It is obvious that the greatest contributions are going to be brought about by today's students, whose creativity will produce spectacular advances.*

In the past two years the major advances arising from chemical ingenuity have been striking, and amply justify this second edition.

In common with other sections of the economy the 2008–09 global recession had a devastating effect on the global chemical industry. Indeed, many of the plans for new plants in Asia, Europe and the USA for the catalytic conversion of glycerol to important chemical building blocks remained unfulfilled. In the USA alone the production of biodiesel in 2009 was 50% lower than in 2008, along with a long list of bankruptcies (J. Jobe, *Biodiesel Magazine*, December 2009). But despite

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this, over the same period the annual global output of biodiesel reached 40 million tonnes, with a number of newer entrants playing their part such as Argentina, India, the Philippines, Brazil and the African continent.

It is now recognized that manufacture of biodiesel using a heterogeneous acid-catalyzed process offers in excess of 50% return on capital and has relatively low start-up costs. Newer plants are sustainable without government subsidy (B. Smith *et al.*, *Ener. Environ. Sci.* 2009, **2**, 262). With oil priced at more than $70 a barrel, despite the economic crisis, it comes as no surprise that the number of countries manufacturing biodiesel is now approaching 100.

The social and economic advantages of independent fuel manufacture are obvious, as is the ability to provide a solution which is adaptable to a variety of feedstocks. Countries producing their own biodiesel are less dependent on non-renewable fuels and at the same time they provide substantial benefits to rural communities.

The enormous potential of the biodiesel by-product glycerol as a versatile feedstock for a whole catalogue of chemicals, polymers and fuels is rapidly becoming appreciated. Many of the new chemical outlets for glycerol developed during the past five years are already in use. In some instances start-up enterprises have been quicker off the mark than traditional large chemical companies.

The second edition of this monograph has been thoroughly revised and updated. New sections have been added to cover such topics as the use of crude glycerol as an antioxidant, as reaction solvent, as lubricant, as a feedstock for methanol and as a fuel additive. We are confident that this new edition will be found valuable by professionals in the chemical and energy industries, including both managers and technologists, and no less by back-room chemists and renewable energy researchers.

Mario Pagliaro, Michele Rossi
Palermo and Milan

Preface to 1st Edition

Whoever is right—Tad Patzek in pointing out that massive biofuel production will cause ecological devastation, or Shell in claiming that its new fields of Jathropa trees will not impact food production—it is impossible to ignore the immense quantities of glycerol resulting from biodiesel manufacture. The volumes of glycerol remaining unsold up to mid-2005 certainly paint a tragic picture of wasted energy and material resources, to say nothing of human intelligence and effort, brought about by the lack of suitable conversion processes for what is the oldest organic molecule known to man. We have even witnessed biodiesel producers experimenting by adding glycerol to animal feed, or spraying it on dirt roads to keep the dust down—and even using it as landfill, as though glycerol were spent nuclear fuel!

Following three or four years of intense research activity, chemical ingenuity worldwide has opened up a number of practical avenues for converting glycerol into value-added products. Many of these are potentially large volume outlets, and may incidentally go some way towards improving the tarnished public image of chemistry. In reviewing and commenting on these achievements this book aims to remind chemical industry professionals, both managers and technologists, of the enormous potential of glycerol as a versatile feedstock for the production of a whole range of chemicals, polymers and fuels. In the ten chapters which follow, readers will find a thorough discussion of new uses for glycerol as a raw material, many of which are already having their impact worldwide.

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For example, during the devastation brought about by hurricane Katrina in 2005 the New Orleans petrochemical refineries were shut down, interrupting the supply of a variety of chemicals, including ethylene and propylene glycols. This led a global manufacturer of cement additives to replace these glycols with crude glycerol from biodiesel refineries (Chapter 3). Again, in 2007 Solvay started its retrofitted plant in Tauvaux, France, where instead of making glycerol from epichlorohydrin as had been done for decades, it began to produce this epoxy resin precursor using glycerol supplied by a French biodiesel producer (Chapter 4). Thirdly, by the time this book is published the world's first plant for the manufacture of propylene glycol from glycerol will be in full production in Atlanta, USA (Chapter 5).

This monograph tells a chemical success story, the conversion of glycerol into value-added products, and it identifies the factors which have brought this about. Whether as a solvent, antifreeze or detergent, or as a monomer for textiles or drugs, new catalytic conversions have been developed for glycerol in the synthesis of products with applications ranging from everyday household items to the manufacture of fine chemicals.

Readers will see the ways in which a number of practical limitations posed by the chemistry of glycerol, such as the low selectivity of traditional catalytic conversions, have been solved by a better understanding of its fundamental chemistry and the application of catalysis technology. In addition they will find in Chapter 10 a discussion of the sustainability issues associated with bioglycerol production. The authors are convinced that chemists and chemical engineers must be in a position to present the "triple bottom line" dimensions—societal, environmental and economic—to the community, the media and to the business world. Indeed, it is an undue emphasis on sustainability on its own which has often led to controversy such as that mentioned above. It has to be accepted that both politicians and ordinary citizens are interested in the arguments for biodiesel and glycerol production, and in turn they want to be reassured that refineries are necessary and environmentally sound. To paraphrase Ozin, emerging biomass-based companies and research centers need young, wise, educated scientists capable of crossing the boundaries between fields and who can explain simply the advantages and problems.

Chemical research on glycerol has shown that, given a strong economic incentive, chemists can rapidly devise a whole set of upgraded processes for biorefineries, and that the integration of these in producing energy and chemicals is not just a romantic dream promoted by green-minded scientists, but an inescapable reality.

Will the biorefinery of the future make use of other platform chemicals apart from glycerol? We have no doubt about it. In 2007, one of us had the good fortune to review University of Peking's Yuan Kou's paper on direct production of fuels from wood lignin. As we write, this seminal work is undergoing further peer-review after in-depth evaluation by editors and referees of *Science* and *Angewandte Chemie*. Yet, besides known problems with scientific publishing, enormous volumes of lignin, a by-product of cellulose manufacture, are burned in power stations, a low quality outlet parallel to that sought for many years for surplus glycerol. In one sense it could be claimed that the low price of oil in the 1990s ($10 to $20 a barrel) applied a dampener on chemical ingenuity for the whole decade, since many developments were put on the shelf until a day in the future when their use would become "economically viable". Today, not only has the price of oil multiplied by a factor of 10, but the concept of energy return on energy invested (EROI) shows that in the USA domestic petroleum now returns as little as 15 Joules for every Joule invested—whereas in the 1930s the figure was 100 Joules (C. Cleveland *et al.*, *Science*, 2006, **312**, 1746). It is exactly this decreasing trend that is forcing society globally to switch from fossil to renewable fuels, until the day when cheap and abundant solar energy becomes a reality. In this evolutionary period biofuels—and biodiesel in particular—will certainly play a role, and it inevitably follows that glycerol will remain a key raw material for many years to come. For example, following the Dumesic findings (Chapter 2) we can readily envisage a time when syngas obtained in high yield from glycerol will be used to synthesize both fuels and methanol by the Fisher–Tropsch process.

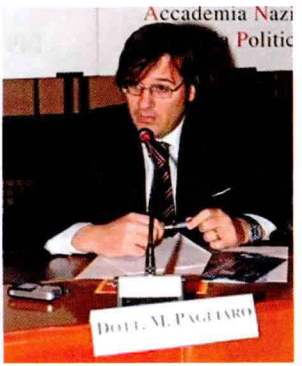
Finally, it is obvious that the greatest contributions are going to be brought about by today's students, whose creativity will produce spectacular advances. To avoid this monograph rapidly becoming out of date it is our intention that it must remain a "living" book, and that readers will have access to periodic updates posted online on the RSC website.

Mario Pagliaro, Michele Rossi
Palermo and Milan

Dedication

This book is dedicated to Francesco and Davide Pagliaro: May they one day enjoy the pleasure of writing

About the Authors



Mario Pagliaro (b. Palermo, 1969) is a research chemist and management thinker based in Palermo at Italy's CNR, where he leads a research group and Sicily's Photovoltaics Research Pole. His research focuses on the development of functional materials for a variety of uses and operates at the boundaries of chemistry and materials science. Between 1998 and 2003 he led the management educational center, Quality College del CNR, using the resulting income to equip his laboratories and establish a research group which currently collaborates with researchers in 11 countries.

Mario holds a PhD in chemistry from Palermo University (1998), the topic of his thesis being the selective oxidation of carbohydrates; mentors were David Avnir in Jerusalem and Arjan de Nooy in the Netherlands. He has also studied and worked in France and Germany. In 2005 he was appointed *Maître de conférences associé* at the Montpellier Ecole Nationale Supérieure de Chimie. Between 1993 and 1994 he worked in the Netherlands, initially at the Rijks Universiteit, Leiden, and then at the TNO Food Research Institute in Zeist. In 1998 he was with Michel Vignon at the Grenoble's CNRS, and in 2001 he joined Carsten Bolm's research group at Aachen Polytechnic. Mario has co-invented a number of novel technologies, some of which have been commercialized. He is author or co-autoher of the books *Flexible Solar Cells, Silica-Based Materials for Advanced Chemical Applications, Nano-Age, The Future of Glycerol, BIPV* and *Il Nuovo Fotovoltaico*; as well of the management books *Scenario: Qualità* and *Lean Banking*. He is the author of five international patents and a large number of scientific

papers. In 2008 he gave the "John van Geuns" Lecture at the University of Amsterdam, and in 2009 he chaired the 10th FIGIPAS Meeting in Inorganic Chemistry held in Palermo July 1 through 4. Since 2004 he has organized the prestigious Seminar "Marcello Carapezza". His website is qualitas1998.net.

Michele Rossi (b. Milan, 1939) is full professor of inorganic chemistry at Milan University, where he has taught in the Faculty of Science until early 2009. He graduated in industrial chemistry at the University of Milan in 1963. In 1974 he became Professor of Inorganic Chemistry at the University of Bari and since 1988 he holds a similar position at the University of Milan. Professor Rossi's current research is in the fascinating world of nanoscience, particularly metal-based catalysis for the activation of small molecules. His research group has discovered the surprising catalytic activity of gold nanoparticles in liquid-phase oxidation of organic compounds. Professor Rossi has been engaged by the World Gold Council for the preparation of gold on carbon catalysts as the reference standard for liquid-phase oxidation. This standard catalyst is in use throughout the world among scientific and industrial researchers.

His scientific activity, the subject of over 150 scientific papers and a number of patents, began at the prestigious school of Lamberto Malatesta and Adriano Sacco, specializing in organometallic chemistry. In one remarkable study, Sacco and Rossi discovered the first example of reversible coordination of molecular nitrogen, at room temperature and pressure, which opened the route to "nitrogen fixation", the front-line inorganic chemistry of the period 1968–1978. From this research arose the now famous compound $CoHN_2(PPh_3)_3$, which has since become a standard feature of chemistry textbooks. During this period he joined Sei Otsuka's group in Osaka, where he spent one year working on low-valency metal complexes. Later he moved into research on the catalysis of fine chemicals synthesis. Application of catalytic hydrogenation and oxidation have been the source of several scientific contributions and patents in the technology of clean processes. Professor Rossi's research group collaborates with a number of other research groups in Italy and abroad, and is a partner in the EU Auricat research project aimed at developing the industrial application of gold catalysis.

Acknowledgements

We wish to express our sincere appreciation to our academic and industrial colleagues who have provided expertise in reviewing a number of the chapters of this book. In many cases they are the leading researchers in the areas covered in the book, and the book itself owes much of its relevance to their admirable scientific efforts.

We acknowledge particularly the assistance of Professors Maria Jerzykiewicz (Wroclaw University), François Jerome (Université de Poitiers), Gadi Rothenberg (University of Amsterdam), Shelley D Minteer (Saint Louis University), Elio Santacesaria (University of Naples), and John Whittall (University of Manchester). Our thanks are also offered to industry researchers Christian Hulteberg (Biofuel–Solution), Katarina Klepacova (Procede Group), Paolo Forni (formerly of Grace Construction Products), Jean-Luc Dubois (Arkema) and Roger Lawrence (Davy Process Technology).

Once again, we would like to thank our research collaborators, especially Rosaria Ciriminna, Cristina Della Pina and Giovanni Palmisano, for their creative input leading to the introduction of alternative uses for glycerol.

Thanks are also due to Don Sanders for his formidable editing of the original manuscript. In addition Merlin Fox of RSC Publishing has been instrumental in producing the second edition of this book.

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