Preface

The growth of interest in the 21st century in the biorefinery concept has been dramatic, if somewhat chaotic and disjointed, with interest and activity in the various relevant disciplines ranging from significant to very limited, and with little connection being made between those disciplines. Biologists and bioengineers have been quick to see the opportunity for white biotechnology, the application of biotechnology to industrial production, in particular through the use of whole cells and enzymes to synthesise products. Such applications are not new – biotechnology has been contributing to industrial processes for some time. For decades, bacterial enzymes have been used widely in food manufacturing and as active ingredients in washing powders. Transgenic *Escherichia coli* are used to produce human insulin in large-scale fermentation tanks, and the first rationally designed enzyme, used in detergents to break down fat, was introduced as early as 1988.

The involvement of other disciplines in the development of biorefineries has been less apparent so far, at least as judged by the literature and attendance at international symposia and other events. Yet, it can be argued that experts in subjects including environmental studies and ecology, social policy and economics, and chemistry and process engineering are all needed to take forward this most essential of societal technological developments. Furthermore, these disciplines need to learn how to work together: interdisciplinarity and multidisciplinarity are the order of the day, including collaboration between technical and non-technical experts and organisations. While white biotechnology is proven, its scope is limited and cannot be expected to answer a very high proportion of the challenges the biorefineries of the future will face. The belief among some early 21st century biologists that by thinking in terms of small molecules they can manage without chemists, is as naïve as the belief among some early 20th century chemists that by thinking in terms of atoms, they can do without physicists.

The reality is that chemists need biologists to learn how to harness the power of biological systems to engineer molecules, while biologists need chemists to understand what to use bioengineering for and how to build up the molecules that it produces to valuable products. Process and chemical engineers are needed to make it practical for industry to actually make the products in the quantities needed and at the rate of production required. But perhaps unlike any previous step change in technology, for the sustainable exploitation of biomass that is so intrinsically linked to the wellbeing of the environment and the survival of life, the scientists and technologists need additional expertise to ensure that we really do achieve economic, environmental and societal benefit, and here we must engage experts from non-technical disciplines.

We have a wonderful opportunity to learn from the mistakes, as well as the successes, of close to a century of petroleum exploitation, two centuries of industrialization and many more centuries of living off the land. These must all come together and work together in a sustainable manner if our standards of living in the developed world are to be maintained and if those of the developing world are to grow. How are we to balance the need for greater consumption that the expectations of the developing world seems to require with diminishing traditional resources and the alarming level of pollution to land, sea and air that our consumption of those resources inexorably creates? In Chapter 1 of this book we look more closely at this apparent dichotomy and argue the case for transmaterialisation – the fundamental change in the resources that we consume (e.g. from fossil to biomass), alongside a massive reduction in the cradle-to-cradle cycle time of these resources, and all done with a much increased level of awareness of ecosystem services. Put these together and we have the basis for future sustainable biorefineries – small and large, using various feedstocks and in various locations, but all producing products that cause neither our generation nor future generations unreasonable stresses on the Earth.

As biorefinery research has been dominated thus far by biotechnology, biorefinery production has been heavily focused on energy products. In fact biorefineries must produce many different products, analogous to petroleum refineries – energy, chemicals and materials are all needed by today's society and in increasing amounts. In Chapter 2 David Turley explores the chemical value of biomass. This includes plant oils, a topic of enormous current interest, due to their value in chemicals as well as fuel, but also as their over-exploitation can lead to major local environmental damage that some believe may even make their overall impact unfavourable. The largest renewable sources of carbon are the carbohydrates and the, currently limited, non-food uses for starch, cellulose and hemicellulose are considered here. Other important biomass components including lignin, waxes and proteins are also reviewed.

The conversion of this enormous natural chemical potential to the actual products we want requires chemical technologies and if we are to keep the overall environmental footprint low and build on the head start afforded by renewable feedstocks, these need to be green chemical technologies. Fran Kerton reviews these in Chapter 3. Apart from the tools of biotechnology, some of the key technologies are likely to be alternative solvents – for extraction of valuable plant chemicals and for chemical processing; alternative activation methods including microwaves (so routinely used by millions of people to convert biomass into food, but undoubtedly with much wider potential for exploitation), ultrasound, electrochemistry (a much underutilised technology, yet with enormous proven value for molecular synthesis and other material and chemical processing) and photochemistry; and catalysis including environmentally friendly heterogeneous catalytic technologies, as well as some highly selective homogeneous catalysis and of course, biocatalysis, including the modifications that chemists have applied to enhance their green credentials such as immobilization (to aid recovery and reuse) and supercritical fluid reaction media.

Apostolis Koutinas and colleagues bring the chemical potential of biomass and the technologies for its conversion together in Chapter 4. The future bioplatform molecules from which many of the future sustainable chemicals will be made are considered, as are the technologies to make them, including fermentations, enzymatic transformations, and various chemical transformations including simple acid catalysis. Lignocellulosics, proteins and vegetable oils, are considered as feedstocks.

Materials from biomass are the subjects of Chapter 5. Carlos Vaca-Garcia looks at biomaterials and biopolymers from biomass. The scope of this chapter is enormous and starts by looking at cellulose itself and the long-used building and clothing materials of society, notably wood and cotton, as well as others, including sisal, ramie, jute and hemp. The particular importance of cellulose, nature's most abundant material, is shown through a consideration of modifications, both physical and chemical, and the uses for major derivatives, notably cellulose esters. Starch derivatives, chitin and its derivative chitosan are among other materials considered. The latter parts of this chapter include a study of biodegradable plastics including PLA, probably the best known 'green' plastic at the time of writing.

The chemical value of a refinery can match that of the fuels: the value of the smaller volume, but higher price chemical components have kept petrorefineries economically viable for close to a century. However, the chemical–energy relationship is symbiotic: the chemicals also need the energy. Most of the new biorefineries of Europe and the Americas have one or more energy products at their heart – most commonly biodiesel and bioethanol, but soon extending to others. The bulk of the biomass carbon will end up in a fuel product and to ensure the overall sustainability and low environmental footprint of the total biorefinery we need to work hard to maximize the energy efficiency, and this is discussed from a largely chemical viewpoint by Mehrdad Arshadi and Anita Sellstedt in Chapter 6. Biomass can be used as fuel in many different ways including solid pellets, liquid fuels, hydrogen, biogas and other fuels for the future, and these are all considered here. The raw materials, the main methods of conversion, the efficiency of conversion, the engineering involved and the by-products are all reviewed.

This book is intended to show that while biomass has biological origins and that biological methods will be an important part of the biorefinery toolkit, biomass is essentially a rich mixture of chemicals and materials that can be extracted for use or that can be converted into other useful products including high value chemicals. When we manipulate biomass we must build on the ideal start for any product lifecycle of a renewable resource, and use green (bio)chemical technologies for transformations to what could be genuinely green and sustainable products. We need to bring the chemistry to the biorefinery as well as take the chemicals from the biorefinery – and we must make sure it's all green chemistry!

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