Glycerol

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A Versatile Renewable Feedstock for the Chemical Industry

Springer

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Preface

The industrial revolution was based on coal, which flourished as the major source of energy and raw material for the chemical industry in the nineteenth century. With the beginning of the commercial exploration of oil fields in the USA, in 1859, the world's energy matrix was gradually changed, and the twentieth century may be defined as the petroleum era. The use of oil as the major source of energy also brought the petrochemical industry, with the production of plastics, which gradually replaced wood, metal and other natural resources in human civilization. At the beginning of the twenty-first century, the world experiences a transition. Oil, coal and natural gas will still play a major role in the energy matrix and production of chemicals, but the scenario must gradually move towards more sustainable energy sources. Climate changes are one of the biggest issues of these days and may bring great economical, environmental and social impacts. The crescent emissions of greenhouse gases since the beginning of the industrial revolution have turned on the yellow light, making the whole humanity think about the destiny of the Earth, up to now, our only home in the vast universe.

Biofuels can be a response to global warming and may help in decreasing carbon emissions. Nevertheless, there are still many developments to be taken, before biofuels could replace a significant part of the oil and coal consumed worldwide. In addition, it will not be the only source of renewable energy in the future, but together with solar, wind, tide and nuclear (based on fusion processes) may provide a more diversified and sustainable energy matrix up to the end of this century.

Bioethanol and biodiesel are the main biofuels used worldwide at the beginning of the twenty-first century. Bioethanol is based on carbohydrate processing, whereas biodiesel relies on the transformation of triglycerides. Both biofuels are facing increased production and consumption in recent years, and the forecast points out for a continuous grow. Biodiesel is produced through the transesterification of vegetable oils and animal fat. Used cooking oils, as well as sewer residues, may also be used. Algae appear as a potential biomass source of biodiesel in the future. Therefore, it is expected that many different raw materials may account for the biodiesel production in the forthcoming years. Nevertheless, no matter the source of raw material, glycerol will always be formed as a by-product of transesterification of triglycerides.

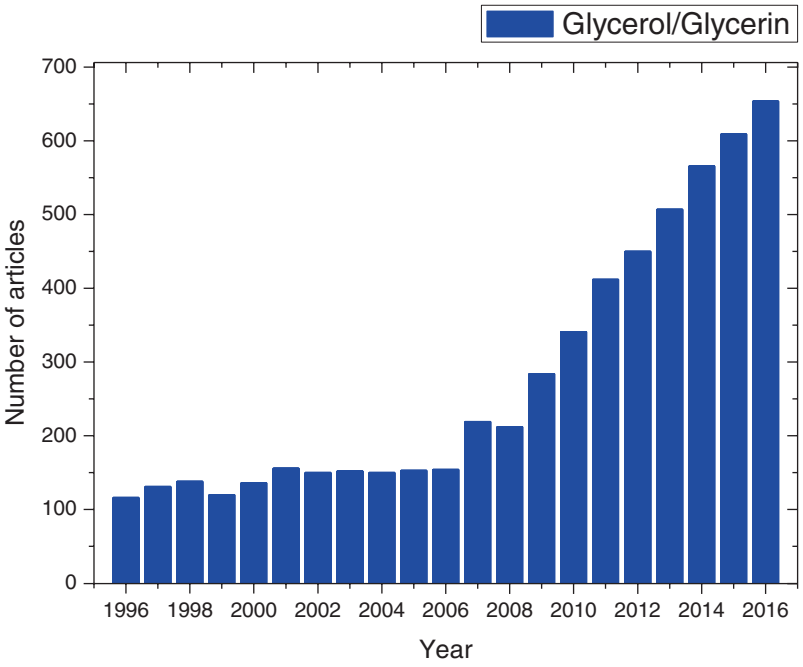

Fig. 1 Number of published scientific articles with glycerol or glycerin as keywords

Hence, its proper valorization will be extremely important to the economic, environmental and social feasibility of the biodiesel, making the whole production chain more sustainable.

This book aims to cover the progresses made in the glycerol conversion to commodities and specialty chemicals. Since the beginning of the widespread use of biodiesel, in the 1990s, there appears a great number of works on the use of glycerol, especially related with its chemical transformation. Figure 1 shows the number of scientific papers published, since 1996, having glycerol or glycerin as keyword. Great interest in the topic is clear, especially in the past 10 years, when the number of papers has skyrocketed. On the other hand, although there have been some review articles published within this time, there is only one book on the use of glycerol that was published about 10 years ago. Thus, taking into account the importance and actuality of the subject, an updated book, covering the major advances in the chemical transformation of glycerol, is highly interesting. This is the major objective of this contribution.

In Chap. 1, the biofuel scenario is briefly discussed, with emphasis on the biodiesel production chain. The chapter also includes discussion on glycerol as a by-product of the biodiesel production, together with other sources of glycerol, such as the chemical synthesis from propene and from algae.

Chapter 2 highlights the utilization of glycerol with a brief discussion on traditional uses, such as in personal care products, in pharmaceuticals and in the food industry. A historic perspective is also included, covering the first identification by the Swedish chemist Carl Scheele and the widespread utilization of nitroglycerine after the development of dynamite by Alfred Nobel. Other uses, such as animal food supplement, in energy generation through combustion or transformation in biogas and in formulations of fluids for enhanced oil recovery are briefly addressed too. The chapter points out the great potential of glycerol as a renewable raw material to the chemical industry, highlighting some potential transformations, most of them discussed in more details in the following chapters. The problem of glycerol purity is also addressed in Chap. 2.

The biotechnological processes of glycerol transformation in high-value chemical products are discussed in Chap. 3. An introduction to the growing importance of the biotechnological processes in the chemical industry is briefly addressed, highlighting the focus on specialty chemicals instead of commodities. Several processes of biochemical transformation of glycerol are then discussed, covering the production of 1,3-propanediol, an important chemical used in the production of textile fibres, ethanol, citric, lactic, succinic and propionic acids, as well as hydrogen and dihydroxyacetone. This later product is widely used in formulations of self-tanning lotions, having a high added-value compared with glycerol.

Chapter 4 is dedicated to the production of commodities from glycerol through thermochemical processes. The chapter begins with a brief discussion on the structure of the chemical industry, showing the three generations of the so-called petrochemical sector. A discussion on the production of renewable ethylene, from ethanol dehydration, and the ethylene-based tree of products is used to address the potential of glycerol as a renewable raw material to the propylene-based tree of products. The chapter covers studies on glycerol hydrogenolysis to propylene glycol, which is presently a commercial process, as well as to propene, which is not yet fully studied, but has great industrial appeal. Glycerol chlorination to epichlorohydrin is another commercial process that shows the potential of this by-product of biodiesel production in the chemical industry. Some aspects of this process in relation to the traditional one, based on fossil sources, are briefly addressed. Glycerol dehydration is also discussed, with emphasis on the production of acrolein and acrylic acid. The chapter ends reviewing studies on glycerol reforming to produce syngas and hydrogen, as well as discussing some developments to transform glycerol in methanol.

The production of specialty chemicals from glycerol via thermochemical conversions is highlighted in Chap. 5. Glycerol derivatives, such as ethers, acetals/ketals and esters, have been extensively studied in the past 10 years, showing great potential as fuel additives. The processes to produce these derivatives and their utilization in the fuel sector are consistently discussed. The chapter also covers the production of glycerol carbonate, a relatively new product that is finding crescent applications every year. The thermodynamic limitations of direct glycerol carbonation with CO_2 are briefly discussed, together with other processes based on the reaction of glycerol with urea. Finally, the oxidation of glycerol to dihydroxyacetone, glyceric and mesoxalic acids, among other products, is addressed in Chap. 5.

The last chapter discusses the conversion of glycerol to specialty and commodity chemicals in the biorefinery context. The chapter begins with a brief comparison between a traditional oil refinery and a biorefinery, based on the conversion of renewable biomass raw materials. The production of specialty chemicals from glycerol is addressed with emphasis on glycerol ethers and acetals/ketals, with high potential to be used as fuel additives, glycerol carbonate and dihydroxyacetone. The main discussions are concerned with the whole sustainability and feasibility of the processes at industrial scale. The chapter ends with a discussion on glycerol hydrogenolysis to propene and glycerol dehydration to acrolein and acrylic acids, as examples of biorefinery processes to commodities. A contextualization in terms of logistics, potential profitability and drawbacks relative to the traditional processes, based on fossil sources, is addressed.

We believe that the book may be a good and updated source of consult to researchers, students and professionals from academy, industry and the government. Our aim is to provide concise information on this subject, but also to cover broad aspects and to include relevant references for further consult of the interested reader.

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