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Glycerol from biodiesel production: Technological paths for sustainability

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ABSTRACT

Increases in biodiesel production have led to a surplus of crude glycerol, which represents a major bottleneck in the biodiesel production chain and has created new challenges to its sustainable use. Although there is a wide range of potential uses for crude glycerol, they are limited by its degree of purity, which affects its physical, chemical and biological properties. This paper presents a review and analysis of patents related to the use of glycerol in the period from 1993 to 2015, showing the quantity and diversity of work related to the search for alternatives to add value to glycerol. It was found that 85.7% of the filed patents fell into four categories of applications: 1) manufacture of chemical products; 2) production of polymer compounds; 3) production of biofuels and biogas; and 4) purification and use of glycerol. In this regard, the development of new technologies for the use of glycerol, without the need for traditional purification steps, are fundamental. This paper portrays the efforts that have been made in this direction and the obstacles that still have to be overcome.

1. Introduction

The use of biodiesel as a renewable fuel that is an alternative to petrodiesel has been seen as an important transition strategy in the search for new energy sources. Biodiesel can be produced from many renewable sources. These include the following types of plant oil: babassu, canola, crambe, palm, oilseed radish, sunflower, jatropha, lupine, soybean, peanut [1], castor bean [2,3], and macaúba [4,5]. It can also be made from animal fat [6], waste cooking oil [7,8] and photosynthetic algae [9–11].

Global biodiesel production has been growing in recent years. In 2016 more than 30.8 million m^3 (Mm^3) were produced, 7.5% more than in 2015. The main producing countries in 2016 were the United States (5.5 Mm^3), Brazil (3.8 Mm^3), Germany (3.0 Mm^3), Indonesia (3.0 Mm^3) and Argentina (3.0 Mm^3). The countries of the European Union produced 10.7 Mm^3, i.e. the equivalent of 34.7% of global biodiesel production, in 2016 [12].

It is estimated that in the future, biodiesel production will grow by around 4.5% annually, reaching 41 Mm^3 in 2022. It is expected that the European Union will remain the main producer and consumer of biodiesel, and that countries such as Argentina, the United States, Brazil, Thailand and Indonesia will continue to lead the biodiesel market [13].

A downside to this promising scenario is that biodiesel production costs are not competitive when compared to the costs of fuels derived from fossil fuels [14–16]. Government policies, fiscal incentives and emissions laws have been deployed in order to encourage the development of the global biodiesel market and assist in overcoming the effect of production costs. However, rapid growth in the biodiesel industry has raised concerns related to ethical issues [17]. In addition, advanced production technologies utilizing the ideal feedstock for biodiesel have had limited success, and glycerol – the main byproduct in this process – is still a major bottleneck in the biodiesel production chain [18,19]. Therefore, finding new uses for glycerol is very important in order to ensure the sustainability of global production of biodiesel. Otherwise, glycerol could become a barrier to increased biodiesel production and threaten the environmental gains from replacing fossil fuels with renewable resources.

Regarding the amounts of glycerol produced in the biodiesel sector, the transesterification reaction produces biodiesel and glycerol at a volumetric ratio of 10:1, that is, for every 1 m^3 of biodiesel, 0.1 of crude glycerol is produced [20]. In 2015, global production was almost 30 Mm^3, and it is estimated that more than 300,000 m^3 of glycerol were produced. The boom in the biodiesel industry means an increase in surplus production of glycerol.

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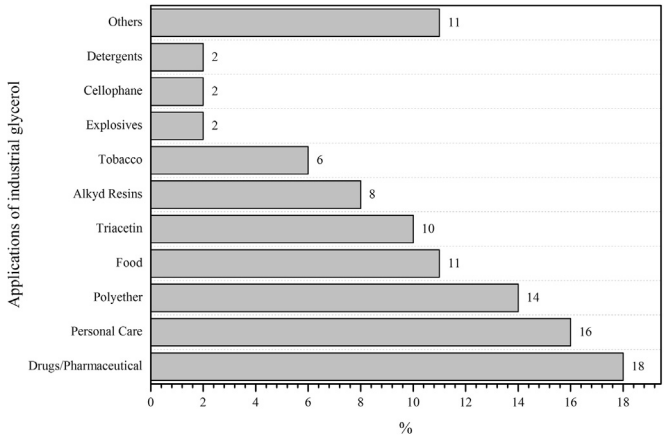

Fig. 1. Traditional applications of glycerol in industry. Adapted from Cornejo et al. [23].

In 2011, it was estimated that 2 million tons (or just 40%) of a total of 5.1 million tons of glycerol were used, the remaining 3 million tons was surplus. Among European Commission directives is a goal of increasing the proportion of biofuels in use, which has led to estimates that global production of glycerol will reach 7.66 million tons in 2020 [18].

Between 2008 and 2012, world production of glycerol increased by 9.3% per year, driven mainly by increased biodiesel production. It is estimated that by 2025 this growth will be 3.5% per year. In 2012, in the global market for oleochemicals, glycerol accounted for about 26% of the volume sold in the segment of chemicals derived from oils and fats of animal and vegetable origin [21].

Glycerol is a versatile renewable raw material used mainly in the chemical industry. It can be used as a humectant in sweets, cakes, meats and cheeses, and also as a solvent, sweetener and preservative in beverages and foods, giving flavor and color to foods and soft drinks [22].

This wide range of industrial applications, coupled with the increased availability of biodiesel, has boosted the world market for glycerol and encouraged the search for new applications, since the traditional uses of glycerol, as shown in Fig. 1, are not able to absorb growing production. Therefore, it is necessary to investigate new alternatives for enhancing its use and avoid market saturation [23]. In recent years, a number of studies of the use of glycerol have been developed [24–30].

The present article is a review of the literature related to innovations in the applications of glycerol from the biodiesel production process. The review included scientific articles present in the Scopus [31] and Web of Science [32] databases and analysis of patents filed with the Brazilian National Institute of Industrial Property (INPI) [33], the Patent and Trademark Office (USPTO) of the U.S. Department of Commerce [34], the European Patent Office (EPO) [35], the World Intellectual Property Organization (WIPO) [36] and the Derwent World Patents Index [37] related to the application of glycerol in new products and processes.

The objective was to gather information on the main advances that allow the use of glycerol as a raw material providing added value in the production of goods. The paper is structured as follows. Section 2 presents the method used to collect the data. Section 3 highlights the most common chemical reactions used to obtain glycerol, various applications in industry, and the main chemical reactions used with glycerol to obtain intermediates and / or chemicals. Section 4 presents some of the applications of crude glycerol derived from biodiesel in the production of chemical products, polymer compounds and biofuels, such as hydrogen. Section 5 presents final considerations.

2. Methodology

This review presents a systematic documentary analysis based on the identification of the main work dealing with the use of glycerol from biodiesel production. The search for alternatives to the use of glycerol from new applications was based on a patent search in the following databases: the Brazilian National Institute of Industrial Property (INPI) [33]; the Patent and Trademark Office (USPTO) of the U.S. Department of Commerce [34]; the European Patent Office (EPO) [35]; the World Intellectual Property Organization (WIPO) [36]; and the Derwent World Patents Index [37]. Also included were published scientific articles related to the terms biodiesel, glycerin and glycerol. Patent filings from 1993 to 2015 were included in the review (Table 1).

In addition to the patent analysis, a literature review was conducted to identify articles published on the theme in a specific period. Since the beginning of the use of biodiesel as fuel, many works on the use of glycerol have appeared, especially related to its chemical transformation. A search was conducted in the Web of Science and Scopus, using the string (glycerol or glycerine or glycerin) and (biodiesel), covering the period from January 1993 to September 2017. The total numbers of articles found were 3555 in the Web of Science and 3960 in the Scopus database. Fig. 2 shows the results, organized by year.

The data clearly show a constant increase in the number of scientific articles in this area and a sustained increase in the interest of researchers in this subject. Between 2008 and 2016, the number of articles increased by about 3.5 times in the Web of Science and practically doubled in Scopus.

The data also indicate that a large number of articles have been published in the last 10 years, mainly in the following areas: chemistry, chemical engineering, engineering, energy fuels, environmental science and biotechnology (Figs. 3 and 4). In both databases, the energy area, where a large proportion of articles on biodiesel are located, includes much of the major research relating to aspects of the production and use of glycerol obtained from biodiesel.

3. Overview of the production chain from biodiesel to glycerol

The terms glycerol (1,2,3-propanetriol), glycerin, and glycerine tend to be used in the literature. However the term glycerol generally applies to the pure substance (Fig. 5), while the expression glycerin applies to commercial products of solutions of glycerol in water, usually

Table 1
Databases searched, terms used and search scope (1993–2015).

Patent Database	Terms used	Scope
National Institute of Industrial Property – INPI [33]	Biodiesel, glycerin and glycerol	Entire database
Patent and Trademark Office of the U.S. Department of Commerce (USPTO) [34]	Biodiesel, glycerin, glycerol, byproduct and coproduct	Issued patents (USPTO-IP) and patent applications (USPTO-PA)
European Patent Office (EPO) [35]	Biodiesel, glycerin, glycerol, byproduct and coproduct	Entire database
World Intellectual Property Organization. This is a global patent organization that collects data from national patent offices (Africa, America, Asia and Europe) (WIPO) [36]	Biodiesel, glycerin, glycerol, byproduct and coproduct	Databases for Africa, Asia, and Europe
Derwent World Patents Index. This is a patent database belonging to the Web of Science (Thomson Reuters) (DERWENT) [37]	Biodiesel, glycerin, glycerol, byproduct and coproduct	Entire database