Chapter

Market Prospecting and Assessment of the Economic Potential of Glycerol from Biodiesel

Alisson Dias da Silva Ruy, Ana Luíza Freitas Ferreira, Antônio Ésio Bresciani, Rita Maria de Brito Alves and Luiz Antônio Magalhães Pontes

Abstract

Glycerol from biodiesel is a potential raw material for synthesis of several products with high added value. The world demand and the market value of these products are important information for defining the best investment for the implantation of a biorefinery. The information is available on websites of social associations, production companies and market consulting companies and can be mined, free of charge. The International Trade Center (ITC), with information on world trade and websites linked to the foreign trade agencies of every country, such as Comex Stat, in Brazil, are relevant search sources. In this context, this work presents procedures and search techniques for prospecting such information. Such a procedure is illustrated through a case study for which a search of market parameters for glycerol and its derivatives was carried out for use in the process design and economic evaluation of an industrial plant. It was found that crude glycerol had a market price close to US$ 170/ton, in 2019. Among its derivatives, acrylic acid, acrylonitrile and 1,3-propanediol have great potential for the development of new processes, within the scope of a biorefinery. Industrially, acrylic acid (US$ 1100/ton) and acrylonitrile (US$ 1500/ton) are produced from propene (US$ 880/ ton) and 1,3-propanediol (US $ 2000/ton) comes from glucose (US$ 460/t) or ethylene oxide (US$ 1200/t), which encourages the development of new sustainable processes.

Keywords: biomass, glycerol, market, economic analysis, industrial processes

1. Introduction

Vegetable biomass contains organic matter from the photosynthesis process and conversion of biological origin compounds into chemicals [1] has attired attention of researchers worldwide. The United States Department of Energy presented a series of chemical products, called platform molecules, which may be synthesized from biomass, generating more complex molecules of interest to society [2]. Biomass is also a raw material for the production of biofuels, representing a renewable alternative, easily accessible and more environmentally sustainable compared to fossil fuels. Among the biofuels, biodiesel has attracted attention since it is produced from simple and abundant raw materials, such as vegetable oils, animal fat and its residues [3].

Biodiesel is one of the most important energy commodities in the world. The USA (6.5 million m^3), Indonesia (6.2 million m^3) and Brazil (5.9 million m^3) were the largest producers in 2019. Germany is the largest producer of biodiesel in the European community (3.2 million m^3), followed by France and Spain. Other countries such as Argentina, Poland, Malaysia and Thailand are also important players in this market, producing more than 1 million m^3 [4]. The production of biodiesel has grown significantly worldwide, which results also in an increase in the amount of glycerol produced as a by-product [5]. Glycerol has great potential for application in the production of high added-value chemicals due to four main factors: its availability; its low commercial value; for being a renewable raw material; and for providing more economically viable alternatives for the biodiesel industry [6]. This may lead to a decrease in biodiesel prices and could improve the glycerol market. Therefore, there is an opportunity to produce value-added molecules, such as acrylic acid, acrylonitrile and 1,3-propanediol, among others [7, 8].

The development of industrial processes that contemplate the conversion of raw materials from biomass into chemical products requires an economic analysis to define the molecules that are of greatest interest to the market. Data can be obtained free of charge from portals such as the International Trade Center (ITC), from the official portals of trade agencies in each country, such as Comex Stat in Brazil and, partially, from websites of market consulting companies. The ITC was developed to provide access to export statistical data and specifications from several countries. As market consulting companies publish detailed reports of the worldwide market assessment of various products, which take into account price, demand and market potential. However, these reports are expensive and difficult to be acquired by researchers at universities and many research institutions.

In this context, this work presents methods and tools, easily accessible and free of charge, to search for information and parameters, analysis of the current market and the economic potential of products. In particular, data on glycerol and three of its main derivatives are analyzed: acrylonitrile, acrylic acid and 1,3-propanediol. Also, a simplified process design is presented for each of the selected derivatives, using the ASPEN PLUS tool.

2. Methods

In order to carry out an economic analysis of a given product of interest, it is important to obtain market data for the base country, where the industrial plant can be implanted, as well as for other countries, for assessment of international trade, threats and opportunities.

The market parameters of glycerol and each of its derivatives to be evaluated were obtained from the International Trade Center (ITC) portal and the Comex Stat portal. The future scenarios were obtained on the websites of consulting companies. This information must be carefully analyzed due to the differences in the assessment among different companies.

ITC is the joint agency of the World Trade Organization and the United Nations that aims to promote business between countries, mainly developing countries, simplify the economy [9], and provide several market analysis tools, covering 220 countries and territories and 5300 products found in the Harmonized System (HS).

The Trade Map is one of the most important and provides, through tables, graphs and maps, performance indicators for imports and exports, international demand, alternative and competitive markets, in addition to a directory of importing and exporting companies [10]. Comex Stat is a portal to access statistical data of foreign trade in Brazil. Every country has a free access consultation tool that quantifies national imports and exports, e.g. Data Web (United States - https://dataweb.usitc.gov/), Stat Can (Canada - https://www5.statcan.gc.ca/cimt-cicm/home-accueil?lang=eng) and ETCN (China - http://www.e-to-china.com).

The chemical products are found on the Trade Map and Comex Stat by using the Harmonized Commodity Description and Coding System, or simply Harmonized System (HS), and the Mercosur Common Nomenclature (NCM), in the specific case of Brazil. The Harmonized System (SH) is a multipurpose international nomenclature for the classification of products, published by the World Customs Organization (WCO). The HS allows participating countries to classify traded goods on a common global basis for customs purposes. It comprises more than 5000 commodity groups; each identified by a six-digit code, from SH2 to SH6, arranged in a legal and logical structure and is supported by well-defined rules to achieve uniform classification (WCO, 2020). The greater the number of digits, the more specific the HS classification becomes, so each country, or group of countries, has defined a common classification, which can have up to ten digits. These nomenclatures can represent a single substance or a group of them, having specific chemical characteristics in common. Usually the commodities and products of great commercialization are dealt with separately; however, the analysis of molecules grouped in the same SH is more difficult. The system is used by more than 200 countries and economies as a basis for their Customs tariffs and for the collection of international trade statistics. Over 98% of the merchandise in international trade is classified in terms of the HS. The HS contributes to the harmonization of customs and trade procedures, and the non-documentary trade data interchange in connection with such procedures, thus reducing the costs related to international trade.

MERCOSUR Common Nomenclature (NCM) is based on the Harmonized Commodity Description and Coding System. The NCM adopts WCO tariff sub-headings (six digits) and adds two more digits to provide a greater level of detail, resulting in eight-digit codes. The MCN has been adopted by the countries that integrate the Argentina, Brazil and Uruguay Block to foster international trade growth, make the creation and comparison of statistics easier, in addition to elaborating freight tariffs and providing other relevant information to international trade.

The ITC Trade Map uses a classification of up to 6 digits, while Comex Stat uses not only the SH, but also the NCM, with 8 digits, specifying more the product under analysis.

The availability of the market parameters in these databases allows the user correlating and interpreting the information in order to economically analyze the product under evaluation. Import and export values, volumes, growth rates, market shares, etc. are obtained from the Trade Map/ITC (worldwide) and the Comex Stat (for Brazil), while the growth forecasts are obtained from the websites of market consulting companies. This procedure was applied to gather information on the market for glycerol, acrylic acid, acrylonitrile and 1,3-propanediol.

The correlation of parameters displayed in graphs and tables is necessary for better evaluation and interpretation of the results. The data can be evaluated by regions or countries with greater market share for a specific product, allowing the visualization of the marketing behavior of these substances during the period under study.

2.1 Search in the international trade Centre

The Trade Map from ITC is accessed by the link https://www.trademap.org/Index.aspx. **Figure 1** shows an example of the search page.

It is possible to perform the search in different ways depending on the purpose of the analysis. One may insert the product code (isolated or group) or the location (country or region), choosing whether the study will be about import or export. The search can be carried out considering one of the five aspects: "Trade Indicators", "Yearly", "Quarterly", "monthly time series" or "Companies". In "Trade Indicators", more specific market data are obtained. It is also possible to choose the way in which the values will be arranged, yearly, quarterly or monthly, and, finally, the main companies that commercialize the product. The monthly, quarterly and yearly trade flows are available from the most aggregated level to the tariff line level. An example is given in the **Figure 2**, considering the option "Yearly Time Series" for the glycerol.

As shown in **Figure 2**, the search can take into account all countries or a specific country. Other criteria can be redefined using the same filters shown in **Figure 1**, such as operations (import, export or exchange balance), time (trade indicators, year, quarter, or month), category (country, product or service). Also, it can be filtered by market parameters (volume, value and others) and unit (depending on the parameter defined by the researcher).

Data such as export values, among others, are generated for each country and period, being initially listed in decreasing order of the values from the last year. According to **Figure 2**, crude glycerol is included in SH6 1520.00, which covers also water and glycerol lyes. In the example, the output data were obtained for the world, specifying the values in dollars of the exporting countries annually. In "Map", the world map shows the expressiveness of each country in different color scales, depending on the commercialized values of the product. In "Graph", the output data can be generated in graphs. In "download", the table of values can be exported to a spreadsheet or text files.

2.2 Search in the Comex Stat

The tool Comex Stat is accessed at "General Exports and Imports" through the link: http://comexstat.mdic.gov.br/pt/home. Results are shown in **Figure 3**, according to the type of operation (exports or imports), period of time and filters of interest. The information may be filtered according to the product code (SH or NCM), country or economic region, means of transport used and how the results should be displayed. If no input is given related to region, the search is carried out all over the world, The option "Net Weight" in Values filter shows the US$ FOB (freight on board) value, which is used to indicate when liability and

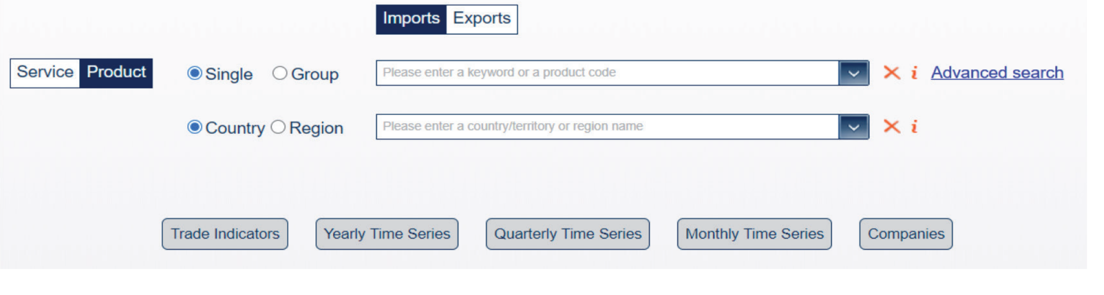
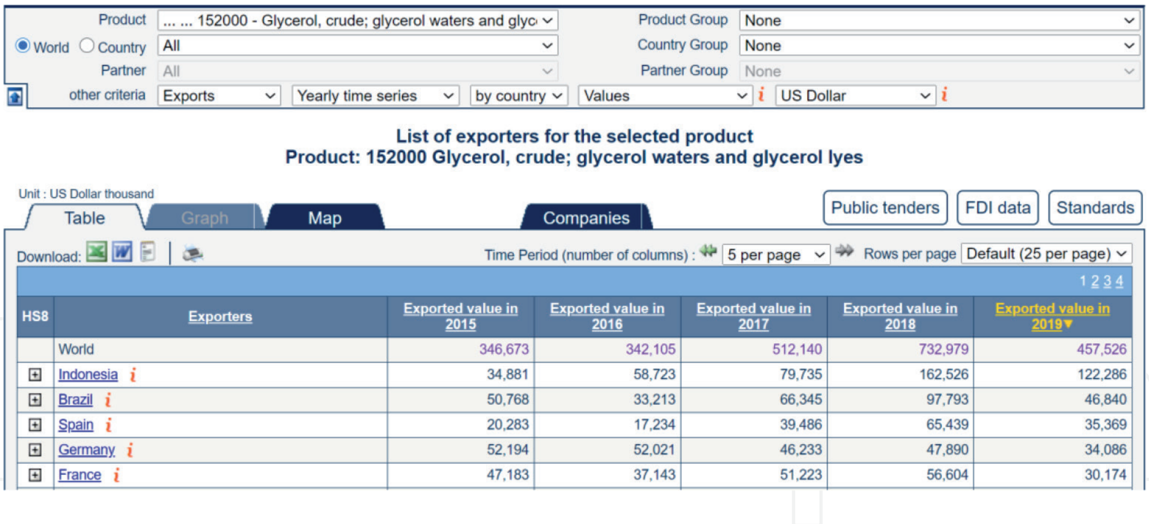


Figure 1.
Search of products in the trade map/ITC.



HS8	Exporters	Exported value in 2015	Exported value in 2016	Exported value in 2017	Exported value in 2018	Exported value in 2019
	World	346,673	342,105	512,140	732,979	457,526
	Indonesia	34,881	58,723	79,735	162,526	122,286
	Brazil	50,768	33,213	66,345	97,793	46,840
	Spain	20,283	17,234	39,486	65,439	35,369
	Germany	52,194	52,021	46,233	47,890	34,086
	France	47,183	37,143	51,223	56,604	30,174

Figure 2.
Example of results for glycerol and yearly time series option.

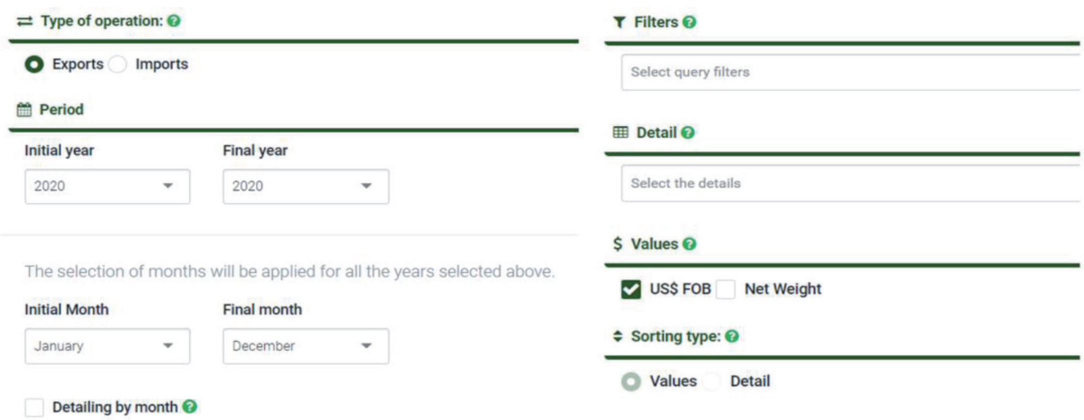


Figure 3.
Search by filters in the Comex Stat tool.

ownership of goods is transferred from a seller to a buyer, and also the amount commercialized in kilogram.

As an example of using COMEX STAT, information for pure glycerol (NCM: 29054500) is evaluated. The results, i.e. the data for the Brazilian annual exports are shown in **Figure 4**.

These data may be exported to a graph to evaluate the trends in imports or exports for the product over the years. Moreover, dividing the US$ FOB by Net Weight, the average annual value for the product is obtained (US$/weight), and it is possible to evaluate the trend of valorization or devaluation over the years. The data may also be exported to a spreadsheet.

2.3 Search in reports of market consulting companies

Websites of most consulting companies present market reports, from which it is possible to get an idea of the future trend analysis for the main producing companies and product participation by region. Typically, these websites can be found using the keywords *global market share* and the name of the desired product.

The market growth forecast is defined based on the Compound Annual Rate of Growth (CAGR), which is the average annualized rate of revenue growth between two given years, assuming that growth takes place at an exponentially compound rate. As the world market is sensitive to constant changes, the forecast of the CAGR may vary yearly and according to the evaluation techniques used by a given

Result

Display type: Horizontal / Vertical — Export data: CSV Excel

Year	NCM Code	NCM Description	US$ FOB	Net Weight
2020	29054500	Glycerol	$26.984.945	68.133.632
2019	29054500	Glycerol	$56.081.624	126.209.238
2018	29054500	Glycerol	$59.853.736	81.925.928
2017	29054500	Glycerol	$36.634.665	60.368.323
2016	29054500	Glycerol	$26.190.292	55.177.640
2015	29054500	Glycerol	$26.488.518	58.074.941
2014	29054500	Glycerol	$16.337.278	30.000.097

Figure 4.
Brazilian annual exports for pure glycerol.

company. Particularly for 2020, the influence of COVID-19 on the growth of product markets has been reported. Due to decreasing in the world growth, the demand for fuels decreased momentarily in 2020 and may return more slowly in 2021.

3. Routes for glycerol conversion

The annual production of biodiesel worldwide has increased in the last two decades. As a result, a large amount of the surplus crude glycerol has been generated. Currently, 90% of glycerol is produced from biodiesel [8] through the reaction of transesterification, which produces biodiesel and glycerol at mass ratio of 10: 1, i.e., for every 10 kg of biodiesel, 1 kg of crude glycerol is produced [11].

The glycerol produced from transesterification contains several impurities, such as: water, soaps, fatty acids and their esters, methanol and catalyst, usually sodium or potassium hydroxide. The removal of these impurities is necessary for the application of glycerol in different kind of industries, such as pharmaceutical, food and cosmetics [8]. Glycerol must reach a specific purity depending on its application, and also on the specification of the contaminants that must be removed through more sophisticated separations [12]. For pharmaceutical industries, glycerol must reach USP (United States Pharmacopeia) grade, which contains 99.5% by weight, while for applications in the food industry, the FCC (Food Chemical Codex) grade is required, with 99.7% by mass [13]. In addition, for application in the production of high added-value molecules, the impurities must be removed as they can significantly inhibit bacterial growth and fermentation (biotechnological processes) or the activity of heterogeneous catalysts (chemical processes) [14].

Glycerol can be converted into chemicals by several different reactions, such as oxidation, dehydration, hydrogenation, acetylation, esterification, etherification, ammoxidation, among others, as shown in **Table 1** [7, 14, 15].

As shown in **Table 1**, several studies have been carried out to convert glycerol into value-added chemicals through catalytic routes. For each reaction, specific homogeneous and heterogeneous catalysts were studied as an active phase, which is responsible for promoting the conversion of glycerol. Although glycerol is a promising alternative to reduce the dependence or even replace conventional production of petrochemical products [14], the good selectivity to desired products at high conversions is still a technological barrier. This is due to glycerol hydroxyls to have similar reactivity, unknown reaction conditions and the lack of efficient catalysts [7].

Conversion of glycerol	Chemical derivatives	Catalysts and active phases
Oxidation	Glycolic acid, hydroxypyruvic acid, tartaric acid, oxalic acid, mesoxalic acid, propionic acid, acrylic acid, citric acid, succinic acid, fumaric acid	Pt/C, Pd/C and Au, Pt-Bi catalysts
Dehydration	Acrolein, acetaldehyde, hydroxypropanone, hydroxypropane, propanaldehyde, adducts, acetone, dihydroxyacetone and polyaromatic compounds,	SiO_2/Al_2O_3, $ZnSO_4$ H_2SO_4, H_3PO_4/ (TiO_2 and SiO_2) Al, V, Sb and Nb oxides Zeolites
Hydrogenation/ Reduction	1,2-Propanediol, 1,3-propanediol, propanol, ethylene glycol, lactic acid, acetol, dichloro-2-propanol	Pt, Pd, Rh and Ru Ni and Cu
Acetylation	Acetins (glycerol mono-, di- and triester)	ZrO_2/SiO_2/ME, ZrO_2/SiO_2/SG, $HClSO_3/ZrO_2$ S-ZrO_2 and H_2SO_4/ZrO_2
Esterification	Mono, di and tri glycerates, glycerol carbonate, polyesters and branched nylons	NaOH, KOH, $NaOCH_3$, $KOCH_3$ $H_3PW_{12}O_{40}/SiO_2$/C Niobic acid /ZrO_2
Etherification	Glycerol tert-butyl ether, methyl butyl ether, 1,3-di-tert-butyl glycerol, 1,2-di-tert-butyl glycerol and 1,2,3-tri-tert-butyl glycerol,	Ru/S, $CuCr_2O_4$ and Cu/Zn CH-SO_3H La and Mg catalysts
Amoxidation	Acrylonitrile	Mo, Bi, Sb, V, Sn, W, Zr, Ti, Ni, Al, P, G and Nb

Sources: Adapted from [2, 7, 14].

Table 1.
High added-value chemicals from glycerol.

The production of 1,3-propanediol, acrylic acid and acrylonitrile are promising products from glycerol. 1,3-propanediol has great economic potential and a recent market, which can be expanded using glycerol as raw material, while acrylic acid and acrylonitrile come from consolidated petrochemical processes, which can be replaced by sustainable glycerol processes. In this context, it is important to evaluate the market and economics of these derivatives, in order to define a proposal for a potential process of production of these molecules from glycerol.

4. Economic analysis

4.1 Glycerol

Glycerol is found in the ITC under the codes SH6 1520.00 and 2905.45. SH 1520.00 refers to crude glycerol, water and glycerol lye. These nomenclatures present glycerol with different concentrations depending on the producing company or country and, therefore, the value of the final sale price is different.

The excess of crude glycerol has promoted a continuous decrease in its market value, reaching US $ 170 / t in 2019. This is one of the main factors to enable the implementation of a process for the production of high added value product. As previously mentioned, the production of 1,3-propanediol, acrylic acid and acrylonitrile are promising products from glycerol. Currently, the industrial production of acrylonitrile and acrylic acid use propylene as raw material, which price was approximately US $ 880/t, in 2019 [10]. The price difference between crude glycerol and propylene opens up a great opportunity for the production of these derivatives from glycerol [16]. 1,3-propanediol is obtained mainly from glucose, by fermentative processes, and ethylene oxide, by catalytic routes [17], whose prices, on average, were US$ 460/ton and US$ 1200/ton, respectively, in 2019 [10]. Thus, there is a good opportunity for developing an economically competitive and sustainable industry, using glycerol as raw material in an integrated biorefinery.

Figure 5 shows the exported values and volumes of crude glycerol considering the five largest exporters: Indonesia, Brazil, Spain, Germany and France. The data were obtained using SH6 1520.00, which includes crude glycerol, water and glycerol lye.

The amount of crude glycerol (SH6 1520.00) exported worldwide reached 2.2 million tons in 2019, representing only US$ 457 million. In **Figure 5a**, it can be seen that Indonesia has the largest export revenue for glycerol, followed by Brazil. Besides these countries, The United States are also a large producer. Germany, Spain and France are also major producers in Europe. Spain has increased its exports considerably, surpassing France and Germany. Due to the great availability of glycerol, there was a considerable drop in prices, represented by the exported values, as shown in **Figure 5b**.

These countries have programs for addition of biodiesel in the conventional diesel due to their strategies for environmental improvement, mainly Indonesia and Brazil. Indonesia represents 26.7% of the world exported value and has the world's daring program for replacing fossil fuel, producing 30% biodiesel in 2020, and an increasing of 40% is expected in the coming years. Brazil will increase domestic consumption by 50% by increasing the percentage of biodiesel in the diesel from 10–15% between 2019 and 2023 [18].

Another SH6 present in the ITC is related to purified glycerol (SH6 290,545), which covers all glycerol that is subjected to different degrees of purification, from the simplest to more complex purification treatment, such as double distilled glycerol. In 2019, purified glycerol was traded at an average of $ 895/ton.

The global market for purified glycerol was $ 2.6 billion in 2019. Asia-Pacific represented the largest market, with approximately 35% of the total, followed by Europe, with 29%, and North America, with about 21%. The growth in these regions can be attributed to the growing adoption of healthy eating styles and the expansion of end-use industries. Glycerol sales are forecast to reach US$ 3.5 billion by 2027, expanding at a 4.0% CAGR. However, due to COVID-19, a severe impact on the glycerol supply chain is expected since the production of biodiesel has been reduced, which may result in the closure of several manufacturing companies.

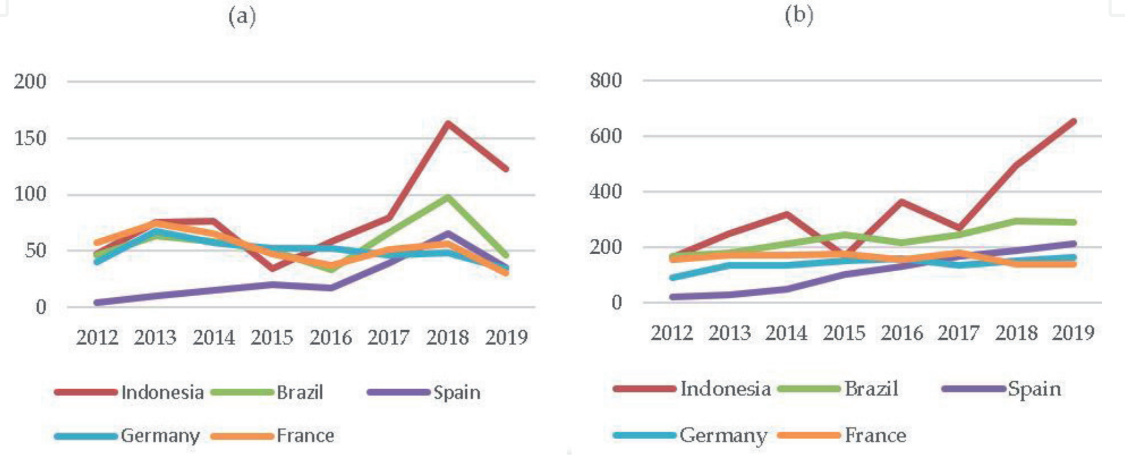


Figure 5.
Exported values and volumes of crude glycerol: (a) Exported values of crude glicerol (million US$/year); (b) Exported volumes of crude glycerol (thousand ton/year).

Europe will be the most affected region, especially in countries such as Italy and United Kingdom, adversely affecting the market growth in the region [19].

Purified glycerol has been largely commercialized worldwide, reaching US $ 1.2 billion in 2019. The main exporters of purified glycerol are shown in **Figure 6**.

Malaysia, since 2012, is the country with the highest exported value and volume (**Figure 6a**). Wilmar International, a large producer of biodiesel, has glycerin purification plants in Malaysia and Indonesia. However, Germany has been standing out in the export of purified glycerol, being the second largest exporter in values in 2019, exporting US $ 236 million, surpassing Indonesia, with US $ 232 million.

Indonesia surpassed Germany in 2018, but in the following year, it saw a drastic reduction in its numbers, exporting smaller values, in US$/year. In 2018, there was the highest peak in the export of purified glycerol, reaching a total 1.8 million tons, with a market value of US $ 1.6 billion. However, it is possible to observe a fall in the values and volumes exported by all countries in 2019, demonstrating the same behavior of crude glycerol (**Figure 6**).

Brazil has reduced considerably the imports of purified glycerol, with a 61% drop in the imported volume from 2014 to 2019. This is due to the implementation of new crude glycerol refining plants from 2014, which generated higher quantities of purified glycerol for internal consumption. Besides being a producer, the country has become one of the major exporters of purified glycerol, tripling the exported volume from 2014 to 2019, reaching US$ 56 million and 126 thousand tons. Comparing the average import and export prices, the country imports a higher cost glycerol, US$ 1275/ton, while exporting about US$ 440/ton. This difference can be justified by the different levels of quality and purity of the product, in addition to the continuous increase of its offer in the world [20].

4.2 1,3-Propanediol

1,3-propanediol (1,3-PDO) is produced from two main routes: biotechnology, developed by DuPont Tate & Lyle, through genetically modified microorganisms that convert glucose into 1,3-PDO; and catalytic, through the hydroformylation of ethylene oxide over cobalt catalysts at high hydrogen pressures. Another way to obtain this compound is from glycerol, however, still without an industrial plant in operation [21].

1,3-PDO is used for the production of polyesters and polyurethanes, being polytrimethylene terephthalate (PTT) the most used, representing 30% of the market. These polymers are widely used in the industry for the production of textile fibers and foam for mattresses, car seats and thermal insulation [22].

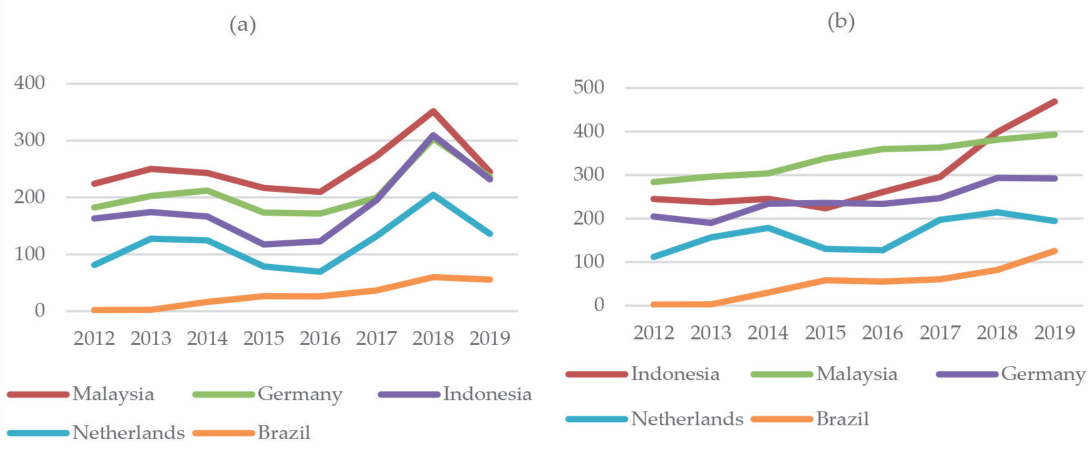


Figure 6.
Exported values and volumes of purified glycerol (SH6: 290545): (a) Exported values of purified glicerol (million US$/year); (b) Exported volumes of purified glycerol (thousand ton/year).

Comparing to polyethylene terephthalate (PET) and butylene terephthalate (PBT), PTT has a high strength, softness and elasticity as differential, and can be used in several segments of clothing, carpets, thermoplastics and monofilaments. 1,3-PDO also has applications in other sectors, such as production of solvents, adhesives, laminates, resins, cosmetics and personal hygiene and cleaning products [17].

North America is the most prominent region concerning the global market of 1,3-PDO, leading the market and having large growth perspective for the coming years. This is due to the high consumption of PTT and the high demand for polyurethane. The 1,3-PDO market in the year 2020 has been valued at US $ 401.7 million with an estimated growth of US$ 292.4 million from 2019 to 2024, presenting a CAGR of 11.4%, already considering the impact caused by the COVID-19. North America is responsible for 74% of this growth [23, 24].

1,3-PDO is not an isolated product in the ITC database, being grouped in SH6 2905.39, which contains the group of the heaviest diols, such as butanediols, hexanediols, but does not consider ethylene glycol and 1,2-propanediol, which are found in SH6 2905.31 and 2905.32, respectively. Thus, the analysis of the 1,3-PDO was performed considering also these compounds.

Since 2013, Germany leads exports of diols, exporting US$ 387 million, which represented 165 thousand tons in 2019, with Merck KGgA and BASF being the main producing companies in the country, mainly of heavier diols. The main world producer of 1,3-PDO is the United States, where DuPont Tate & Lyle is located, which represents the majority of exports of this product in the country. According to the **Figure 7**, the United States was the second most expressive country in the diol market, having exported US $ 355 million and 176 thousand tons in the same year.

China has been highlighted in the export of diols found in SH 2905.39 since 2013, more than doubling its exports. Until 2019, it handled 96 thousand tons, representing US$ 161 million. However, the country also stands out as the largest importer since 2013, having imported US$ 339 million and 220 thousand tons in the last year, as shown in **Figure 8**.

The great representativeness of China in the global scenario is explained by the high demand for diols and their derivatives, including 1,3-PDO, for which it has factories in the country, with emphasis on Zhangjiagang Glory Biomaterial Co., Ltd. and Haihang Industry Company Ltd.

Brazil has no expressiveness in the 1,3-PDO market, which is an isolated product, with NCM 2905.39.20.

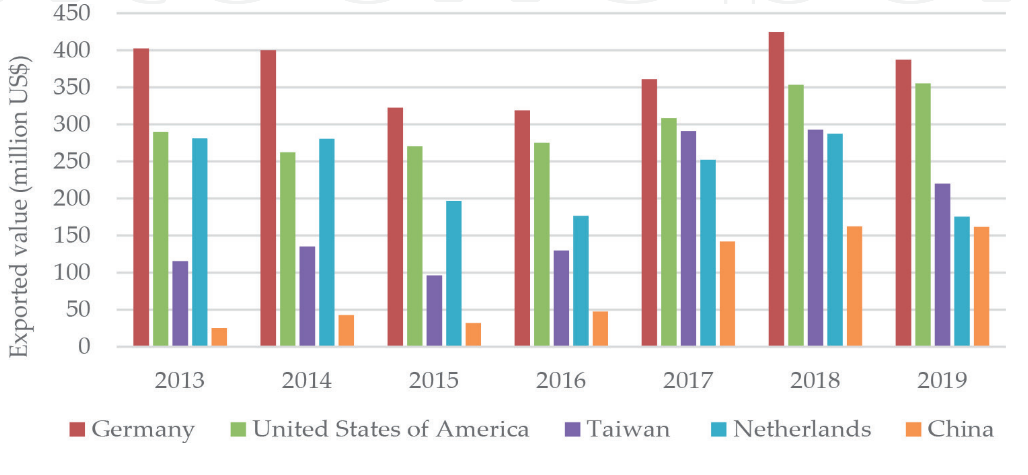


Figure 7.
Main exporters of SH6 2905.39 related products.

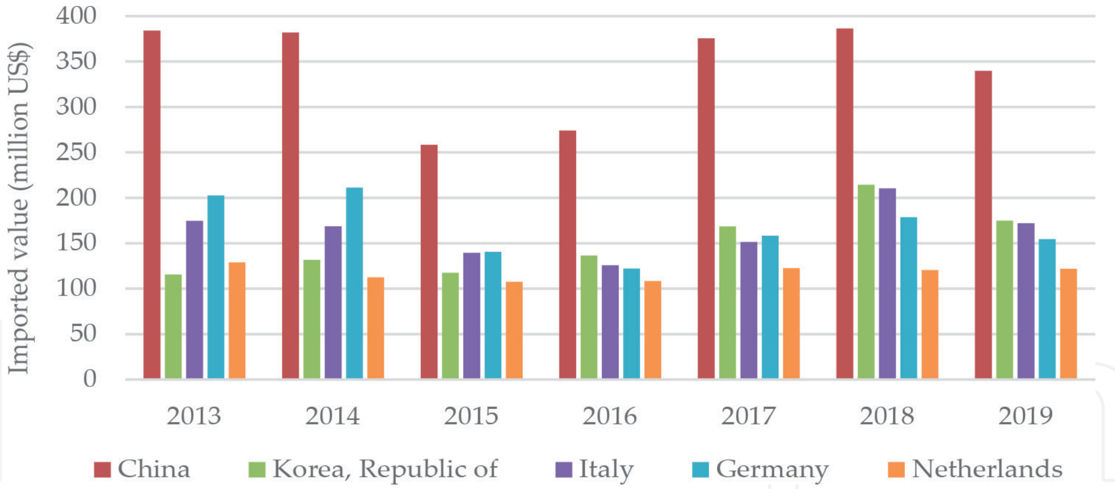


Figure 8.
Main importers of diol alcohols, except ethylene glycol and 1,2-propanediol (SH6 2905.39).

4.3 Acrylonitrile

Acrylonitrile is produced on a commercial scale through ammoxidation of propylene by catalytic routes, using bismuth-molybdenum oxides as catalysts [25]. Acrylonitrile is used in the manufacture of thermoplastics and textile fibers. Its main applications include ABS thermoplastic resin, acrylic fibers, carbon fibers, nitrile rubber, among others [26]. In 2019, acrylic fibers were responsible for most of the use of acrylonitrile, followed by ABS, a thermoplastic resin used in the construction, automotive and consumer goods industries.

Before COVID-19, growth forecasts for the acrylonitrile market were more promising, showing a 4.3% growth in CAGR for the coming years compared to the US$ 11.8 billion market in 2019 [27]. However, information released in [28] shows a lesser prospect of growth after the outbreak of the pandemic, forecasting a market of US$ 10.9 billion in 2020 and forecast to reach US$ 12.4 billion in 2024, with 2.2% CAGR. The growing demand for acrylic fibers and ABS and composites, such as carbon fiber, are the drivers of the growth of this market.

Figure 9 shows the largest exporters of acrylonitrile in the world. Acrylonitrile is isolated in SH6 2926.10. According to the data available at the ITC, 1.6 million tons of acrylonitrile was exported worldwide in 2019, with an average export value of US $ 1.486/ton, representing a trade of US $ 2.4 billion.

The United States is the largest exporter of acrylonitrile since 2013, with US$ 533 million in 2019. In 2018, the country exported more than 504 thousand tons of the product, representing 31% of global exports.

In 2019, INEOS Nitriles, one of the main producing companies, announced the closure of the plant located in Teesside, United Kingdom, with capacity of 300 thousand tons [29]. With the decline in trade in 2020 due to the pandemic, the withdrawal from the market of this expressive quantity may contribute to a smaller drop in the value in US $ /weight of acrylonitrile in 2020 and 2021.

China, since 2013, is the largest importer of acrylonitrile, with US$ 484 million in 2019 (**Figure 10**). According to the ITC, the average import price for acrylonitrile this year was US$ 1622/ton. Between 2014 and 2018, there was a drastic decrease in Chinese imports, from 152 thousand to 59 thousand tons.

In Comex Stat, acrylonitrile is an isolated product with NCM 2926.10.00 [20]. Brazil is an exporter of acrylonitrile, ranking eighth worldwide in 2019 [10]. In 2018, Brazil exported 83 thousand tons of acrylonitrile, representing about US$ 150 million. Brazil's representativeness in this market is due to the presence of Unigel,

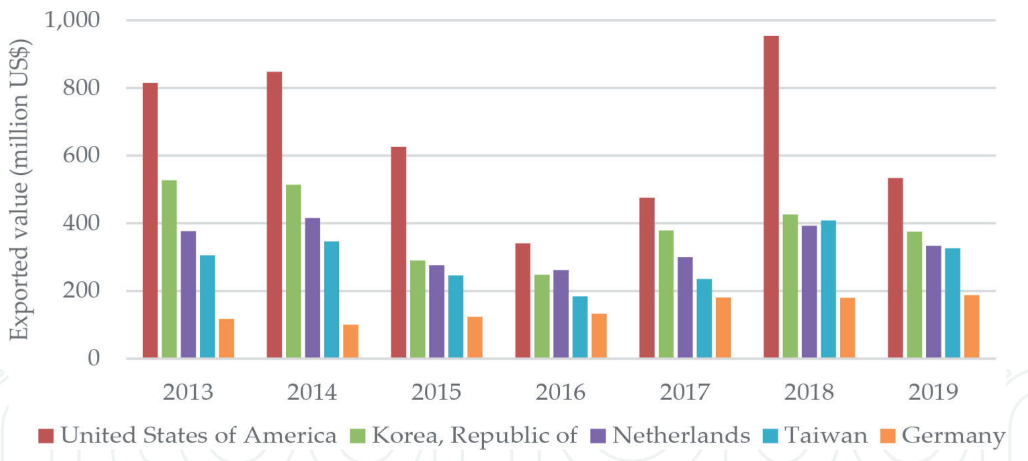


Figure 9.
The largest exporters of acrylonitrile.

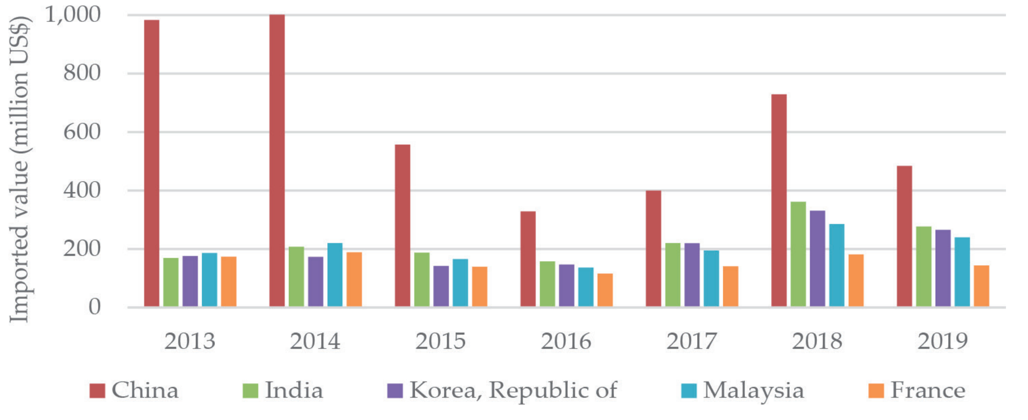


Figure 10.
Main importers of acrylonitrile.

which allocates a large part of its production for export. Unigel is the only producer in the southern hemisphere of the product with a nominal capacity of 100 thousand tons/year [30].

4.4 Acrylic acid

Acrylic acid is produced by the oxidation of propene in gas phase, over bismuth and molybdenum catalysts [16]. However, there is a potential to obtain acrylic acid from glycerol, being a more sustainable alternative to the use of petrochemical compounds [31].

Acrylic acid is applied in the production of polymers, latex, paints, leather finishing and paper coatings, in the textile sectors, in the production of surfactants, among others [32]. Superabsorbent polymers are the most represented segment in the market, being used in diaper production, water treatment and crude oil extraction.

The acrylic acid market may reach US$ 21 billion in 2027 [33]. In 2019, the volume handled in the acrylic acid market was 6.3 million tons and is expected to reach 8.3 million tons in 2025 [34]. The acrylic acid market mainly covers the Asia-Pacific region, with India and China accounting for 70% of product demand. The market has been driven by the growth of construction sectors, superabsorbent polymers and automobile industries, mainly in China, India and Brazil.

In the ITC portal, acrylic acid and its salts are included in SH6 2916.11. In 2019, world trade reached 774 thousand tons at an average price of US$ 1100/ton.

Saudi Arabia has become a major producer and has become the largest exporter of the product since 2015, surpassing China and Germany, selling 195 thousand tons in 2019, which represented US$ 217 million (**Figure 11**). This is due to the implementation of the new petrochemical complex in the country, which produces large amounts of acrylic acid [35]. Petroleum & Chemical Corporation and BASF SE, located in China and Germany, respectively, are responsible for a large part of the production of acrylic acid in the world and are highly representative of the market.

Taiwan was the largest importer in 2019, a position occupied in previous years by the United States and Belgium. The country imported 77 thousand tons, moving a value of US$ 71 million (**Figure 12**). China is also a major importer of acrylic acid, occupying the fourth position in the world ranking in 2019, with a large domestic demand for its derivatives. Some of these countries may not be producers, only selling acrylic acid.

Belgium has been the lead in imports of acrylic acid since 2013, losing its position to Taiwan, United States and China in 2019, since it has opened new plants producing acrylic acid and superabsorbent polymers [36].

In Brazil, acrylic acid is found in NCM 2916.11.10. Since 2014, there has been a significant decrease in external dependence on acrylic acid, with a reduction of 80% in the imported values, reaching 11 thousand tons and US$ 1293/ton in 2019.

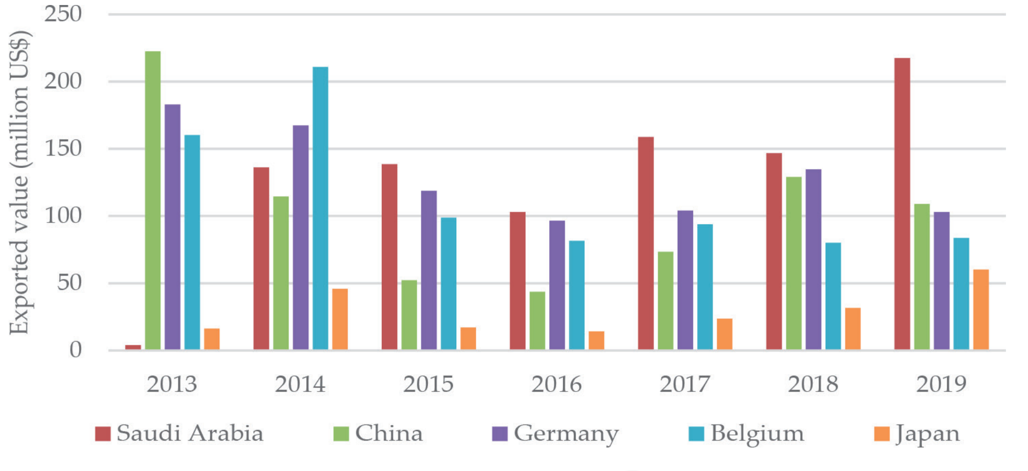


Figure 11.
Main exporters of acrylic acid and its salts.

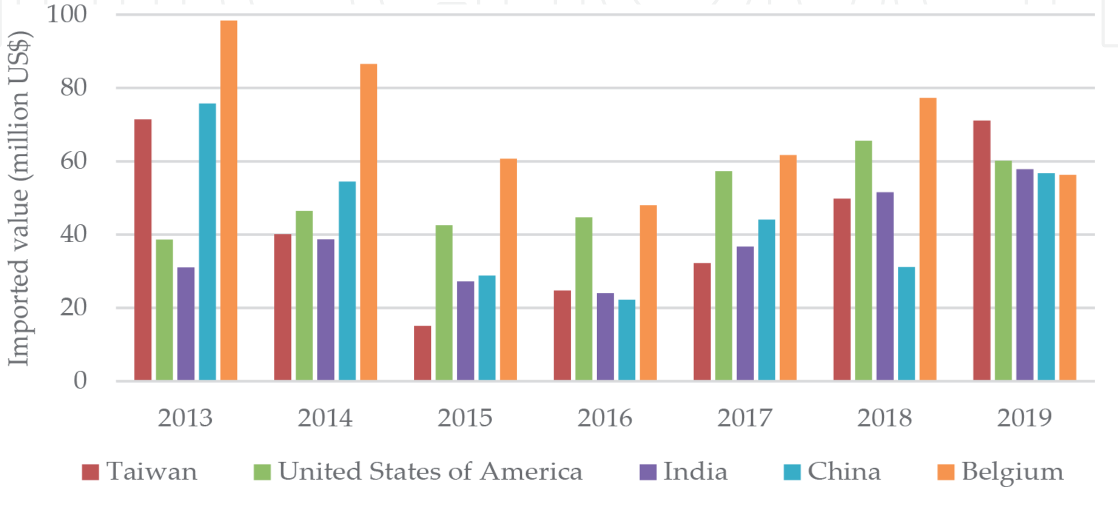


Figure 12.
Main importers of acrylic acid and its salts.

The decrease in the imported volume was due to the entry of Brazil into the acrylic acid market since 2014. This scenario was influenced by the investments made by BASF and Braskem, which, in 2014, carried out a large acrylic acid production project, adding domestic market and positively influencing Brazil's trade balance. In this sense, there was a considerable increase in the exported value and volume of acrylic acid in the country. In 2014, there were no records of exports of this product in the country, starting in 2015, when it reached the quantity of 7 thousand tons. In 2019, Brazil exported 18 thousands tons with an export value of US$ 26 million at an average price of US$ 1466/ton.

5. Conclusions

The growing worldwide use of biodiesel, an alternative renewable fuel, has generated large amounts of crude glycerol, a byproduct in its production, which presents large opportunities for application, after purification. Purified glycerol is a high-value and commercial chemical that may be used in a large number of applications, including its conversion into value-added products. Among them, 1,3-PDO, acrylonitrile and acrylic acid are promising products.

Commercial information about these products can be obtained from open websites of social associations, producing companies and market consulting companies free of charge. The careful analysis of these information shows there is high added-value when producing 1,3-PDO, acrylonitrile and acrylic acid from glycerol due to the difference between the prices of the products generated and the raw material.

This work shows that there is great potential for economic feasibility for the development of processes, in an integrated biorefinery, for the industrial production of chemicals from glycerol.

In addition, the effective use of glycerol as raw material for the production of chemicals, conventionally obtained from fossil raw material, may contribute to the reduction of using non-renewable natural resources and to the development of a greener chemistry.

Acknowledgements

The authors gratefully acknowledge the support of the RCGI – Research Centre for Gas Innovation, hosted by the University of São Paulo (USP) and sponsored by FAPESP – São Paulo Research Foundation (2014/50279-4) and Shell Brasil.

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES – Personnel Coordination of Improvement of Higher Level) - Finance Code 001.

The authors also gratefully acknowledge the financial support of the FAPESB – Bahia Research Foundation and CAPES National Exchange Program in partnership with Universidade Federal da Bahia and Universidade de São Paulo.

Conflict of interest

The authors declare that there are no conflicts of interest to disclose. The funding sources were not involved in the analysis and interpretation of data, neither in the writing of the manuscript, nor in the decision of submission for publication. This decision was based entirely on technical relevance and conjuncture pertinence of the study, based solely on the judgment of the authors.

Author details

Alisson Dias da Silva Ruy[1,2], Ana Luíza Freitas Ferreira[1], Antônio Ésio Bresciani[2], Rita Maria de Brito Alves[2]* and Luiz Antônio Magalhães Pontes[1]

1 Departamento de Engenharia Química, Universidade Federal da Bahia, Rua Prof. Aristides Novis, no. 02, 2nd floor, Federação, 40210-630, Salvador, Bahia, Brazil

2 Departamento de Engenharia Química, Universidade de São Paulo, Escola Politécnica, Av. Prof. Luciano Gualberto, no. 380, Tv. 3, 05508-010, São Paulo, SP, Brazil

*Address all correspondence to: rmbalves@usp.br

References

[1] Lietti L. Glycerol valorization towards a biorefinery [thesis]. Politecnico Di Milano; 2017.

[2] Werpy T, Petersen G. Top Value Added Chemicals from Biomass Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas. National Renewable Energy Lab., Golden, CO (US). 2004. DOI: 10.2172/15008859.

[3] Singh D, Sharma D, Soni SL, Sharma S, Sharma PK. A review on feedstocks, production processes, and yield for different generations of biodiesel. Fuel. 2020;262:116553. DOI: 10.1016/j.fuel.2019.116553.

[4] Tiseo I. Global biodiesel production by country 2019 [Internet]. 2020. Available from: https://www.statista.com/statistics/271472/biodiesel-production-in-selected-countries/ [Accessed: 2020/07/28]

[5] Gebremariam SN, Marchetti JM. Economics of biodiesel production: Review. Energy Convers Manag. 2018;168:74-84. DOI: 10.1016/j.enconman.2018.05.002.

[6] Quispe CAG, Coronado CJR, Carvalho JA. Glycerol: Production, consumption, prices, characterization and new trends in combustion. Renew Sustain Energy Rev. 2013;27:475-93. DOI: 10.1016/j.rser.2013.06.017.

[7] Bagheri S, Muhd N, Yehye WA. Catalytic conversion of biodiesel derived raw glycerol to value added products. Renew Sustain Energy Rev. 2015;41:113-27. DOI: 10.1016/j.rser.2014.08.031.

[8] Wang Y, Xiao Y, Xiao G. Sustainable value-added C3 chemicals from glycerol transformations: A mini review for heterogeneous catalytic processes. Chinese J Chem Eng. 2019;27:1536-42. DOI: 0.1016/j.cjche.2019.03.001.

[9] ITC. International Trade Centre (ITC) [Internet]. 2020. Available from: https://www.tfafacility.org/international-trade-centre

[10] ITC. International Trade Centre - Trade Map [Internet]. 2020. Available from: https://www.trademap.org/

[11] Vivek N, Sindhu R, Madhavan A, Anju AJ, Castro E, Faraco V, et al. Recent advances in the production of value added chemicals and lipids utilizing biodiesel industry generated crude glycerol as a substrate – Metabolic aspects, challenges and possibilities: An overview. Bioresour Technol. 2017;239:507-17. DOI: 10.1016/j.biortech.2017.05.056.

[12] Kaur J, Sarma AK, Jha MK, Gera P. Valorisation of crude glycerol to value-added products: Perspectives of process technology, economics and environmental issues. Biotechnol Reports. 2020;27:e00487. DOI: 10.1016/j.btre.2020.e00487.

[13] Ardi MS, Aroua MK, Hashim NA. Progress, prospect and challenges in glycerol purification process: A review. Renew Sustain Energy Rev. 2015;42:1164-73. DOI: 10.1016/j.rser.2014.10.091.

[14] Hejna A, Kosmela P, Formela K, Piszczyk Ł, Haponiuk JT. Potential applications of crude glycerol in polymer technology – Current state and perspectives. Renew Sustain Energy Rev. 2016;66:449-75. DOI: 10.1016/j.rser.2016.08.020.

[15] Veluturla S, Archna N, Rao DS, Hezil N, Indraja IS, Spoorthi S. Catalytic valorization of raw glycerol derived from biodiesel: a review.

Biofuels. 2016;9:305-14. DOI: 10.1080/17597269.2016.1266234.

[16] Braga ER, Mustafa G de S, Pontes D de A, Pontes LAM. Economic analysis and technicalities of acrylic acid production from. Chem Ind Chem Eng Q Available. 2020;26:59-69. DOI: 10.2298/CICEQ180111025B.

[17] Ruy AD da S, Alves RM de B, Hewer TLR, Pontes D de A, Teixeira LSG, Pontes LAM. Catalysts for glycerol hydrogenolysis to 1,3-propanediol: A review of chemical routes and market. Catal Today. 2020. DOI: 0.1016/j.cattod.2020.06.035.

[18] International Biofuels. Indonesian B40 biodiesel plan back on track as palm oil prices improve [Internet]. 2020. Available from: https://biofuels-news.com/news/indonesian-b40-biodiesel-plan-back-on-track-as-palm-oil-prices-improve/ [Accessed: 2020/08/08]

[19] Grand View Research. Glycerol Market Size, Share & Trends Analysis Report By Source (Biodiesel, Fatty Acids, Fatty Alcohols, Soap), By Type (Crude, Refined) By End Use (Food & Beverage, Pharmaceutical), By Region, And Segment Forecasts, 2020-2027 [Internet]. 2020. Available from: https://www.grandviewresearch.com/industry-analysis/glycerol-market [Accessed: 2020/07/26]

[20] Comex Stat. [Internet]. 2020. Available from: http://comexstat.mdic.gov.br/pt/home

[21] Samudrala SP. Glycerol Transformation to Value-Added 1,3-Propanediol Production: A Paradigm for a Sustainable Biorefinery Process. In: Glycerine Production and Transformation-An Innovative Platform for Sustainable Biorefinery and Energy. IntechOpen; 2019. p. 24. DOI: 10.5772/intechopen.83694.

[22] Shi G, Xu J, Song Z, Cao Z, Jin K, Xu S, et al. Selective hydrogenolysis of glycerol to 1,3-propanediol over Pt-WOx/SAPO-34 catalysts. Mol Catal. 2018;456:22-30. DOI: 10.1016/j.mcat.2018.06.018.

[23] Markets and Markets. 1,3-Propanediol (PDO) Market worth $870 million by 2024 [Internet]. 2019. Available from: https://www.marketsandmarkets.com/Market-Reports/1-3-propanediol-pdo-market-760.html [Accessed: 2020/08/10]

[24] Business Wire. COVID-19 Impacts: 1,3-Propanediol (PDO) Market Will Accelerate at a CAGR of Over 11% Through 2020-2024 | Growing Polyester Applications Across Various Industries to Boost Growth | Technavio [Internet]. 2020. Available from: https://www.businesswire.com/news/home/20200814005012/en/COVID-19-Impacts-13-Propanediol-PDO-Market-Accelerate-CAGR [Accessed: 2020/08/15]

[25] Liebig C, Paul S, Katryniok B, Guillon C, Couturier JL, Dubois JL, et al. Glycerol conversion to acrylonitrile by consecutive dehydration over WO3/TiO2 and ammoxidation over Sb-(Fe,V)-O. Appl Catal B Environ. 2013;132-133:170-82. DOI: 10.1016/j.apcatb.2012.11.035.

[26] Rezaie F, Pirouzfar V, Alihosseini A. Technical and economic analysis of acrylonitrile production from polypropylene. Therm Sci Eng Prog. 2020;16:100463. DOI: 10.1016/j.tsep.2019.100463.

[27] Grand View Research. Acrylonitrile Market Size, Share & Trends Analysis Report By Application (Acrylic Fibers, Adiponitrile, Styrene Acrylonitrile, Acrylonitrile Butadiene Styrene, Acrylamide, Carbon Fiber), By Region, And Segment Forecasts, 2020-2027

[Internet]. 2020. Available from: https://www.grandviewresearch.com/industry-analysis/acrylonitrile-acn-market [Accessed: 2020/07/21]

[28] Market Watch. Acrylonitrile Market 2020 is expected to see magnificent spike in CAGR with Global Industry Brief Analysis by Top Countries Data which includes Driving Factors by Manufacturers Growth and Forecast 2024 [Internet]. 2020. Available from: https://www.marketwatch.com/press-release/acrylonitrile-market-2020-is-expected-to-see-magnificent-spike-in-cagr-with-global-industry-brief-analysis-by-top-countries-data-which-includes-driving-factors-by-manufacturers-growth-and-forecast-2024-2020-08-10 [Accessed: 2020/08/13]

[29] Ineos Nitriles. INEOS announces launch of consultation on the potential closure of Seal Sands Acrylonitrile Plant [Internet]. 2019. Available from: https://www.ineos.com/news/shared-news/ineos-announces-launch-of-consultation-on-the-potential-closure-of-seal-sands-acrylonitrile-plant/ [Accessed: 2020/08/01]

[30] Unigel. Acrílicos [Internet]. 2020. Available from: https://www.unigel.com.br/index.php/acrilicos/ [Accessed: 2020/08/01]

[31] Li X, Zhang Y. Highly Efficient Process for the Conversion of Glycerol to Acrylic Acid via Gas Phase Catalytic Oxidation of an Allyl Alcohol Intermediate. ACS Catal. 2016;6:143-50. DOI: 10.1021/acscatal.5b01843.

[32] Buitelaar MM, Van Daatselaar E, Van Teijlingen DG, Stokvis HI, Wendt JD, De Sousa Ribeiro RJ, et al. Process Designs for Converting Propylene Glycol to Acrylic Acid via Lactic Acid and Allyl Alcohol. Ind Eng Chem Res. 2020;59:1183-92. DOI: 10.1021/acs.iecr.9b04334.

[33] Globe News Wire. Acrylic Acid Market To Reach USD 20.19 Billion By 2027 | Reports and Data [Internet]. 2020. Available from: https://www.globenewswire.com/news-release/2020/08/12/2076817/0/en/Acrylic-Acid-Market-To-Reach-USD-20-19-Billion-By-2027-Reports-and-Data.html [Accessed: 2020/08/12]

[34] Expert Market Research. Global Acrylic Acid Market to Grow at a CAGR of 4.7% Over the Forecast Period of 2020-2025 [Internet]. 2020. Available from: https://www.expertmarketresearch.com/pressrelease/acrylic-acid-market [Accessed: 2020/08/02]

[35] Volkova M. Tasnee cuts feedstock to affiliates SEPC, SPC by 41% after drone attacks [Internet]. 2019. Available from: http://www.mrcplast.com/news-news_open-358733.html [Accessed: 2020/08/02]

[36] Alperowicz *N. Nippon* Shokubai inaugurates acrylic acid, SAP units in Belgium [Internet]. Chemical Week. 2018. Available from: https://chemweek.com/CW/Document/98987/Nippon-Shokubai-inaugurates-acrylic-acid-SAP-units-in-Belgium [Accessed: 2020/08/09]