

REVIEW

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The glycerol biorefinery: a purpose for Brazilian biodiesel production

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Abstract

According to estimates from the International Energy Agency, global energy consumption will increase by at least one third, between 2010 and 2035. The additional power required will be provided not only by fossil sources but also by renewables. While the world energy matrix is supplied only by 13.2% from renewable sources, Brazil has different scenery with renewables accounting for 42.4% of the energy matrix. This work aimed to evaluate the potential use of oleaginous in biorefineries considering the produced quantity, prices, and costs of raw materials and products. Considering the availability of these raw materials, the results showed significant opportunities that can be exploited in Brazil, within the biorefinery concept. Soybean oil is the main raw material for biodiesel production in Brazil, although there are many other vegetable oils with potential for this purpose. Related to the production costs, the soybean biodiesel has higher costs than diesel. Then, this biofuel is only produced due to Brazilian regulatory rules and public subsidies. In order to become this production favorable in the market environment, it is essential to aggregate value to all byproducts and residues generated along the biodiesel production chain. Glycerin is a byproduct of biodiesel that could be used, in a glycerol biorefinery concept, as raw material for the production of value-added products through chemical, biochemical, or thermochemical routes.

Keywords: Biorefinery; Oleaginous; Soybean; Biodiesel; Glycerin; Biofuels; Chemicals; Energy; Prices and costs

Introduction

Nowadays, most of the energy consumed in the world comes from non-renewable sources, such as petroleum, coal, and natural gas. The world energy matrix uses only 13.2% from renewable sources, while the Brazilian scenario differs from this context using 42.4% of these sources, according to 2012 statistical data. They are represented mainly by sugarcane biomass (15.4%), hydraulic and electric (13.8%), natural gas (11.5%), and firewood and charcoal (9.1%). The participation of renewable sources in the energetic matrix is among the highest in the world, although there has been a slight reduction (1.8%) from 2011 to 2012, due to lower supply of hydropower and ethanol [1].

Factors such as Brazil's vast territory and favorable weather conditions expand the possibility of using water and biomass for energy production. Among the biomasses, the main are sugarcane, oilseeds, and lignocellulosic materials (e. g., crop residues and wood chips). Notwithstanding, many Brazilian industrial sectors that use biomass as the

main raw material have envisioned its use not only to produce energy, but in a wider perspective using the concept of biorefinery. For these sectors, the application of this concept is a great opportunity for growth and market expansion.

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals [2]. A biorefinery is not a completely new concept. Many of the traditional biomass converting technologies such as sugar, starch, and pulp and paper industries use aspects connected with this approach. However, several economic and environmental drivers such as global warming, security of supply, energy supply, high energy costs, and agricultural policies have also directed those industries to further evolve their operations into biorefineries [3].

The combinations involving raw materials, conversion/technology processes, and final products are almost unlimited in the biorefinery concept. The final decision about what product will be prioritized in a biorefinery (biofuels, chemicals, or bioenergy) will depend on the availability of raw materials, technological knowledge, public policies, regulations, and market dynamics.

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Considering the availability of raw materials and favorable conditions of price and costs, Brazil has significant opportunities that can be exploited in the biorefinery concept. Thus, this work aimed to present the overview of the Brazilian biodiesel production and the perspective of glycerin use in the biorefinery context.

Review

Raw materials for biodiesel production

In 2004, due to the necessity to expand the supply of energy from biomass, the Brazilian Government introduced biodiesel in the national energy matrix, through the National Program for Production and Use of Biodiesel [4]. In 2005, was established optional addition of 2% biodiesel to petroleum diesel (named B2), which became mandatory from January 2008. This percentage was increased successively by the National Energy Council (CNPE) up to 5% (B5) in January 2010.

In Brazil, currently, there are 64 biodiesel plants authorized for operation by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP), with a total production capacity of 7 million m³/year [5]. In 2012, more than 2.5 million m³ of biodiesel were produced [6], which corresponds to 36% of the current installed capacity. This production placed Brazil in the third position in the world ranking of biodiesel producers.

The main commercial route used in the biodiesel production is the transesterification process of vegetable oils and fats with alcohols, in the presence of a basic catalyst. This reaction results in three molecules of fatty acid monoalkyl esters, which compose the biodiesel, and one molecule of glycerol or glycerin (byproduct) [7].

In Brazil, there are more than 200 species of plants like fruits and grains that can produce oil, with different potentialities and natural adaptations to environmental conditions, which can be used to produce biofuels or other value-added products [8], but only some of them have been used for biodiesel production. Data on production of oilseeds and fat used for this purpose are shown in Table 1.

Figure 1 presents the contribution of each oil source used for Brazilian biodiesel production in April 2013.

The soybean is the main raw material used. Most of the national soybean production (about 44%) is exported in the form of grain, 7% is stocked, and 49% is processed domestically for obtaining 79% of soybean meal and 21% of oil. Seventy-seven percent of this oil is used for food and biodiesel production [12]. In April 2013, the soybean oil used for biofuel production represents more than 2.0 million m³ [13]. The soybean is the main raw material for biodiesel production as a consequence of some important issues, such as technological domain of the crop, scale of production, and the success in establishing the productive chain across the country [8].

Figure 2 displays the growth in the use of the main sources of oils for biodiesel production. Although the role of soybean oil in the biodiesel production is really the most important, the use of fat in this matrix has increased substantially, probably, because it is a residue and its cost is lower than oilseeds. The main barrier for the expansion of fat in biodiesel matrix is the high number of saturated fat acids present in this material.

There is an expectation that the regulatory framework will be increased to B10 by the Brazilian Government. If this actually occurs, it will be urgent to increase the raw material supply through the diversification in the production of oilseed crops in various regions of the country.

Prices and costs of soybean biodiesel

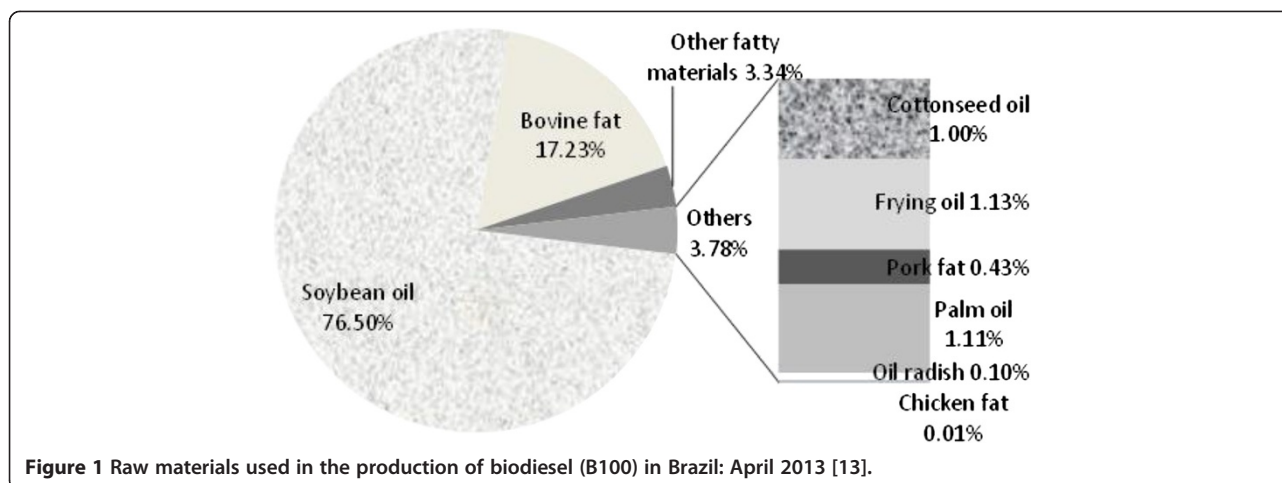
The price of biodiesel depends greatly on the price of soybean oil in Brazil. In Figure 3, it can be seen that there is a strong correlation between the nominal prices of biodiesel, practiced in the auctions of the National Petroleum Agency (ANP), and the prices of soybean oil. The correlation found between these two variables in the period of January 2011 to November 2013 was 0.73. The National Petroleum Agency uses it largely in the price of soybean oil for pricing in auctions.

With the launch of the National Biodiesel Program (PNPB) establishing the mandatory blending and the scheduled increase in the proportion of biodiesel in fossil diesel, there was a consolidation of the biodiesel market in Brazil. The growth of investments in the structure of

Table 1 Brazilian production of oilseeds and bovine fat in 2011 [9-11]

| Product | Harvested area (ha) | Production (tonnes) | Oil production (kg ha ⁻¹) | Main producing state |
|----------------------|---------------------|---------------------|---------------------------------------|----------------------|
| Soybean | 23,968,663 | 74,815,447 | 540 | Mato Grosso |
| Cottonseed | 1,405,135 | 5,070,717 | 360 | Mato Grosso |
| Palm (bunch) | 109,080 | 1,301,192 | 4,000 | Pará |
| Bovine fat | Na | 750,000 | Na | São Paulo |
| Peanut | 106,679 | 311,459 | 800 | São Paulo |
| Castor beans (berry) | 208,476 | 120,166 | 705 | Bahia |
| Sunflower | 62,535 | 77,932 | 630 | Mato Grosso |
| Canola ^a | 42,400 | 52,000 | 500 | Rio Grande do Sul |

Na, not applicable. ^aProduction refers to the 2011/2012 season and not the calendar year.



production of biodiesel allowed for an increase to 5% blending with 3 years in advance. Achieving this goal has been attributed to the ability of the industry to meet the market needs, as well as the will of the Brazilian Government in the growth of the use of this energy source [17].

The price of biodiesel in the country is set at auctions and it is fixed for a period of 3 months. On the other hand, the soybean oil is a commodity and its price is set by the market. As with other agricultural commodities, after 2002, there was a rise in the price of soybean oil, a fact that reduced substantially the margins of biodiesel processing plants. More recently, there was a fall in the price of soybean oil, reaching US\$0.99/L in November 2013 [16]. This fall has been attributed to the high amount of soybean harvested in Brazil, which has enhanced the availability of raw material for biofuel production. Moreover, the decline is also attributed to the worldwide availability of vegetable oils and excess capacity of the biodiesel facilities in the country (next to 60%) [18].

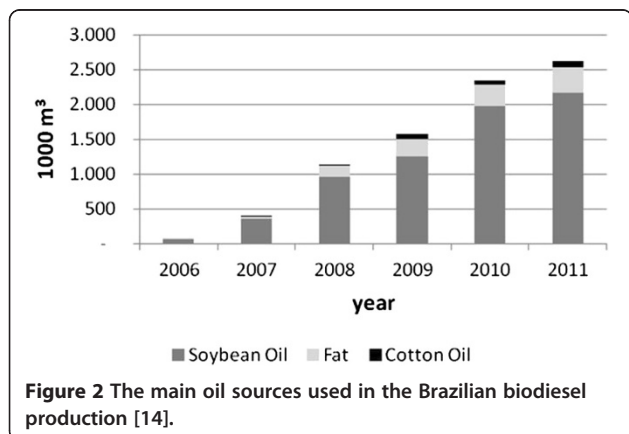
Thus, there was a drop in sales prices of B100 at auctions in 2013. The average price of biodiesel in the ANP auctions in 2013 was US\$0.90/L, well below the price established in October 2012 (US\$1.16/L). Even with this

drop in current prices and reduced profit margins, other factors allow the plants to continue to produce biodiesel and expand its production capacity as the growth potential in underexplored markets is high [17].

Table 2 shows the prices and production costs of diesel and biodiesel. In 2013, the average selling price of diesel in the distributor was US\$0.88/L [15]. As transport costs, profit margins, and taxes account for 70% of this value [19], it is estimated that US\$0.26/L corresponds to the production cost of diesel.

Different authors estimate different cost of biodiesel production in Brazil [19,20]. These costs undoubtedly vary according to the production process as well as the raw material. The cost of soybean biodiesel can reach values between US\$0.63/L and US\$1.25/L, excluding taxes, shipping, and producer profit margin. This value is well above the values of the production cost of diesel (US\$0.26/L).

The high cost of biodiesel production by alkaline transesterification is bound mainly to the high cost of soybean oil, which corresponds to 77% of total manufacturing costs [20]. Soybean is considered the main source of raw material with enough availability to meet the demand for biodiesel in the country.



Challenges and opportunities within the concept of glycerol biorefinery

It is estimated that 90 m³ of biodiesel produced by transesterification generates approximately 10 m³ of glycerin. Figure 4 shows the increase of glycerin production which follows the biodiesel production growth in the period from 2005 to 2011. If the use of B10 is implemented in Brazil, 5.56 million m³ biodiesel would be produced, corresponding to approximately 600,000 m³ of glycerin, which is much higher than the national demand. Furthermore, glycerin has a low market value.

The increasing production of glycerin is not only a Brazilian reality; other countries such as the USA [21]

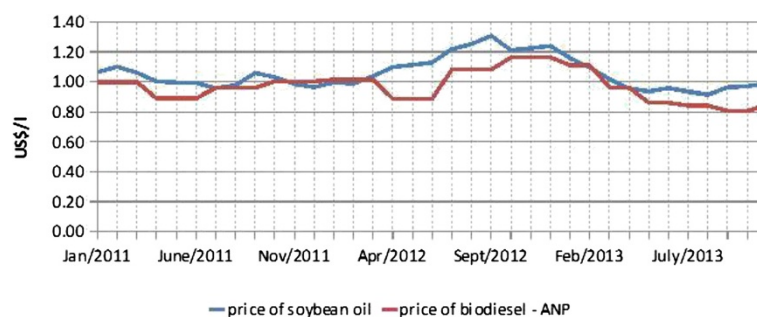


Figure 3 Evolution of biodiesel prices in the ANP auctions and the prices of crude soybean oil (quotation = R\$2.30/US\$). Source: author's calculations based on [15] and [16].

and Germany also have growth in the production of crude glycerin, which is directly related to the increase in the production of biodiesel.

In addition to the excessive amount of glycerin produced, another important issue is the quality of this material. As the main production process of biodiesel is a chemical route using basic catalysts, crude glycerin contains diverse impurities such as alcohol, traces of the catalyst, esters, and salts that hinder its direct application in several industrial processes. Nowadays, the main industrial sectors that consume glycerin worldwide are cosmetics, soaps, and pharmaceuticals [22,23] that require glycerin with certain degree of purity. The purification of crude glycerin obtained from biodiesel production to transform it into analytical grade is not economically favorable for sectors that work with lower value-added products [24].

The crude glycerin produced in Brazil is mostly used to generate heat by burning it in industrial furnaces and boilers, as in biofuel production, besides potteries and steel companies. Also, Brazilian glycerin has been exported to China [25].

Brazil exported 16,400 tonnes of glycerin with revenue of US\$5.4 million, equivalent to US\$0.30/kg of glycerin [26]. However, exports of glycerin decreased more than

45% in March of 2013 [27], resulting in a large accumulation of this byproduct in biodiesel plants.

Since there is a global trend of continuing increase in the consumption of biodiesel, it is necessary to search for different technological solutions for crude glycerin in order to add value to the productive chain of biodiesel within the biorefinery concept. Similarly to the sugarcane biorefinery, it has been proposed for glycerol biorefinery [28]. Glycerin may be used as raw material for the production of value-added products through chemical, biochemical, or thermochemical routes, as shown in Figure 5 [23,24,28-32].

Currently, another interesting solution can be to apply crude glycerin from vegetable oil biodiesel production as raw material for animal feed. Some reported data indicate that the use of 10% crude glycerin as a pig and catfish complement feed maintains their growth with normal performance [30].

Ethanol, hydrogen, and syngas could be used directly as fuels or as intermediates in chemical synthesis. Chemical compounds as polyols and organic acids are very important as building blocks. They are used in industrial sectors such as cosmetic, pharmaceutical, automobile, and chemical industries [33].

Table 2 Comparison of prices and costs of diesel and soybean biodiesel [15,19,20]

| Description | Price/cost as of 2013 (US\$/L) |
|---|--------------------------------|
| Price of diesel in the refinery [15] | 0.69 |
| Price of diesel in the distribution [15] | 0.89 |
| Production cost of diesel (estimated in this paper) | 0.26 |
| Average price of biodiesel [15] | 0.90 |
| Cost of biodiesel production (alkaline transesterification with a residual oil from the pre-treatment step of oil) [20] | 0.63 |
| Cost of biodiesel production [19] | 0.65 |
| Cost of biodiesel production (conventional alkaline transesterification) [20] | 1.25 |

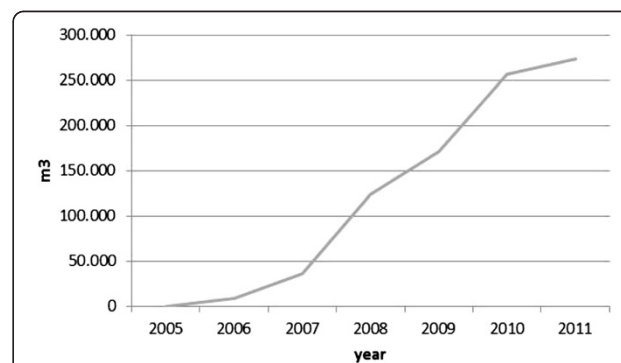
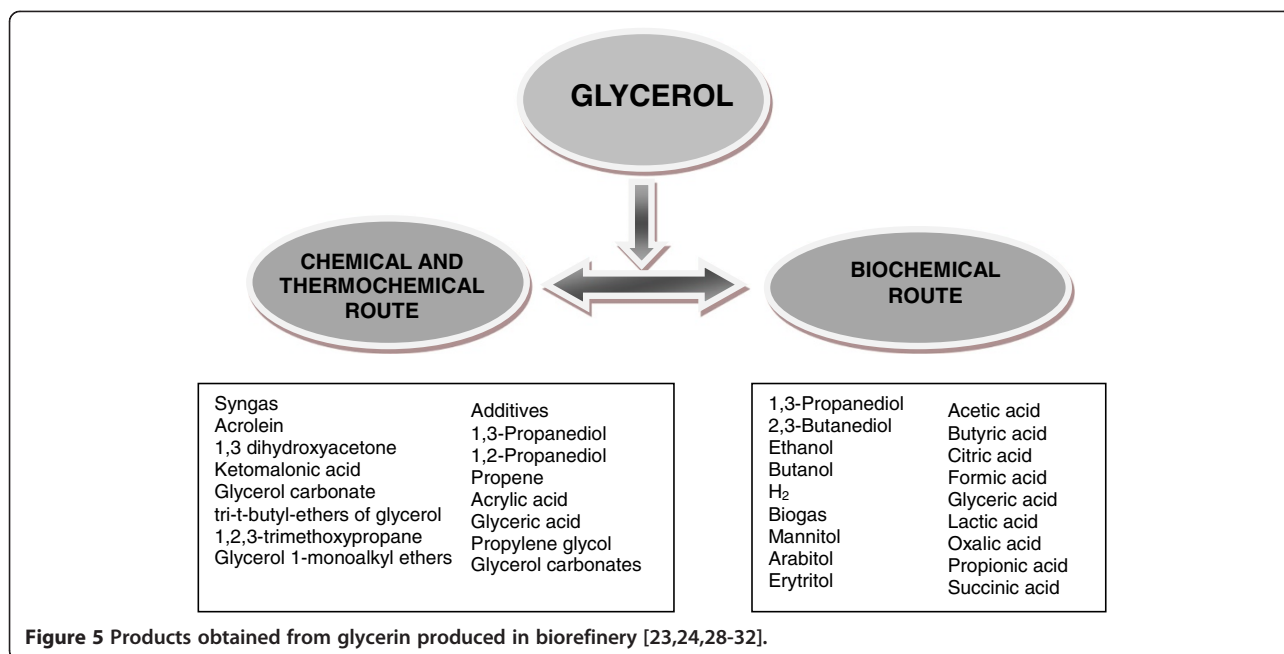


Figure 4 Glycerin generated in the production of biodiesel (B100) in Brazil: 2005 to 2011 [14].



Glyceric acid may be used in chemical and pharmaceutical industries as a building block and for the production of polymers and surfactants. Lactic acid can be processed to make acrylic acid or 1,2-propanediol used in polyester resins and polyurethane. Succinic acid is largely used for manufacturing health-related products and as building block to produce precursors that are converted into green solvents, pharmaceutical products, and biodegradable plastics. Polyols are used in food, pharmaceutical, and medical industries. They are used to improve the nutritional profile of food products due to their low caloric content, low insulin-mediated response, and non-cariogenicity. Polyols and their derivatives also have other industrial applications, including the production of polyurethanes, plastifying agents, resins, surfactants, and intermediates for producing hydrocarbons [23,24,28-33].

The chemical routes used to transform glycerin include selective oxidation, etherification, dehydration, hydrogenolysis, and reforming [23,34-37]. In the selective oxidation, the oxidation of primary hydroxyl groups yields glyceric acid and tartronic acid, both of which are commercially useful compounds. Dihydroxyacetone (DHA), an important fine chemical, is obtained from the oxidation of the secondary hydroxyl groups, while ketomalonic (or mesoxalic) acid results when all three hydroxyl groups are oxidized [34,38].

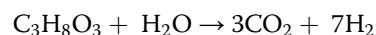
Alkyl ethers can be synthesized by the reaction of glycerol with alkenes and preferentially with isobutylene in the presence of an acid catalyst. Ether derivatives of glycerol reduce emissions of particulate matter, hydrocarbons, carbon monoxide, and aldehydes, when incorporated in

standard diesel fuel containing 30% to 40% of aromatic compounds [34,39].

Dehydration of glycerol may follow two pathways. The dehydration of the secondary hydroxyl group yields 3-hydroxypropanal, which undergoes a dehydration step, leading to the formation of acrolein. On the other hand, the dehydration of the primary hydroxyl group results in 1-hydroxyacetone, also known as acetol [23].

Hydrogenolysis is a catalytic chemical reaction that breaks a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to result in molecular fragments. Propylene glycol (1,2-propanediol (1,2-PD)) and 1,3-propanediol (1,3-PD) could be obtained through the hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen [23,36].

One promising way is to use glycerin to produce synthesis gas via steam reforming [40]. Overall, glycerin steam reforming can be represented by the following reaction [37]:



Another process used to produce synthesis gas from glycerol is the aqueous phase reforming (APR), using aqueous solutions of glycerol and a catalyst [41]. Synthesis gas can be used to produce hydrocarbons (through Fischer-Tropsch synthesis), methanol, hydrogen, isobutene, and isobutane [42]. BioMCN has been producing methanol from synthesis gas obtained from glycerin since 2010 in Delfzijl (Netherlands) [35].

One process widely known for the valorization of glycerin is the synthesis of epichlorohydrin. This chemical is employed in the production of epoxy resins. Advanced Biochemical (Thailand) Co., a subsidiary of Vinythai (shareholders are Solvay and PTT), is producing 100,000 t/year of epichlorohydrin in Thailand (Map Ta Phut) using Solvay technology (Epicerol®). A new plant of Vinythai in China (Taixing) should become operational in the second half of 2014, also with capacity of 100,000 t/year and using the Epicerol® technology. In this process, glycerol reacts with HCl, yielding a mixture of 1,2-dichloro-3-propanol

and 1,3-dichloro-2-propanol, which is treated with NaOH resulting in epichlorohydrin. The Dow Chemical Co. and Spolchemie (Czech Republic) have also developed processes to convert glycerol to epichlorohydrin [23,34,35,43-45].

Figure 6 shows some products and their intermediates obtained by biotechnological pathway of glycerol (glycerin) conversion.

The route of biotechnological valorization of glycerol can follow three different pathways. Yeast and filamentous fungi convert glycerol to polyols and organic acids by

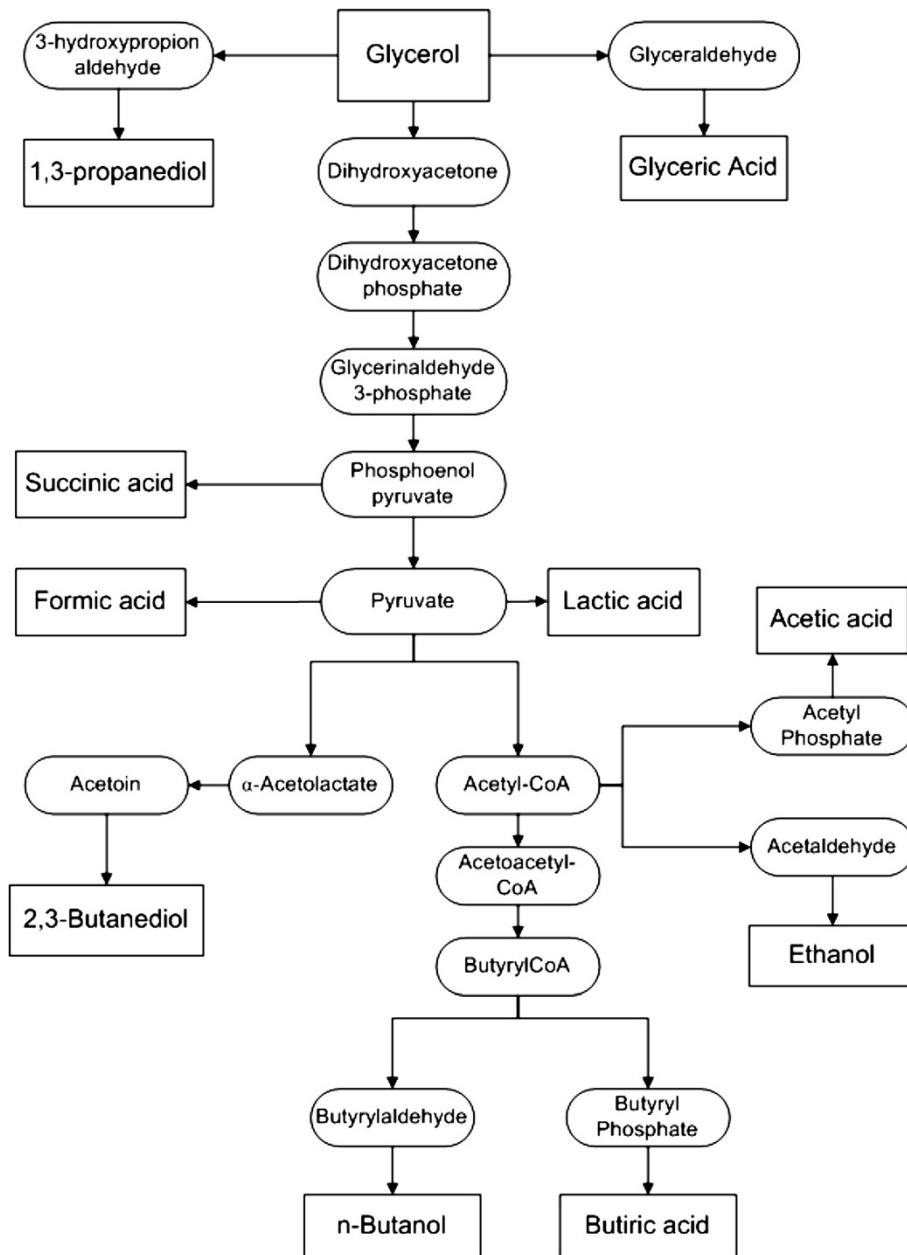


Figure 6 Products obtained from glycerol bioconversion metabolism [28,29,46,47]. Products and glycerol are enclosed in boxes and the main intermediates are enclosed in circles.

aerobic process. Enterobacteriaceae produces butanol and 2,3-butanediol using anaerobic way. Additionally, *Escherichia coli* and other bacteria produce lactic and glyceric acids and dihydroacetone under microaerobic conditions. Succinic acid can be produced by aerobic and microaerobic pathways, while 1,3-propanediol and ethanol can be obtained by anaerobic and microaerobic conditions [28,29,46,47].

Notwithstanding, there are some aggregate-value bioproducts that can be obtained from glycerin by biotechnological route. Although there are several works in the literature and patents, commercial initiatives are still rare. Some examples of industrial scale production are described below; however, there is no information about industrial initiatives in Brazil.

The chemical companies BASF and Cargill and industrial biotechnology company Novozymes are developing bio-based technologies to produce acrylic acid from renewable feedstocks. Currently, acrylic acid is produced by the oxidation of propylene derived from the refining of crude oil. Using biotechnology route, these companies have worked to develop microorganisms that can efficiently convert renewable feedstock, among them are glycerol, into 3-hydroxypropionic acid, which is one possible chemical precursor to acrylic acid [48]. The companies have carried out this precursor production in pilot scale, but they intend to increase for commercial scale still in 2014.

1,3-propanediol has showed to be a scientific and technological interest product. An Asia (METabolic EXplorer) and European initiatives (Propanergy and Glyfinery Projects) have been carried out to construct pilot and industrial plants to obtain this product from glycerin raw material. In all cases, the biotechnological route and the biorefinery concept are applied, including the production of biogas and other aggregated-value bioproducts. To develop the European projects, partnerships between private companies and universities were established [49-51].

Posada et al. [52] evaluated the conversion of raw glycerol to nine added-value products obtained by chemical (synthesis gas, acrolein, and 1,2-propanediol) or biochemical (ethanol, 1,3-propanediol, lactic acid, succinic acid, propionic acid, and poly-3-hydroxybutyrate) routes. The results showed that not only quality requirements were successfully reached but that all the processes were profitable. More income can be earned from 1,3-propanediol and 1,2-propanediol production, while less income would be obtained from hydrogen (synthesis gas) and succinic acid.

According to recent analysis of technical papers, the most studied chemical products obtained from glycerin are 1,3-propanediol, hydrogen, and propylene glycol. On the other hand, propylene glycol, acrolein, and dichlorohydrin were the most cited chemical products in patents.

Additionally, the main chemicals obtained from operating plants are propylene glycol and epichlorohydrin [53].

In this context, if glycerin is used in Brazil or worldwide as raw material for the production of fuels and value-added products in the glycerol biorefinery concept, it could increase balance of trade through the sale of these products, and it can prevent the accumulation of glycerin in companies when exports are unfavorable.

Conclusions

Brazil stands out on using biomass as an energy source. In addition, many raw materials have great potential for use in biorefineries. Among these raw materials are oilseeds such as soybeans, besides forest biomass, sugar cane and other biomass. Considering the availability of these raw materials and favorable conditions of price and costs, the results showed significant opportunities that can be exploited in Brazil in the biorefinery concept.

Soybean oil is the main raw material used in the production of biodiesel in Brazil. Despite increased use of biomass of soybean in the Brazilian energy matrix, petroleum products remain the most economically viable. The cost of production of soybean biodiesel in Brazil (US\$1.25/L) is well above the values of the production cost of diesel (US\$0.26/L). This is certainly a challenging factor that encourages the consolidation of biorefineries in Brazil. Besides biodiesel from soybean oil, the application of the biorefinery concept aimed the production of a wide range of products. The production of chemicals and biofuels from glycerin biodiesel byproduct is one of the main challenges within the concept of biorefinery. Some products as polyols, organic acids, alcohols, syngas, and biogas could be obtained from this industry that could be called 'glycerol biorefinery'.

Both biochemical and chemical route, including thermochemical processes, are essential and complementary in a biorefinery. It is not yet possible to define the best technologies and products for oleaginous chains that are under development, but at the present time, all of them must be considered. The possible combinations of raw materials, conversion/technology processes, and final products are practically unlimited in the biorefinery concept.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MCTD and ELS wrote the Abstract and the 'Introduction' and 'Raw materials for biodiesel production' sections. DTS wrote the section 'Prices and costs of soybean biodiesel'. All authors participated in the writing of 'Challenges and opportunities within the concept of glycerol biorefinery' and the 'Conclusions' sections. All authors read and approved the final manuscript.

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