Chapter

Integrated Soybean Biorefinery

Fernando Luiz Pellegrini Pessoa, Hugo Villardi, Ewerton Emmanuel da Silva Calixto, Erika Durão Vieira, Ana Lucia Barbosa de Souza and Bruna Aparecida Souza Machado

Abstract

The concept of biorefinery is analogous to that of petroleum refineries, but it uses renewable raw materials. However, the main objective of the biorefinery is to transform renewable agricultural materials into numerous and different commercially applicable products, allowing a viable economic competitiveness to traditional petrochemical refineries. In this chapter, we present a proposal for a biorefinery integrated from soybean as raw material, demonstrating its potential in this sector. In addition, special focus was given to the high value-added products present in the soybean oil deodorizer distillate (SODD), such as tocopherol, fatty acids, and squalene, which can be applied in the food, pharmacy, and cosmetic industries. In conclusion, the use of soybean raw material as a biomass in a biorefinery presents numerous environmental and economic advantages as high value-added products are formed. It is important to highlight that in this highly evolved integrated biorefinery model, the additional benefits of operational and administrative synergies will emerge over time.

Keywords: biorefinery, soybean, biomass, oil, fatty acids

1. Introduction

Due to the environmental concerns and the likely depletion of fossil fuel oil, the scientific community has been increasingly striving to seek raw materials from renewable sources to enable sustainable growth, thereby reducing dependence on oil. In this perspective, the concept of biorefinery is perfectly connected in this scenario, since its main objective is to transform renewable agricultural materials into numerous and different commercially applicable products, allowing a viable economic competitiveness to traditional petrochemical refineries [1, 2]. Biorefinery applications integrate several important areas of research, such as product and process engineering, biofuel generation, biotechnology, agronomy, agroecology, and environmental impact assessment, among others [3].

Soybean (*Glycine L.*) accounts for 60% of the world's oilseed production, followed by cottonseed (*Gossypium herbaceum L.*), which accounts for 10% of the global production [4]. Global soybean production in 2016 was 324 million tons, a significant increase of 17% compared to 2013. The United States, Brazil, and Argentina are the largest soybean producers in the world, with a production that occupies more than 80% of the world production of this oilseed [5]. Brazil is the country with the greatest potential for expansion of the cultivated area, being the largest producer and exporter of soybeans and their derivatives worldwide.

From the soybean processing, bran that is rich in protein is mainly used in animal feed, and oil, in addition to its application for the production of biodiesel, is also used for human consumption and product development (chemicals, food, and cosmetics). In general, 78–80% of the grain is transformed into bran, and 18–20% of the grain results in oil, the remainder being fibrous material from the low value-added shell used as feed [6]. Soybean seeds contain on average 40% protein, 20% lipids, 34% carbohydrates (soluble and insoluble), and 4.9% ash. Among these large groups of biomolecules are important macro- and micronutrients and biologically active components such as isoflavones, tocopherols, saponins, phytosterols, as well as essential fatty acids, especially linoleic acid and linolenic acid [7].

Of the lipid fraction, most of the crude oil components are triglycerides (99%), and the remainder are phospholipids, unsaponifiable material, and free, saponifiable fatty acids. These non-saponifiable materials are extracted from the crude oil in the last purification step and in this fraction contain some high value-added products such as vitamin E (tocopherols) and terpenes, in particular squalene [8].

In this context, this chapter aims to present and discuss the application of soybean as a raw material for biorefinery, with a special focus on the exploitation of high value-added products present in the soybean oil deodorizer distillate (SODD), such as tocopherol, fatty acids, sterols, and squalene.

2. Biorefinery: concepts and potential of soybean application

The concept of biorefinery is analogous to that of petroleum refineries, but it uses renewable raw materials. In turn, the International Energy Agency defines that biorefining is the sustainable synergistic processing of biomass in different ingredients applied to food and tradable feeds, chemicals, materials, and energy in the form of fuels and heat.

The industrial unit integrates equipment and processes of biomass conversion in the production of fuels, electricity, heat, and refined products. It is worth noting that the concept of biorefinery has been explored in recent years by numerous researches, since it has become the best option to transform different biomass systems into products that can be applied in different industrial sectors [9–11]. According to Navarro-Pineda et al. [12], a biorefinery can be defined as a unit that integrates equipment and processes to convert biomass into other high value-added products, including, for example, fuels and chemicals.

Different studies conceptualize biorefinery as a form analogous to petroleum refineries, which use fossil feedstocks to generate fuels and chemicals. According to Maity [13] just as petroleum refineries can obtain intermediary products for the generation of other products, biorefineries, regardless of the type of raw material used, also generate intermediate products to obtain numerous products. However, de Jong et al. [14] highlighted in their work some similarities and differences when they performed a comparative analysis between biorefineries and refineries. According to the authors, the main similarity is related to the quantity of intermediate products that both generate. However, the nature of the raw material is considered as the main difference which could significantly differentiate the concept of both, since the raw material used in refineries is a homogeneous material, while biomass, applied to the biorefineries, is an extremely complex and heterogeneous matrix.

Biorefinery systems have been considered as sustainable systems due primarily to the renewability of the biomass used in this process [15]. However, there are some controversies regarding the sustainability of some types of biorefinery systems, since sustainability is not based exclusively on renewability or the environmental dimension, and therefore other economic issues must also be taken into account [15]. Recent studies also highlight the importance of conceptual and methodological developments for sustainable biorefineries. According to Azapagic [16], integrated biorefineries use various biofeedstocks to produce biofuels, energy (electricity and heat), and chemicals. In order to maintain sustainability, the main factor for the development of integrated biorefineries is the production of biofuels for transportation, with the coproducts helping to maximize the value of raw materials.

Based on this context, soy has enormous potential as a raw material for a biorefinery, proving to be ideal for the process. According to Abdulkhani et al. [5], compared to other conventionally used raw materials, soybean contains all the components necessary to make up a biorefinery unit. For example, from the transesterification reaction, the virgin oil extract can be used to produce biodiesel, while the residual soybean straw can be used to produce different products, such as biomaterials, biofuels, and biochemical.

Thus, soybean refining is composed of a set of processes that aim to transform crude oil into edible oil. The refining process aims to improve the appearance, odor, and flavor of the oil, which occurs with the removal of certain components of the crude oil. There are two types of refining, the chemical and the physical, and these definitions are related to the process for the removal of the fatty acids in the oil, which are considered as unwanted components.

In the chemical refining, saponification of the acids occurs through an alkaline solution, which dilutes the soaps generated in water for the later removal of the process by separators. In turn, the physical refining is characterized as a process that separates the acids using the difference of their volatility, in relation to the triglyceride present in the oil.

The main steps involved in the refining process are degumming (hydration), neutralization (deacidification), bleaching (clarification), and deodorization [17]. **Figure 1** shows a simplified scheme for the extraction and refining of soybean oil.

The removal of traces of components responsible for undesirable odors and flavors occurs in the stage called deodorization. The operation takes place in a stripper, where the steam (1–3%) is injected into the soybean oil under low pressure (1–6 mmHg) and sufficient temperature to vaporize the fatty acids and the odoriferous compounds and to remove them from the oil. The deodorization temperature is variable because it directly affects the vapor pressure of the volatile constituents to be removed and thus directly affects the removal rate of these components [18].

It should be noted that the SODD contains products of high value-added that have uses in various sectors of the food, pharmaceutical, and cosmetic industries, for example. According to Lee et al. [19], this residue concentrates tocopherols and tocotrienols that present great value added, since it has antioxidant activity as vitamin E.

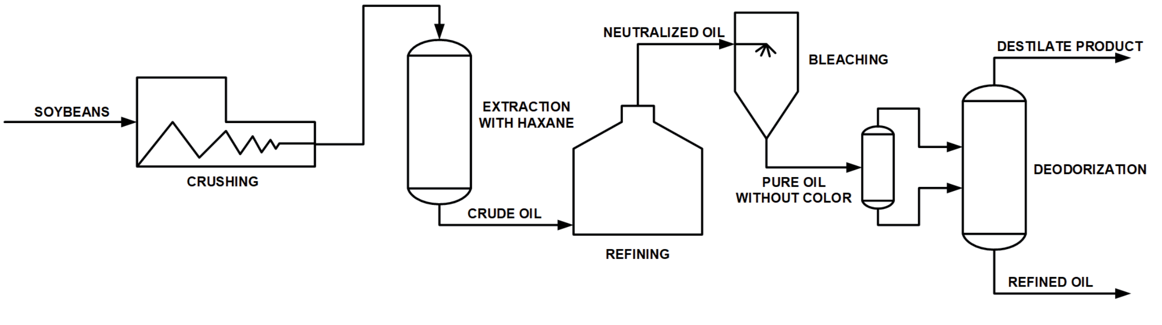

Figure 1.
Simplified flowchart for refining soybean oil.

In the recent study by Jones et al. [20], it was argued that biorefinery is an ideal strategy for the sustainable use of biomass on a large scale in the bioeconomy, resulting in an important competitive co-production of food and feed, for example, and with the production of bio-based products and bioenergy with great socioeconomic and environmental benefits. In addition, to ensure adequate sustainability, the appropriate location of industrial plants is particularly important to contribute to economic, social, and sustainable objectives, so it should not be done superficially [21]. **Table 1** presents some works that use, discuss, or propose different raw materials for the development of a sustainable biorefinery. Some conversion

Material and biorefinery	Target	Comments	Reference
Hemicellulose based integrated forest biorefineries	Specially chemical, biomaterials, commodity bioproducts, biofuels and sugars	Use of a prehydrolysis method that produces a recoverable hemicelluloses sugars stream Kraft, pulp mill, dissolving pulp mill	[23]
Enzyme biorefinery platform	Bioethanol production using enzyme and the biochemical platform	Development in fermentation and culturing technique to improve enzyme production and the pretreated solid after of hydrothermal process as the inducer in the enzyme production for advances in biofuels	[24]
Microalgal biorefinery	Convert CO_2 in chemicals for biofuels, food, feed, and high-value products Obtain proteins, lipids, pigments and carbohydrates	Separate operation units: laboratory-scale research, culture, and downstream processing The fractionation of microalgal components (downstream processing), remains the most expensive step	[25]
Biorefinery based on *Theobroma grandiflorum* (copoazu) fruit	Pasteurized pulp, antioxidant extract, biofertilizer, biogas, oil seed, essential oil, ethanol, and polyhydroxybutyrate (PHB)	A biorefinery based on copoazu could be considered as an opportunity to promote rural development with the participation of small-scale producers as feedstock suppliers	[26]
Biorefinery for avocado (*Persea americana* mill.)	Microencapsulated phenolic compounds extract, ethanol, oil and xylitol	Attractive opportunity for an integrated processing of the fruit into a series of valuable products, using the pulp, peel and the seed of the fruit	[27]
Integrated sunflower-based biorefinery	Production of antioxidants, protein isolate and poly(3-hydroxybutyrate)	Integration of the proposed processing scheme in a sunflower-based biodiesel plant could lead to the development of a sustainable biorefinery	[28]
Biorefinery with different mixtures of forestry, olive and grape pruning, sunflower waste and sawdust	Ethanol, dimethylether (DME), synthesis gas and electricity	Possibility of obtaining 42,700 T y^{-1} of ethanol with a purity of 96%, which supposes a 16.5% of the Spanish national production in 2016, and 137,850 T y^{-1} of DME, with a purity of 99.99%	[29]
Biorefinery process of corn cob bagasse	Polyoses, acetone–butanol–ethanol, polysaccharides and lipid	Approximate 87.7% of the polysaccharides were converted into valuable biobased products (~175.7 g/kg of acetone–butanol–ethanol along with 36.6 g/kg of lipid)	[30]

Table 1.
Publications that use, discuss, or propose different raw materials for the development of a biorefinery.

technologies are consolidated at a commercial scale, but others are still under development or study [22]. In the study by de Jong et al. [14], the advantages and opportunities for different types of biorefineries were discussed, as well as some disadvantages and threats to their implementation and sustainability, and analyzed in a comparative way with petrochemical refineries.

2.1 Main components of SODD

As previously discussed, SODD is a by-product of the soybean oil refining process, being considered as a complex mixture of compounds such as free fatty acids, hydrocarbons, and sterols, such as tocopherols, a class of large natural antioxidants with vitamin E activity [31]. For example, SODD has been studied as a great alternative to marine animals as natural source of squalene (from shark) and as a raw material for the production of fatty acids, tocopherols, and phytosterols [32]. In this section we present the main compounds in SODD with the objective of showing the potential of soybean for the development of an integrated biorefinery.

2.1.1 Tocopherol

Tocopherols are the most widely distributed antioxidants in nature, being present in the form of four homologous isomers (α, β, γ, and δ) and because they have activity as vitamin E are widely used as antioxidants and food additives. In turn, a vitamin is defined as an organic compound that is essential for exerting different normal physiological functions of the organism, being necessary in small quantities [33]. Thus, vitamin E, and more specifically the α-tocopherol isomer, is widely used by industry mainly because of its antioxidant properties, which are attributed to numerous beneficial effects on human health [34].

Based on the Brazilian production, an estimate shows that the range of tocopherol available for commercialization is 7–12% of tocopherol in SODD. Considering the production of refined oil in 2016, according to the Brazilian Association of Vegetable Oil Industries [35], 7.9 million tons were produced, since deodorized distillate is equivalent to approximately 0.1% of all refined oil produced, and it can be concluded that there is an amount of tocopherols available from the SODD of 490–840 t, as reported by Araújo et al. [36].

2.1.2 Fatty acids

Other components of great interest in SODD are fatty acids. According to Barros et al. [37], acids present in oils are constituted, on average, by carboxylic acids containing 4–30 carbon atoms, and the use of these for the production of biofuel becomes advantageous, as it is shown as a potential substitute to refined oils for the production of biofuel, since these have competition from the food industry.

The distillate obtained in the deodorization of soybean oil has a composition dependent on the type of refining provides a SODD with less fatty acids (40–50%) due to the saponification used in the process, of the acids, produces a more acid by-product (70–80% of fatty acids) [38].

2.1.3 Squalene

Squalene is an important bioactive compound concentrated in intermediate by-products and waste streams during the refinement of soybean oil [39]. Squalene is defined as a natural dehydrotriterpenic hydrocarbon formed by six double bonds ($C_{30}H_{50}$) and diffused in the animal and plant kingdom [40]. Squalene is widely applied in the preparation of cosmetics as a natural moisturizer and in cholesterol biosynthesis [32, 41] as well as used for the development of stable emulsions for vaccine adjuvants [42, 43], mainly due to their safety recognized by the World Health Organization [44] . For commercial purposes, it is mainly obtained from liver oil from some deep-sea sharks.

SODD and sunflower oil deodorization distillate are by-products most appreciated for the high quality of squalene [45]. Bondioli et al. [46] recovered squalene in high purity (90%) and with excellent yield (about 91%) from olive oil deodorization distillate, whereas Gunawan et al. [47] obtained squalene with almost 96% purity and 93% recovery in the second fraction of the process using SODD, demonstrating the potential of this by-product to obtain squalene. An Indian patent also describes the use of SODD for obtaining high-purity squalene for application in cosmetics and medicaments, for example [48].

2.2 The soybean biorefinery

The usage of oil for the fuel synthesis is based on the transformation of triglycerides in esters. The most common way to synthesize those substances is by the transesterification of the refined oil. Although the regular transesterification process provides high conversion rates and have a relatively operational simplicity, some problems comes along, such as (1) low energetic and production efficiency; (2) need to adjust the raw material; (3) the use of high toxicity intermediate products; (4) generation of a significant by-product volume (glycerol) with a level of contamination that requires high investments to its use or discharge; (5) the use of methanol which, besides toxic, needs fossil fuels, as raw material, to be produced in the form of energy; (6) difficulty in recycling the catalyst; (7) need to remove the glycerol from biodiesel; and (8) high environmental impact associated.

The sector must deal with those barriers and other operational issues, e.g., soy price and physical properties which turn the production less attractive. Therefore, governments are obliged to subsidize the biofuel production, since they are pressured to meet oil demand provided by law.

For this reason, the biodiesel production feasibility is only possible due to governments' incentives such as tax relief and the market guarantee, as well as its appeal, under the label of "green product," to the final consumer.

In this regard, the biorefinery concept fits perfectly, because in addition to using residual raw materials, it manages to generate value-added products, which help the lucrative process. However, waste oils demand different technologies than the usual ones, and in this case, one of the solutions for technically and economically viable biodiesel production is the use of processes that use solvents under supercritical and subcritical conditions. Thus, one of the steps of a biorefinery would be the production of esters and glycerin with low level of contaminants.

The limitations have encouraged many studies to synthesize green fuels that overcome the shortcomings of their predecessors. These have been called second-generation biofuels [49]. Another factor is the generation of glycerin as a by-product. This presents an increase in the costs of the process, as it is not easily treated for use as raw material and so cannot be discarded. The synthesis of propylene from glycerin does not demand as high a purity as is required for the cosmetics area and has a wide market [50]. Thus, the evaluation of a methodology that uses residual sources and generates esters and glycerin without catalysts presents a high socioeconomic potential.

The objective is the esterification of residual raw materials in super- and subcritical environments to obtain esters and glycerin for the synthesis of propene and polymers.

The second integrated process is the extraction of high value-added waste products from the refining of vegetable oils. Using SODD, which has significant amounts of free fatty acids (potential source to produce esters), tocopherols (widely used in the cosmetics industry), and sterols (used in the formulation of vitamin supplements in the cosmetics industry), biorefinery is a great generator of high value-added products.

A process which separates the products efficiently and with high purity will provide raw material for the synthesis of esters and quality raw material for the cosmetic and medicinal sectors. The separation with supercritical fluid (CO_2) allows to obtain products without the contamination of solvents, thus allowing a commercialization of the same with greater purity. The fatty acids obtained are used for the synthesis of esters in a subcritical environment and contemplate the third part of the biorefinery.

Due to the composition of the oils, a supercritical environment would be required to promote triglyceride/alcohol contact and hence esterification. This concept arose from the need of sources with high triglyceride content, since these substances and alcohols are not miscible, and under the conditions evaluated, the whole reaction medium would be in a single phase, favoring the reaction. However, fatty acid-rich materials, such as deodorization distillates and the residual frying oils, are soluble in alcohols; thus, milder conditions were enough for the synthesis of esters [51–53].

According to Villardi et al. [54], the subcritical environment is excellent for the synthesis without catalyst using SODD. The authors report excellent conversions with methanol at 200°C and alcohol/SODD ratio of 10–105 minutes (99.5%). When ethanol was used, the conversion reduced by 12.4% under the same conditions, showing that the acidic character of the alcohol directly influences the results. The work further compared the results with the synthesis using acid catalysts and concluded that catalyst with less synthesis is as efficient as acid to produce esters through acid sources.

In addition, if the fuel market is not attractive, the esters can be burned as fuel because of the calorific value of the esters. They are also applied as drilling fluid, for example, if it undergoes treatments that comply with the legislation specific to such use.

2.2.1 The flow sheet

This topic presents a short overview of the biorefinery concept to a soybean crushing and refining facility and presents some applications for most of the residues produced during the process. The energetic requirements and the number of residues generated during soy protein concentrate (SPC) and soy protein isolate (SPI) processes were obtained by simulations. This study reinforced the idea to direct the straw and hulls to fulfill the energetic demand of the crushing, refining, and biodiesel production facilities and to provide electricity to the rest of the process.

The main residues produced by the refining process are gums, soap stock, spent bleaching earth (SBE), and deodorizer distillate product. Lecithin can be obtained from gum residues. Biodiesel can be produced from soap stock and spent bleaching earth. Concentrated tocopherols are obtained from deodorizer distillate, and the electrical energy is produced from soybean molasses generated during the concentration of proteins from soybean meal.

Figure 2 illustrates the major steps of a soybean crushing and refining facility, as well as the main products and the residues generated.

After the hull and straw removal, the soybean flakes are sent to the soybean oil extraction. In this step, the most common method used to extract is the direct solvent extraction with hexane as solvent. It consists of three basic steps: the seeds' preparation, oil extraction, and oil/meal desolventizing.

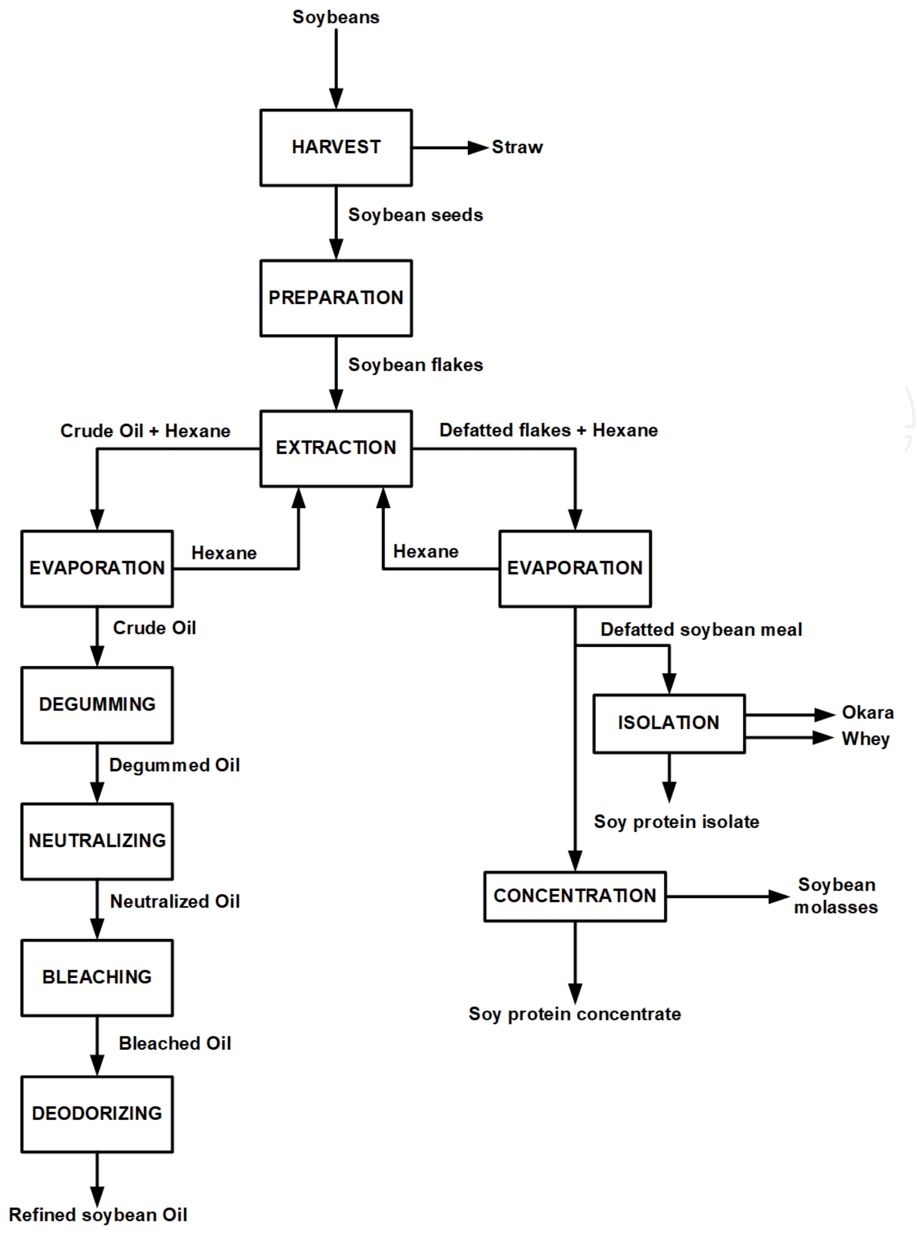

Figure 2.
Overview of the main steps and residues in a soybean biorefinery.

The next main step is the chemical refining of the soybean oil which aims to remove the unwanted oil components with minimal effect on triacylglycerols and minimal loss of the desirable components.

After the oil extraction present in the soybean meal, the protein content in the meal becomes even more concentrated, and for an achieved concentration of 65–72% dmb, it can be sold as soy protein concentrate. Using a different process, the meal can achieve 90–92% dmb and be sold as soy protein isolate.

The residues produced along the soybean refining process have commercial value or can be used as a source of energy for the plant itself. One of these residues is the straw.

Every year around 220 million tons of soybeans and an equivalent amount of straw are produced globally [55]. The straw is composed of stem, leaf, and pod husk, varying its global composition. Another residue is the hull, which is part of the seed that has the highest carbohydrate concentration. It consists of 86% carbohydrates, 9% proteins, 1% lipids, and 1% ash (w/w dry basis). The hull occupies around 8% of the seed [56].

Another kind of residue present in the soybean crude oil is the gum. The process to remove it is called degumming process. It aims to remove phospholipids from crude soybean oil, in order to improve its physical stability and facilitate further refining. Without this process, phospholipids can lead to dark-colored oils and act as precursors to off-flavor compounds [55]. The processed phosphatides present in vegetable oil are also known as lecithin. This substance is widely used in the cosmetic, food, and pharmaceutical industries because of its large amount of surfactant and bioactive properties.

The degummed oil is sent to a process to neutralize the crude oil during the refining process. This process produces a residue called soap stock. It has around 6% of the initial value of the crude oil volume feed used in the refining with around 35% of total fatty acids. Soap stock is basically formed by water, free fatty acids, neutral oil, phospholipids, unsaponifiable matter, proteins, and mucilaginous substances. It can be used to produce biosurfactants and rhamnolipids with a yield of 75% [57]. However, research has concentrated its efforts to take advantage of the high free fatty acid content of the soap stock for biodiesel production.

The neutralized oil goes to the bleaching process to remove residual soaps, phosphatides, and oxidizing bodies, breaking down peroxides into lower molecular weight carbonyl compounds, to facilitate their removal during deodorization operations. The residue generated by the bleaching process is called spent bleaching earth. The oil recovered from SBE is used to produce coating systems that demand good mechanical properties and mild chemical resistance.

The bleached oil is sent to a deodorizing process. The residue of this step is known as SODD. It aims to remove aldehydes, ketones, and some volatile substances that affect the refined oil flavor and odor, such as fatty acids, tocopherols (also known as vitamin E), sterols, and squalene.

The usage of most of the soybean meal is for animal feed, human diet, and industrial purposes [56]. It is due to not only its high protein content but also for its nutritional quality. Soy proteins are widely used as functional ingredients in food systems. They can also be hydrolyzed by acids, alkalis, or enzymes. The effects of hydrolyzed proteins have been tested for human use in sports' nutrition, malnutrition, postsurgical recovery, burn recovery, gastric repair, muscle damage recovery, infant formulas, and allergic individuals [55]. The possible uses of soy proteins in industry include the production of adhesives, plastics, and textile fibers.

Another kind of residue is the soybean molasses. It is a residue of the protein concentration present in defatted soybean flakes using aqueous alcohol extraction. Its composition may vary depending on the soybean variety, growing conditions, location, and year. However, the main components of soybean molasses are carbohydrates and smaller amounts of monosaccharides. Soybean molasses also contain proteins, lipids, minerals, and phytochemicals (plant compounds that might affect human health), such as isoflavones and saponins [55].

The last process is the manufacturing of the soybean protein. It generates two residues with exploiting potential: (1) the okara (also known as spent flakes or cotyledon fiber) and (2) a liquid fraction called whey. These are also the names of the residues from soy milk and tofu production. The soy soluble polysaccharides also refer to all soluble saccharides present in the whole soybean.

The process showed in **Figure 2** can be integrated with a cogeneration system to provide electricity to the rest of the refinery. The other routes to produce glycerol and biodiesel from all the residues generated are also illustrated in **Figure 3**. It is possible to have a broader view of production of transportation fuels, bioenergy, and high value-added products.

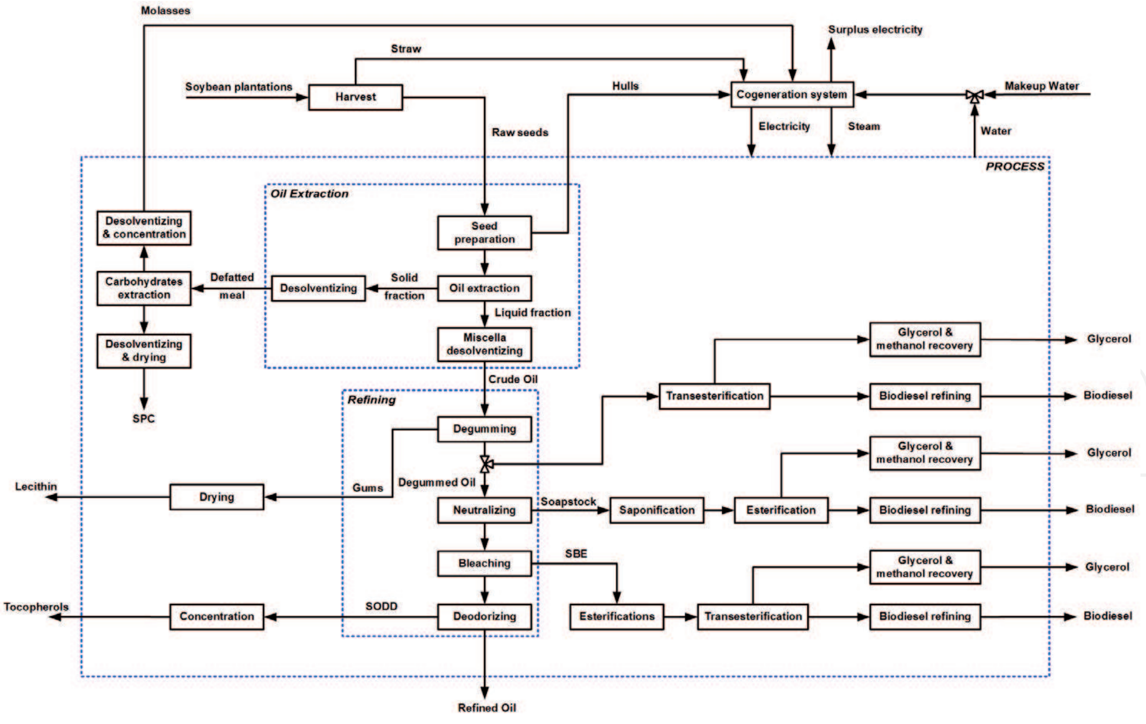

Figure 3.
The integrated biorefinery concept.

There are different studies and proposals of integrated biorefineries in the literature, as discussed by Oliveira [58]. For example, Forster-Carneiro [59] analyzed integrated biorefineries that use agro-industrial residues in Brazil, and the results indicated that the sugarcane has the highest agronomic availability, followed by soybeans. In this work we have been able to demonstrate an approach in relation to the SODD generated and the obtaining of high value-added products when discussing an integrated biorefinery for soybeans, relating, for example, the inherent complexity of its structure.

3. Conclusions

As discussed in this chapter, due to the environmental problems of recent times, numerous research efforts for the development of new raw and sustainable resources for the production of food, materials, and energy have been addressed in different studies. With the technological advance and increased investments in this area, many biorefineries are already in operation to minimize the problems caused by traditional refineries. Based on this context, we highlighted the importance and potential of soybeans through an integrated biorefinery concept.

In addition, we demonstrated that the use of soybean raw material as a biomass in a biorefinery presents numerous environmental and economic advantages as high value-added products are formed. These products can be applied in different sectors of the chemical, pharmaceutical, cosmetic, and food industries, thus contributing to the use of the products generated. It is important to note that in this highly evolved integrated biorefinery model, the added benefits of operational and administrative synergies will emerge over time. The implementation of integrated biorefinery of soybeans, specifically in Brazil, is very interesting considering the country's expertise regarding biofuel technology already applied to soybeans.

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Conflict of interest

The authors have no conflict of interest.

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