Chapter

Routes to Aggregate Value to Soybean Products

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Abstract

This chapter presents routes to aggregate value to soybean oil products by sustainable and economical sources for biofuels. The traditional production routes, such as pyrolysis, allows, by mixing oils and plastics, to generate bio-oils with high burning power. One example of an alternative route is single-step interesterification, where the methyl acetate reacts with the triglycerides in the oil, forming fatty acid methyl esters and triacetin as a by-product. This is a great advantage of this route, as in addition to its commercial value being greater than that of glycerol, it can be mixed with biofuel without changing its characteristics. The main objective is present routes that may reduce cost in general, in addition to generating co-products that allow an increase in the process added value.

Keywords: soybeans products, aggregated values, triglycerides, triacetin, methyl esters

1. Introduction

Originated from Asia, soy is the largest oilseed in volume, production and international trade. In terms of food, soy is the main source of protein and the second most consumed oil in the world, only behind palm [1]. Furthermore, it has an importance that involves the development of a productive complex including the processing of the bean and its main products: crude oil and bran; also, its use for animal food edible oil and fuel (see **Figure 1**).

The soybean industrial processing can be summarized in two steps: (1) the crude oil production with soybean residue; (2) Crude oil refining to obtain other products (e.g.: refined oils, margarine, hydrogenated fat).

The volume of soy sold is extremely important for the economy, especially for the main world producers, such as Brazil. In order to have a positive trade balance, Brazil needs to export tons of primary products, which have low unit values to offset the import of value-added products, such as electronic appliances and machines. In addition, processing soybeans increases the job offer, further heating up the economy. Therefore, adding value to the soy production process is very important for a country's economy.

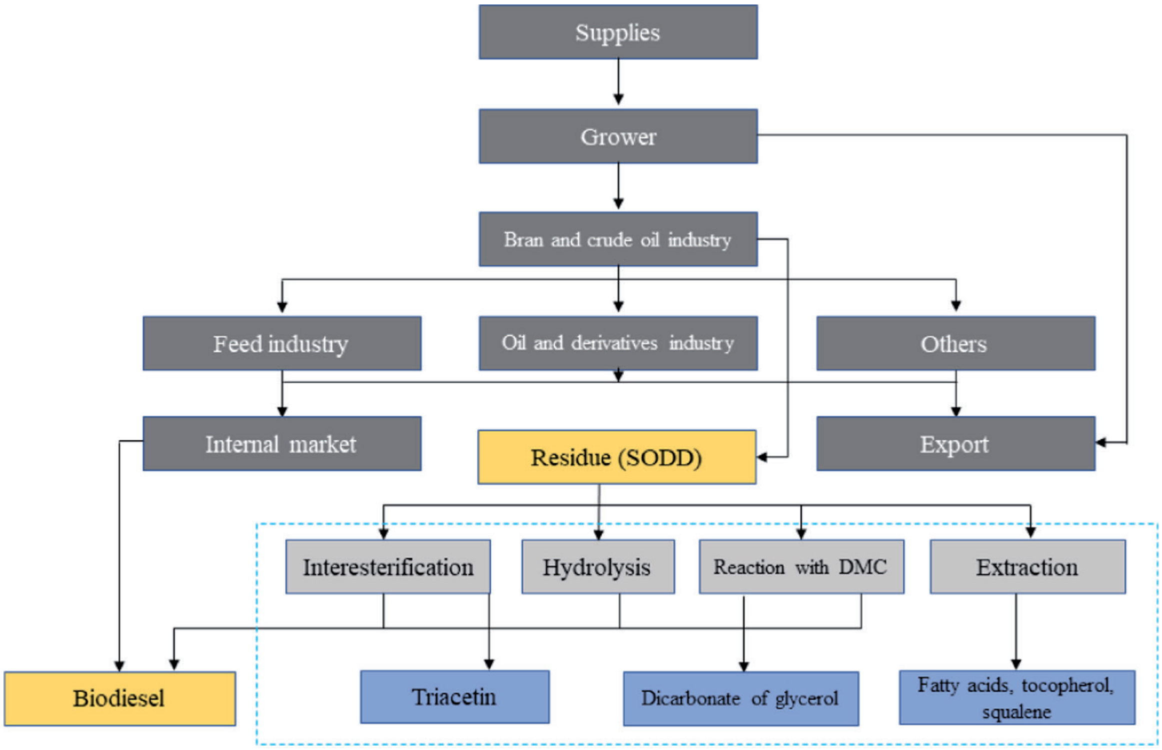

Figure 1.
Soy production chain.

Based on this, this chapter aims to discuss and present routes for the processing of soy, especially the Deodorized Soybean Oil Distillate (DSOD) and viable options to produce biodiesel to add value to the soy chain.

2. Oil refining

Refining consists of a set of processes that aim to transform crude oils into edible oils. The refining process aims to improve the appearance, odor and taste of the oil, which occurs with the removal of certain components from the crude oil. There are two types of refining, chemical and physical. These names are related to the process of removing unwanted fatty acids in the oil. The main steps in the refining processes are: degumming (hydration), neutralization (deacidification), whitening (clarification) and deodorization.

The removal of traces of components responsible for undesirable odors and tastes occurs in the step called deodorization. According to Sangoi and Almeida [2], the reduction of free fatty acids contained in oils promotes the removal of flavors and odors, at a range of 0.01% to 0.03%, eliminating the undesirable characteristics of the oil. This step generates a residue known as a distillate from soybean oil deodorization. According to Ma and Hanna [3], this substance is concentrated in tocopherols (vitamin E), sterols and fatty acids. DSOD is obtained from the precipitation of an aqueous phase during deodorization, and the compounds of interest are insoluble in water [4].

According to Aranda and Morlock [5], to produce a ton of biodiesel 0.91 tons of fatty acids are needed. According to Fontana [6], 0.1% of DSOD are generated in the refining of soybean oil, which would provide a quantity of 6440 tons of fatty acids, considering a production of 9.2 million tons of oil, according to Abiove [7] and an average percentage of 75% of fatty acids in DSOD. These values show the potential of the residue, increased by the logistical facility, as it is found in oil refining industries, unlike residual oils, which have a high logistical cost and variable production.

3. Sludge extraction

The most interesting components present in the sludge are fatty acids, however some works have evaluated the potential of other components such as sterols, tocopherols and squalene.

There are studies in the literature that evaluated the extraction of components from the deodorized distillate, such as sterols using supercritical extraction. The results show a recovery of 76% with a purity of 60%, both by weight. These substances are important because they act in the reduction of cholesterol in the blood, being of great interest to the pharmaceutical industry [8]. Similar works using enzymes are also presented and recovery of up to 87.7% of sterols [9].

4. Biodiesel

Biodiesel is currently an important biofuel of global interest, as it is considered a sustainable energy source of renewable origin [10]. As the most used raw material for production is refined soy oil, the production of fuel has the potential to close the carbon cycle [11]. In addition, the use of biodiesel generates less pollutants than fossil diesel, mainly CO_2, CO and SO_2, although it presents higher NO_x emissions [12, 13].

Brazil is a major world producer of biodiesel, ranking second in production volume in 2021, totaling approximately 6.9 billion liters, only behind the United States, which will produce more than 8.5 billion liters [14].

Another option to add value with deodorized distillate is direct esterification, that is, the synthesis of fatty acids to esters. This pathway was evaluated in a subcritical environment, as fatty acids are miscible in ethanol, unlike triglycerides, which are constituents of refined oils. These conditions, even though they demand high temperatures, dispense with the catalyst separation step, allowing for greater gains in the process. Some studies point to a 97% conversion of fatty acids into esters using subcritical environments at 100°C [15].

The economic potential of a complete process is available in the literature [16]. The work evaluated the potential of DSOD for the supercritical synthesis of esters and recovery of squalene. The squalene recovered was 31 g per kg DSOD with 98% purity by weight, the esters had a purity of 88% plus a mixture of tocopherols and sterols. The results of the economic analysis show, for the worst scenario, that is, with higher raw material values and lower product sales, a gross margin (MB) of 35% and the contribution margin index (BMI) of 29% for DSOD. These indicators are presented in Eq. 1 and 2.

$$MB = \frac{Product\ Revenue\,(PR) - Raw\ Material\ Cost\,(RMC)}{Product\ Revenue\,(PR)} \tag{1}$$

$$MB = \frac{Product\ Revenue\,(PR) - Operational\ Cost\,(OC)}{Product\ Revenue\,(PR)} \tag{2}$$

Other alternative routes are discussed in this chapter. The focus is on the synthesis of biodiesel via chemical reactions other than transesterification via heterogeneous, enzymatic and medium catalysis conventional supercritical, which promote the synthesis under different conditions.

As the formation of glycerol as a by-product is linked to the transesterification of triglycerides by alcohols, other supercritical routes propose to use other reagents for the same purpose – methyl acetate, acetic acid and dimethyl carbonate –, generating by-products of greater economic value than glycerol. These alternative routes, therefore, have all the advantages and disadvantages mentioned for the supercritical transesterification process, with the difference that they present more economically attractive by-products [13].

5. Interesterification with methyl acetate

This route consists of a single step, in which the interesterification between the methyl acetate and the triglyceride of the oil takes place, forming the fatty acid methyl esters and the triacetin as a by-product. The reaction, like the transesterification, occurs in three reversible steps: in the first, a triglyceride molecule reacts with a methyl acetate molecule to form a FAME (fatty acid methyl esters) and monoacetyl diglyceride molecule. Then, one molecule of monoacetyl diglyceride reacts with the second molecule of methyl acetate to form another of FAME and diacetyl monoglyceride; finally, diacetyl monoglyceride reacts with a methyl acetate molecule to form the third FAME molecule and triacetin, as can be seen in **Figure 2**.

If fatty acids are present in the oil, they are esterified by methyl acetate in FAME, generating acetic acid as a by-product. Other parallel reactions that can occur are the hydrolysis of triglycerides due to the presence of water, forming fatty acids and glycerol. This, in turn, reacts with acetic acid derived from esterification, forming triacetin and water [17, 18].

Triacetin formed as a by-product is the great advantage of this route. Although, its commercial value is greater than that of glycerol, the sale of biodiesel with this substance in its composition can be even more advantageous as it will increase the volume of biofuel generated, now a mixture of FAME and triacetin. Thus, there would be no need to purify triacetin in the process [18].

This final product alternative is only possible because triacetin, in addition to being miscible with fatty acid methyl esters, does not influence the fuel properties in a way that leaves them out of the pattern. Important properties of biodiesel as a fuel, such as kinematic viscosity, pour point, cloud point, cold filter plugging point,

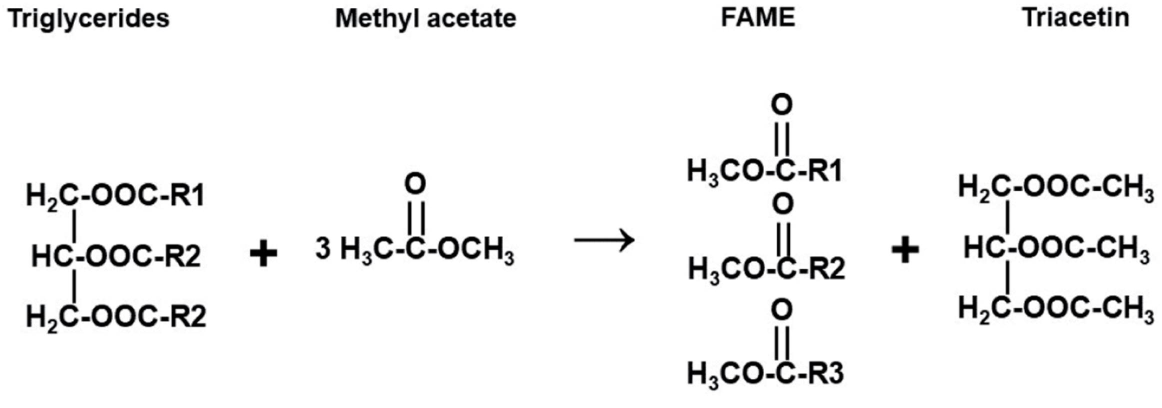

Figure 2.
Overall FAME synthesis reaction from triglycerides and methyl acetate.

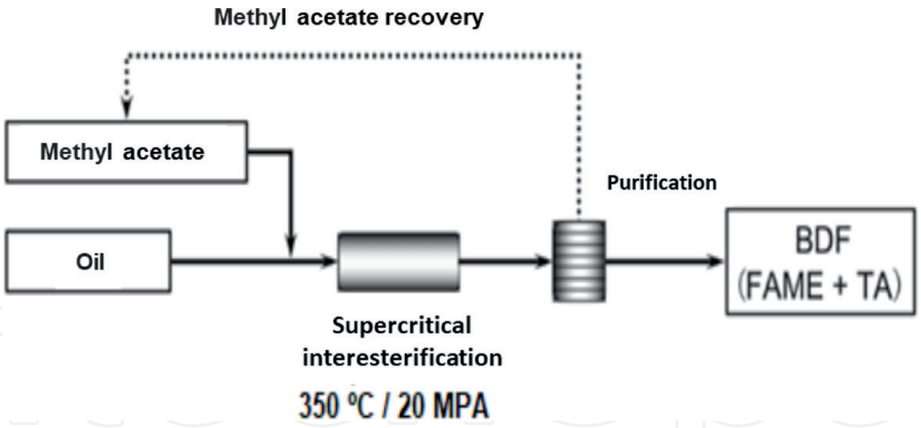

Figure 3.
Simplified diagram for the interesterification process with methyl acetate. Source: [18].

flash point and cetane number, are not changed with the addition of the by-product, remaining within European and North American standards [19]. However, due to the influence on the heat of combustion and density of the biofuel, the ideal is a mixture with a maximum of 10% by mass of triacetin - the European standard establishes 900 kg/m^3 as a density limit, as well as the Brazilian legislation on ANP [18, 20, 21].

Figure 3 shows a preliminary scheme for the process was proposed by Saka and Isayama [18].

6. Acetic acid hydrolysis and methanol esterification

This route consists of two steps: in the first, triglycerides, when reacting with acetic acid, are converted into fatty acids, which are esterified by methanol to FAME. The main justification for this route is the adoption of reaction temperatures of up to 300°C, avoiding thermal degradation of the esters.

6.1 Step 1: reaction with acetic acid

The route begins with the breakdown of triglycerides in the oil by acetic acid, a reaction in which one mole of triglyceride reacts with three moles of acid, forming one mole of triacetin and three moles of fatty acid, as shown in **Figure 4**. The reaction also takes place in three reversible steps: first, an acetic acid molecule reacts with a triglyceride molecule, forming a fatty acid molecule and a monoacetyl diglyceride molecule, which reacts with another acetic acid molecule to form the second fatty acid molecule and diacetyl monoglyceride; this reacts with the last acetic acid molecule to form again fatty acid and finally triacetin [22].

Regarding the cost of raw materials, acetic acid is a viable obtaining reagent because it is a commodity of the chemical industry, mainly used for the production of the acetate monometer of vinyl, for the production of polyvinyl acetate (PVA) [23].

6.2 Step 2: supercritical esterification with methanol

The second reaction of this route takes place in just one reversible step, in which a fatty acid molecule reacts with a methanol molecule, forming a FAME molecule and a water molecule, as shown in **Figure 5**.

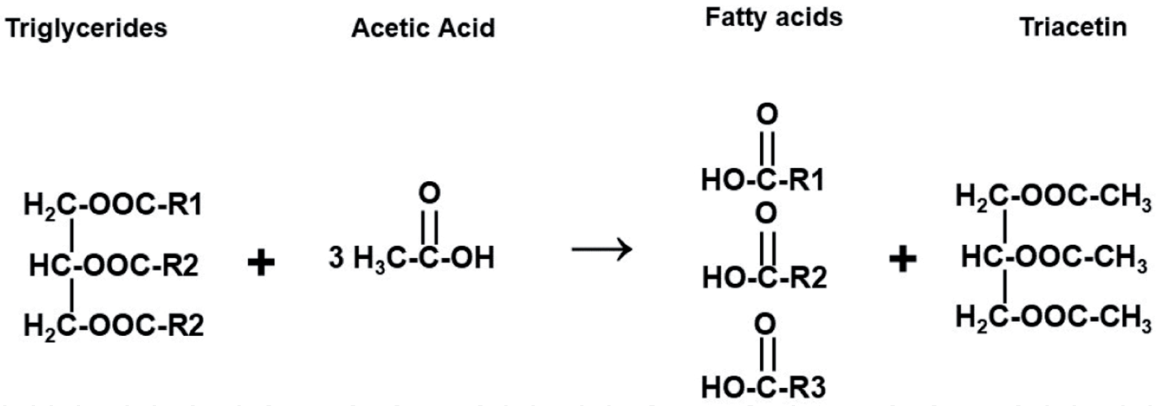

Figure 4.
Hydrolysis reaction between triglyceride and acetic acid. Source: [22].

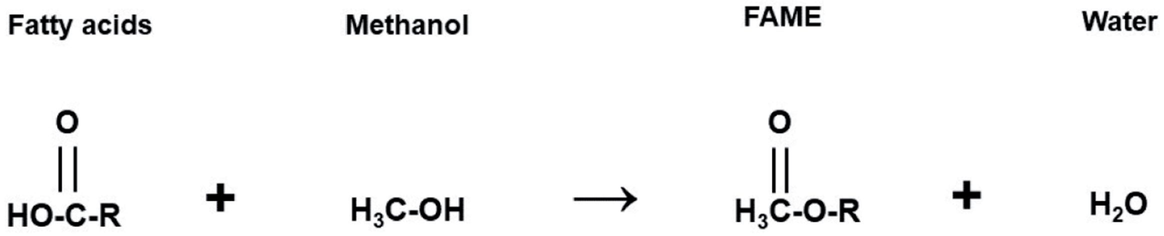

Figure 5.
Esterification reaction between fatty acids and methanol.

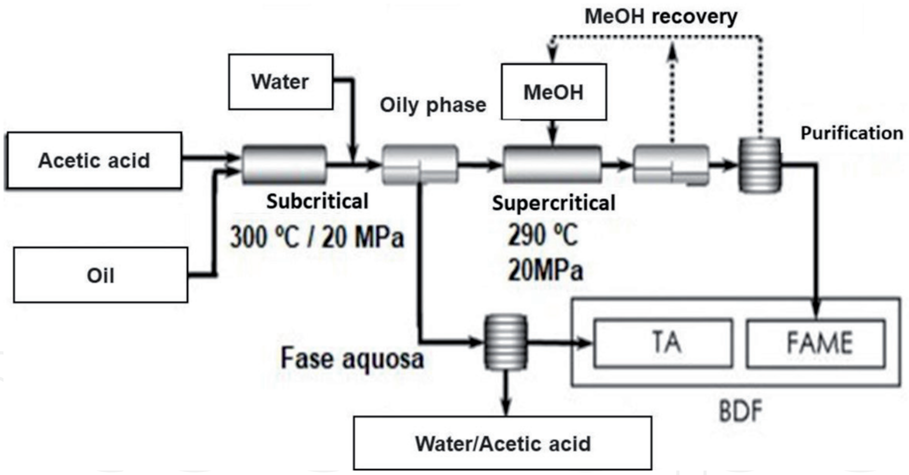

Figure 6.
Diagram of the process of hydrolysis with acetic acid and esterification with methanol. Source: [22].

After step 1, where the oil reacts with acetic acid through subcritical hydrolysis, the reaction products are separated by aqueous washing, from which triacetin and acetic acid are recovered in the step aqueous and fatty acids are taken to the second reactor with methanol under supercritical conditions for esterification. A phase separator is used to recover some of the excess methanol, followed by an unspecified scrubber that will separate the rest of the methanol and water from the FAME. The aqueous phase of the first stage is also subjected to unspecified purification to obtain triacetin, which will be mixed with FAME and, thus, composes the biodiesel in the final product. Performing an intermediate separation between the two steps can be advantageous to reduce the size of equipment in the second step. However, this imposes successive heating and cooling on the process, increasing energy expenditure, which can be one of the biggest disadvantages of this route [22].

Literature reports a yield of 95% in mass compared to the oil used in the first step, with only 2 minutes of reaction at 300°C and 15 minutes of reaction at 270°C. This approach to this process is interesting because, in addition to avoiding the saturation of the triacetin market, a phenomenon observed for glycerol, it is possible to increase the net production of FAME [24]. Saka et al. [22] suggested a diagram for this route, shown in **Figure 6**.

7. Reaction with dimethyl carbonate (DMC)

The third route is to obtain FAME from a reaction between triglycerides and dimethyl carbonate. Unlike all the other pathways described, this reaction takes place in two reversible steps: in the first, a DMC molecule reacts with a triglyceride molecule, releasing two FAME molecules and an intermediate, the fatty acid glycerol carbonate (FAGC - fatty). acid glycerol carbonate). In the second step, the FAGC molecule reacts with the second DMC molecule to form a FAME molecule and the by-product of the route, glycerol dicarbonate [25]. The reaction and its stoichiometry are shown in **Figure 7**.

DMC is an attractive reagent because it can be considered a green alternative in the organic synthesis industry and has several applications as a methylation and carbonylation agent. It is a non-toxic and biodegradable substance, which is obtained by environmentally interesting routes. The most used industrial route today is the oxidative carbonylation of methanol with carbon monoxide and oxygen, catalyzed by copper(I) chloride. As methanol and carbon monoxide can be obtained from biomass synthesis gas, obtaining biodiesel using DMC from this route would only use reagents of renewable origin [26–28].

Another important point is the fact that DMC does not decompose at temperatures lower than 390°C, so using it as a reagent in supercritical processes is viable [29].

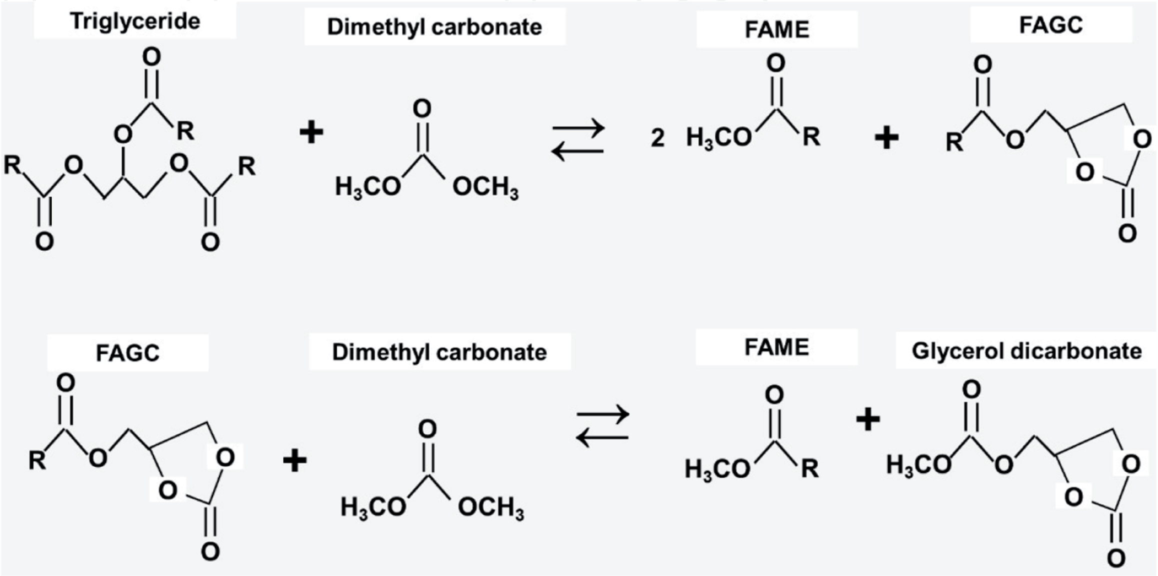

Figure 7.
Two-step reaction with dimethyl carbonate. Source: adapted from [25].

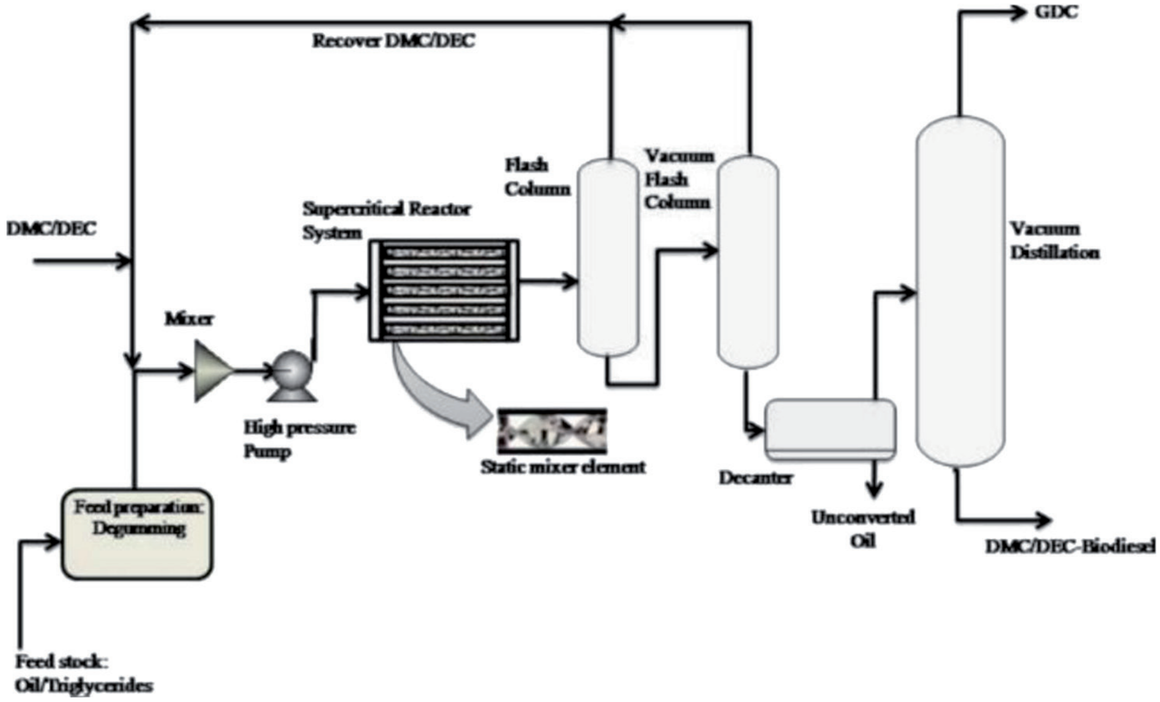

Figure 8.
Process using DMC as a reagent, producing FAME and glycerol dicarbonate (DCG) as products. Source: [30].

Biodiesel production by this route via supercritical process was studied using crude oils of *Jatropha curcas* and *pongamia pinnata* as raw material and DMC and diethyl carbonate as reagents, in a batch reactor, optimizing parameters such as molar ratio, temperature and reaction time. For all experiments, carried out at 15 MPa, the highest conversion obtained was for the system with *pongamia* oil and DMC, which shows that dimethyl carbonate is more reactive than diethyl carbonate [30].

The two-stage route, as well as for the methanol and acetic acid routes, has the advantage of being able to apply milder process conditions to avoid product degradation. However, this pathway generates glycerol as a by-product, although this can be converted to glycerol carbonate, a compound with greater added value, when reacting with DMC [29, 31].

The mixture of FAME and glycerol dicarbonate can be used as biodiesel, without harming its properties, as well as with triacetin. After the reaction to obtain FAME and the removal of excess dimethyl carbonate, the remaining product – FAME and DCG – was analyzed, showing that its properties were within the parameters established by the American and European standards. However, as it is an intermediate for glycerol carbonate, a compound with a high market value, glycerol dicarbonate and FAME can also be separated in a distillation column, depending on the strategy and economic feasibility of the process [30]. The complete flowsheet for the described process is shown in **Figure 8**.

8. Conclusions

This chapter shows the potential of soy as a raw material for a biorefinery, that is, obtaining several high added value products through different technological routes. The residues of this oilseed can be used to obtain these products with high added value without competing with the food sector. Routes that make the production of biodiesel viable are real and technically feasible, in addition to the generation of co-products of greater interest such as: tocopherols, sterols, squalene, triacetin, DCG. Another interesting point is the flexibility that some products allow when generated together with the esters, as they do not interfere with the quality of the biofuel. Soy has a wide range of exploration possibilities, and its production follows the pace of industrial production. Studies that make its development economically viable are the biggest challenge, as the technical feasibility is well consolidated.

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Conflict of interest

The authors have no conflict of interest.

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