UNIVERSIDADE FEDERAL DE SÃO CARLOS
CENTRO DE CIÊNCIAS EXATAS E TECNOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

SOYBEAN BIOREFINERY WITH RESIDUES EXPLOITATION: PROCESS ASSESSMENT

CRISTINE DE PRETTO

DOCTORAL THESIS

UNIVERSIDADE FEDERAL DE SÃO CARLOS
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BIORREFINARIA DE SOJA COM APROVEITAMENTO DE RESÍDUOS: AVALIAÇÃO DE PROCESSO

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CRISTINE DE PRETTO

Thesis submitted to Graduate Program in Chemical Engineering of Federal University of São Carlos in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemical Engineering, area of concentration in Chemical Process Research and Development

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RESUMO

A soja é uma matéria-prima renovável e o processo de produção de farelo e óleo refinado de soja gera alguns resíduos que podem ser aproveitados, de forma que o conceito de biorrefinaria pode ser aplicado a esse processo produtivo. Dessa forma, esse trabalho objetivou analisar a aplicação do conceito de uma biorrefinaria a uma instalação processadora de soja, buscando aplicação para os resíduos produzidos durante o processo. Para isso, primeiro coletaram-se informações e dados na literatura sobre o processo tradicional de produção de farelo desengordurado e óleo refinado de soja e os resíduos gerados durante esse processo foram identificados. Uma vez identificados os resíduos do processo, dados na literatura acadêmica sobre possíveis aplicações para esses resíduos foram coletados. A seguir, o processo tradicional de produção de óleo de soja refinado e farelo desengordurado foi simulado por meio de um software comercial. A quantidade de resíduos gerados e as demandas energéticas do processo foram obtidas. A quantidade de resíduos gerados durante o processo de fabricação de proteína de soja concentrada (PSC) e proteína de soja isolada (PSI) também foi calculada. Posteriormente, uma aplicação para os resíduos gerados (exceto os resíduos do processo de produção de PSI) foram simulados no mesmo software e os resultados foram analisados. Verificou-se que utilizando a casca e a palha da soja, toda a necessidade energética, tanto térmica quanto elétrica, do processo de produção de farelo, óleo refinado e biodiesel a partir do óleo degomado é satisfeita e até mesmo uma quantidade adicional de energia elétrica pode ser gerada, ainda mais quando o biodiesel também é usado como combustível na caldeira. Quatro resíduos são gerados durante o processo de refino do óleo: gomas, borra, terra clarificante gasta com óleo residual e destilado desodorizado. A partir das gomas, pode-se produzir a lecitina de soja. Da borra e terra clarificante gasta com óleo residual, pode-se produzir biodiesel, mas mais resíduos são gerados e mais vapor é consumido quando comparado à produção de biodiesel a partir do óleo degomado de soja. Os tocoferóis presentes no destilado desodorizado podem ser concentrados e vendidos devido às suas propriedades antioxidantes. O melaço da soja, gerado durante o processo de concentração das proteínas do farelo, também pode ser usado para a geração de energia elétrica.

Palavras-chave: biorrefinaria de soja; cogeração de energia; demanda energética; aproveitamento de resíduos

ABSTRACT

Soybean seed is a renewable feedstock and the production process of soybean meal and soybean refined oil generates residues that can be exploited, in such a way that the biorefinery concept can be applied to this production process. For this reason, this work aimed to analyse the employment of the biorefinery concept to a soybean crushing and refining facility, exploiting applications for the residues generated during the process. For that, first, information and data from literature about the traditional manufacture process of soybean meal and refined soybean oil were collected and the residues produced during this process were identified. Once the residues were recognized, data in academic literature about possible applications for the residues were collected. Next, the traditional process for producing soybean refined oil and defatted meal was simulated using a commercial simulator. The amounts of residues generated and energetic requirements were calculated. The amount of residues generated during soy protein concentrate (SPC) and soy protein isolate (SPI) process production were also obtained by simulations of these processes. Following, an application for each residue (except for SPI residues) was simulated in the same software and the results were analysed. It was verified that soybean straw and hulls could fulfill the energetic demand of the crushing, refining and biodiesel production process and even a surplus of electricity could be generated, especially when biodiesel was also used as a boiler fuel. Four residues from refining process are generated: gums, soapstock, spent bleaching earth and deodorizer distillate. From gums, it is possible to produce lecithin. From soapstock and spent bleaching earth, biodiesel can be generated, although it generates more residues and consumes more steam than the production of biodiesel from degummed oil. From deodorizer distillate, it is possible to concentrate tocopherols, which is an antioxidant and can be sold for its antioxidant properties. Soybean molasses generated during the concentration of proteins from soybean meal can also be used for electrical energy production.

Keywords: soybean biorefinery; energy cogeneration; energy demand; residues exploitation

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1 INTRODUCTION

With global warming and land and river pollution, the implementation of production systems that are more sustainable has become a worldwide concern. In 1992, in the city of Rio de Janeiro, Brazil, the United Nations (UN) held the Rio-92 conference, with the presence of representatives from 172 nations, to discuss sustainable development as the main theme (United Nations, 1992). One of the causes of global warming is attributed to the use of petroleum derivatives as fuels. Furthermore, there are doubts over the remaining time that existing oil reserves will be able to meet global demand (Sánchez and Cardona, 2008; Bergeron et al., 2012; Kurian et al., 2013). In addition, few countries possess significant oil reserves, and many are dependent on imports. Especially after the petroleum crisis in the 1970s, there have been moves towards greater autonomy in terms of energy independence. This happened in Brazil, with creation of Proálcool, a program that encouraged the production of ethanol from sugarcane (Soccol et al., 2005; Kurian et al., 2013). It is true, however, that the stabilization of the oil barrel price and the problems faced by plants as lack of management and the withdrawal of subsidies led a large number of sugarcane facilities to break, thereby decreasing the strength of this Program. On the other hand, an increase on global efforts to produce renewable energy has also been seen (Andrade et al., 2009).

The biorefinery concept addresses the search for more sustainable systems. Similar in concept to traditional petroleum refineries, a biorefinery converts biomass (its feedstock) into marketable chemicals, fuels, and products. It takes advantage of the different biomass components and intermediates, maximizing the value derived from the biomass by producing high-value, low-volume products, which enhances profitability, together with low-value, high-volume fuels to meet the nation's energy needs (United States Department of Energy, 2014).

Renewable biomass comprises all the organic material that derives from plants, including algae, trees, crops, and organic wastes, which can be renewed (McKendry, 2002; Yang et al., 2013). Cereal and oilseed crops can be used as feedstocks for the establishment of whole-crop biorefinery systems. There are significant amounts of crop residues, and a variety of waste grain fractions are generated during harvesting and grain milling. These residues can be converted into high-value foods and industrial bioproducts (Bergeron et al., 2012). An example of a biomass suitable for a whole-crop biorefinery is soybean. Soybean is a crop of global proportions and importance. In the 2015/16 harvest, soybean production was 312 million of metric tons (MT), accounting for about 60 % of the total global oilseed production.

Its meal represented 71 % (219 million MT) of all meal produced worldwide and its oil 29 % (52 million MT), behind only of palm oil, with 34 % of the total share (United States Department of Agriculture (USDA), 2016).

Around 85 % of global soybean production is destined for the crushing industry, and the main products are soybean meal and soybean oil. About 98 % of the soybean meal produced is employed as animal feed, and the remaining 2 % is used to manufacture soy flours and proteins. Of the oil fraction, 95 % is consumed as edible oil, while the remainder is used for industrial products such as fatty acids, soaps, and biodiesel (Ng, 2011).

Due to the global scope and importance of soybean and its products, and the drive to develop more sustainable production systems, the possibility of creating a whole-crop biorefinery based on soybean, exploiting the possibility of finding an application for residues generated during soybean processing would be interesting.

1.1 OBJECTIVES

Bearing the exposed in mind, this work aims, as a general objective, to analyse the employment of the biorefinery concept into a soybean crushing and refining facility, exploiting applications for the residues produced during this process. For this, the following specific objectives are envisioned:

- Collect data in academic literature about traditional soybean crushing and refining installations and identify the residues generated;
- Collect data in academic literature about possible applications for the residues generated during traditional soybean seed processing;
- Simulate this traditional process with the data collected in a commercial simulator;
- Select an application found for each residue, simulate this exploitation process in the same commercial software and analyse the results obtained;
- Evaluate the soybean biorefinery both in terms of energetic fulfillment and surplus electricity generation ability.

1.2 THESIS ORGANIZATION

Apart from this introductory chapter, this thesis has five more chapters. Chapter 2 seeks to provide a brief literature review of the most important features of soybean processing and a survey in scientific literature about possible applications for the residues generated during the processing of soybean seeds into refined oil and soybean protein concentrate.

Chapters 3 and 4 present the simulation of this process attached to a biodiesel production section, where biodiesel is produced from a fraction of degummed oil that is diverted from the refining process (a step of soybean oil processing) to the biodiesel production. Based on process information, the amount of residues generated and utilities demanded are quantified. However, the difference between Chapters 3 and 4 lies on the fact that each one explores distinct options for a soybean processing facility. In Chapter 3, the process is specified such as the amount of degummed oil diverted to biodiesel is kept fixed in 50 %, half of defatted meal produced is destined to soybean protein concentrate (SPC) production and the other half to produce soybean protein isolate (SPI). With this process specifications, the residues generated and utilities required are evaluated. Chapter 4, on the other hand, does not deal with any further processing of defatted meal (into SPC or SPI), but assesses a flexible process, in which the amount of degummed oil diverted to biodiesel production can be varied. Furthermore, a cogeneration system coupled to the plant is also simulated and it is evaluated whether the energetic demand of the whole process can be entirely fulfilled by burning in the boiler residues of the process and/or produced biodiesel.

Based on the survey conducted in Chapter 2, on the research group expertise in which this work is inserted and on the strengths and limitations of the process simulator used, Chapter 5 presents an integrated process, in which each residue generated during the traditional soybean processing is used as feedstock of new process steps in order to obtain a process of commercial value. Some integration opportunities are also discussed.

Finally, Chapter 6 discusses the conclusions the work can provide, presents some final remarks, and to finalize, suggestions for future works are exposed.

2 LITERATURE REVIEW AND STATE OF ART

2.1 INTRODUCTION

To study the possibility of obtaining a biorefinery from a soybean crushing facility that seeks to find an application for each residue generated during the traditional process, it is important to have some key information:

- What are the components of soybean seeds and how do they influence the process and the products?
- What are the process steps performed in a traditional soybean crushing facility and the residues generated during these steps?
- What is the composition of each residue and is there any, and, in case there are more than one, which are the possible applications for these residues?

This chapter aims to answer these questions and assist, therefore, on structuring a soybean-based biorefinery.

2.2 SOYBEAN SEED COMPOSITION

Soybean composition can vary, but typical values of the contributions of the major components in dry and wet matter are given in Table 2.1. The wet matter values are based on the usual moisture content of stored mature beans. The major components present are proteins (40 %, on a dry matter basis), followed by carbohydrates (35 %) and lipids (20 %) (Liu, 1997).

Table 2.1 – Distribution of major components in soybeans in percentage of the seed weight

	Water (%)	Proteins (%)	Lipids (%)	Carbohydrates (%)	Ash (%)
Dry matter	-	40	20	35	5
Wet matter	13*	35	17	31	4.4

* Water content of stored mature beans (necessary to ensure storage stability).
Source: Liu (1997).

Besides the major components, soybean seeds also possess minor components. Some of these minor components were found to have good effects in animal and human health; some others, have negative effects, whether in animal and human health or in stability and storage of soybean processed products. Sections 2.2.1 to 2.2.5 provide a better, but still brief, description of soybean components.

2.2.1 Proteins

Most of the proteins present in soybeans, accounting for 60-80 % of the total, are storage proteins that have the role of providing a source of nitrogen and carbon for the developing seedling. These proteins are also known as globulins, since they are soluble in salt solution, and can be divided into glycinins and conglycinins (Liu, 1997; Taski- Ajdukovic et al., 2010; Žilić et al., 2011). Glycinin is a hexamer, where each subunit consists of an acidic and a basic polypeptide, linked by a disulfide bond. Only a small portion of glycinin is glycosylated, and it has a molecular mass of around 360 kDa. As for conglycinins, there are three types: α-conglycinin, β-conglycinin, and τ-conglycinin. β-conglycinin, which has been most widely studied, has a molecular mass of around 180 kDa, and takes the form of a trimer. All its subunits are glycoproteins and contain 4-5 % of carbohydrates.

Along with these main proteins, other soybean proteins can be classified into four groups or fractions, according to their sedimentation coefficients (Liu, 1997; Taski-Ajdukovic et al., 2010; Žilić et al., 2011):

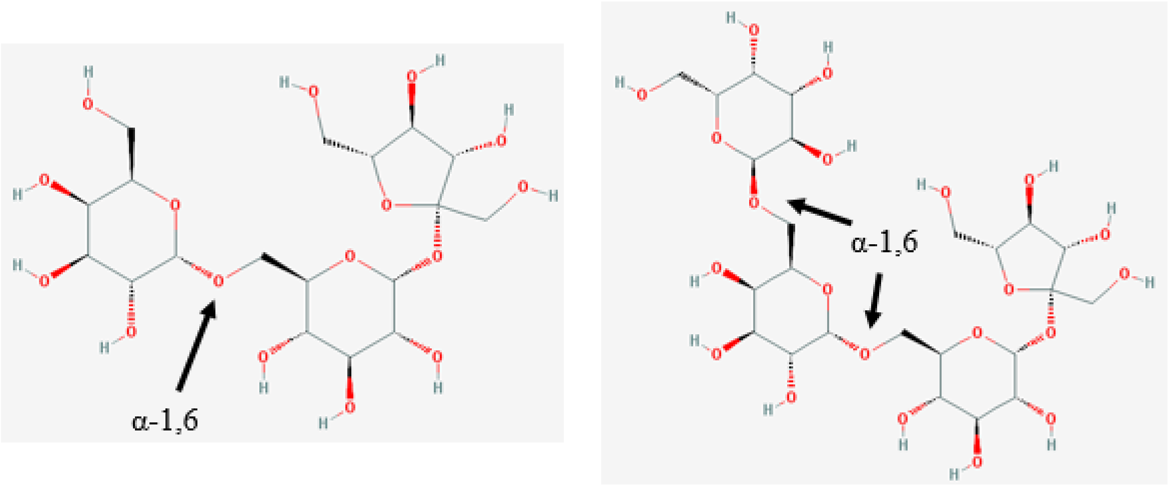
- 2S is a heterogeneous fraction and includes Kunitz and Bowman-Birk trypsin inhibitors, cytochrome C, and α-conglycinin. This fraction accounts for 20 % of the total extractable proteins.
- 7S is also a heterogeneous fraction, encompassing β- and τ-conglycinin, α-amylase, lipoxygenase, and lectin (lectin is also known as hemagglutinin). It accounts for about one third of the extractable proteins.
- 11S is a pure glycinin fraction, representing a third of the extractable proteins.
- 15S is another pure fraction, constituted by polymers of glycinin, and represents 10 % of the extractable proteins.

Kunitz and Bowman-Birk trypsin inhibitors, lipoxygenase, and lectins are known antinutritional factors, and lipoxygenase promotes the oxidation of fatty acids, compromising the quality of soybean products. This problem can be overcome by inactivation of these molecules with moist heat (Liu, 2004).

2.2.2 Carbohydrates

Dry soybeans contain about 35 % of carbohydrates, which can be divided into soluble and insoluble compounds. Among the soluble carbohydrates, raffinose and stachyose (Figure 2.1) are found in proportions of between 0.1 % and 0.9 %, and between 1.4 % and 4.1 %, respectively (on a dry matter basis). Humans and other monogastric animals are not endowed with the enzyme α-galactosidase, necessary for hydrolyzing the α-galactosidic linkage (α-1,6 type) present in these oligosaccharides. The intact sugars therefore pass directly into the lower intestine, where they are metabolized by microorganisms that contain the enzyme. The result is production of flatulence and other undesirable side effects. These carbohydrates, together with certain proteins (described above) and phytates, are the antinutritional factors present in soybeans. While proteins and phytates can be treated with heat to remove their antinutritional activity, the carbohydrates are heat resistant. An attempt to improve the quality of soy carbohydrates involves the hydrolysis of raffinose and stachyose to their monomeric units, so that they can be digested by monogastric animals.

Insoluble carbohydrates that are also found in soybeans include cellulose, hemicellulose, pectin, and trace amounts of starch (Liu, 2004).



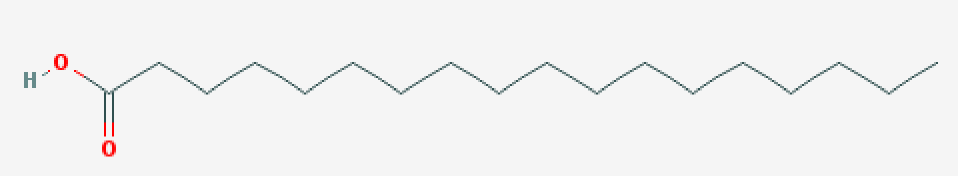
(a) Raffinose (b) Stachyose

Figure 2.1 – Carbohydrates raffinose and stachyose. Source: adapted from National Center for Biotechnology Information (2016a, 2016b)

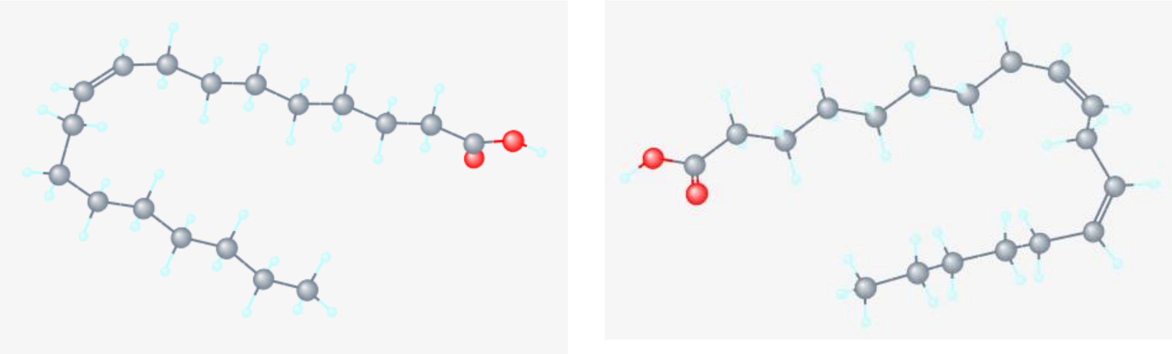
2.2.3 Lipids

Lipids usually account for around 20% (dry basis) of the seed mass, and include triacylglycerols, free fatty acids, phospholipids, tocopherols, phytosterols and squalene.

Fatty acids (a carboxylic acid with a long aliphatic chain, Figure 2.2) in its free form occurs in mature undamaged seeds less than 1%. Most of fatty acids present in soybean are linked to other molecules (Johnson et al., 2008). Fatty acids in its free form are not desired in refined oil since they can affect oil stability, but they can be used as feedstock for biodiesel production.



(a) Stearic acid



(b) Oleic acid

(c) Linoleic acid

Figure 2.2 – Some common fatty acids present in soybean. Source: (National Center for Biotechnology Information, 2016c, 2016d, 2016e)

Triacylglycerols, neutral lipids, each consisting of three fatty acids and one glycerol that links the three acids (Figure 2.3), are the major constituents of refined soybean oil, responsible for more than 99% of its composition (Liu, 1997). The triacylglycerols of soybeans mainly consist of linoleic acid, followed by oleic, palmitic, linolenic, and stearic acids.

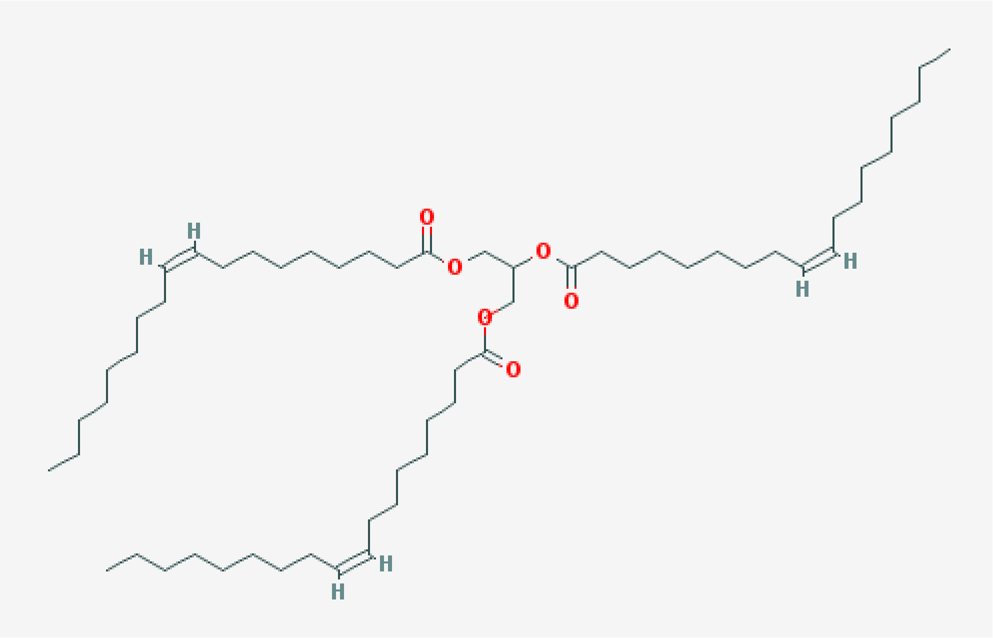
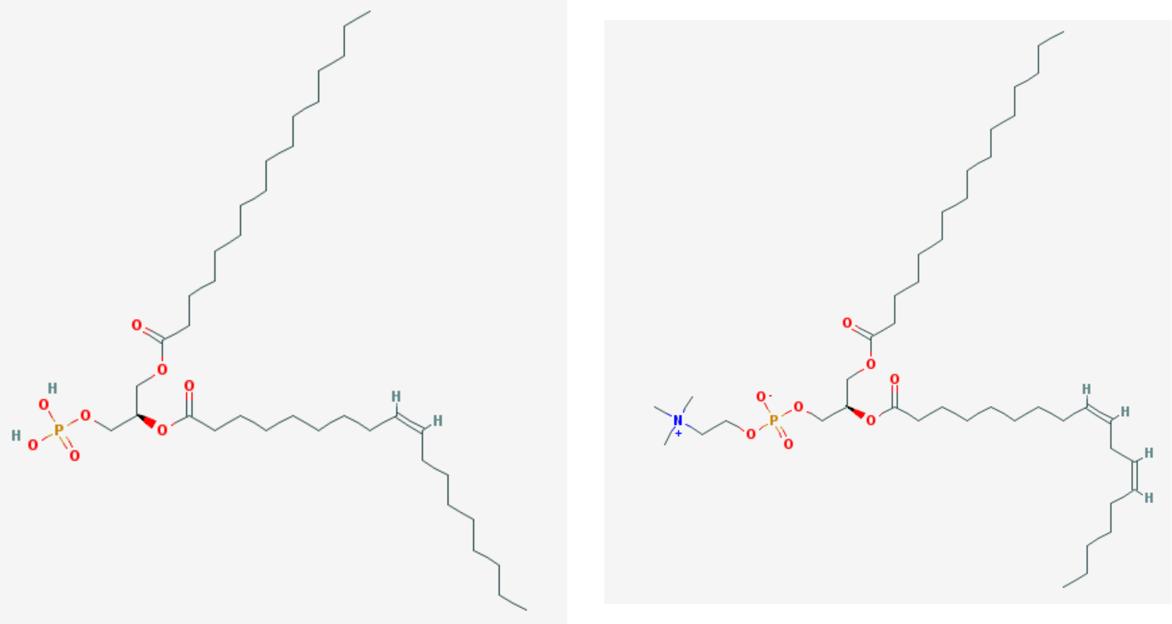


Figure 2.3 – Triolein, an example of a triacylglycerol. Source: National Center for Biotechnology Information (2016f)

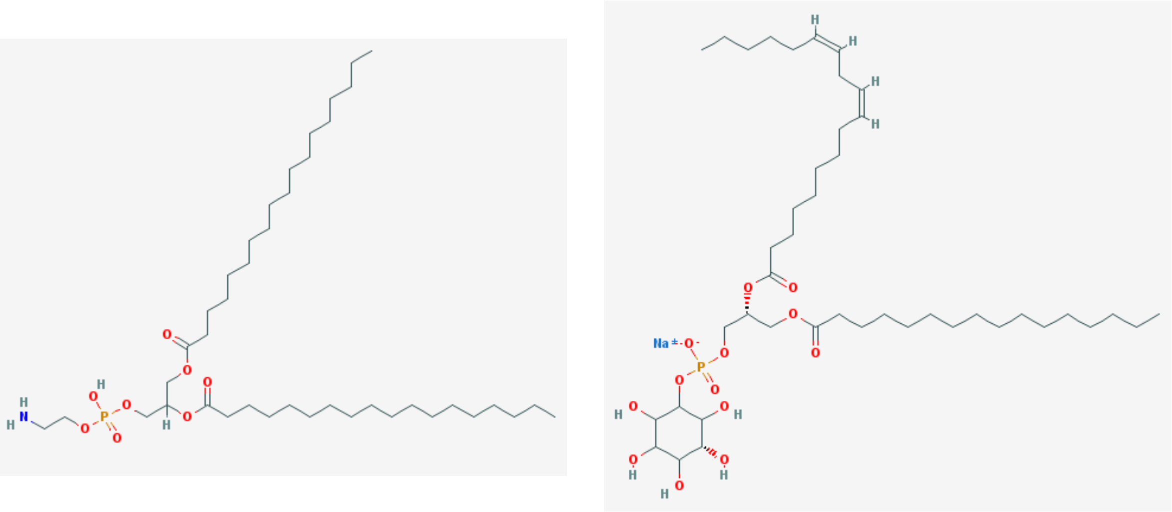
Phospholipids are polar lipids formed by a glycerol molecule linked to two fatty acids and to a phosphate linked, usually, to an organic base or a polyhydroxy compound (Akoh and Min, 2008). The phospholipids present at highest concentrations in soybeans are phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, and phosphatidic acid (Figure 2.4). Phospholipids are not desired in refined soybean oil, but they possess important emulsifying properties and, after their removal during the oil refining process, can themselves be submitted to a refining process prior to use in the food and other industries. Crude soybean oil possess 1.5-2.5 % of phospholipids in its composition, while refined oil retain 0.003-0.045 % (Gunstone, 2011).

Sphingolipids (Figure 2.5), as phospholipids, are polar cell membrane lipids, and are also found in soybeans, but they are typically present in much lower concentration than phospholipids (Johnson et al., 2008). Soybean seed has an average of 11 mg of sphingolipids per gram of the seed dry weight (Wang et al., 2006).



(a) Phosphatidic acid

(b) Phosphatidylcholine



(c) Phosphatidylethanolamine

(d) Phosphatidylinositol

Figure 2.4 – Examples of (a) Phosphatidic acid, (b) Phosphatidylcholine, (c) Phosphatidylethanolamine and (d) Phosphatidylinositol (in its sodium salt form). Source: National Center for Biotechnology Information (2016g, 2016h, 2016i, 2016j)

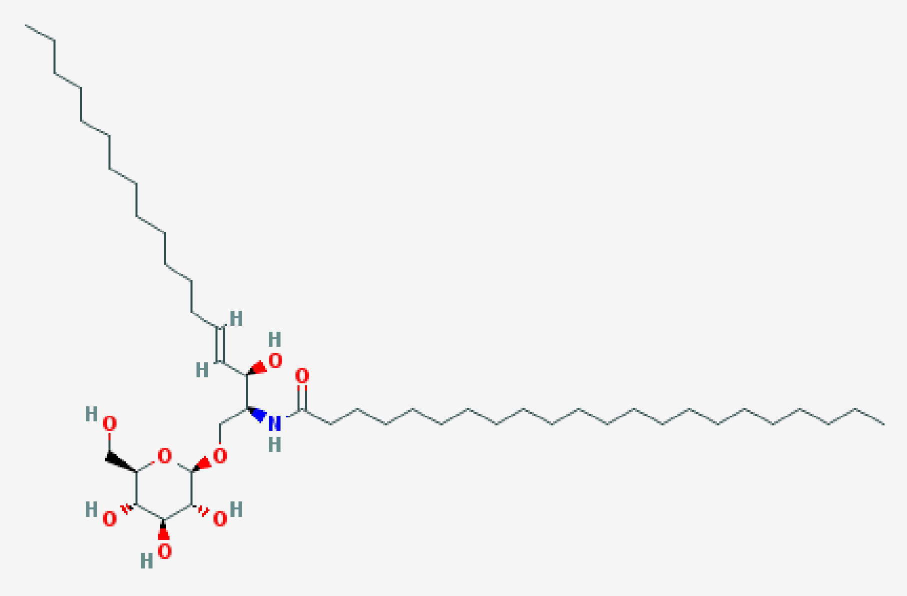
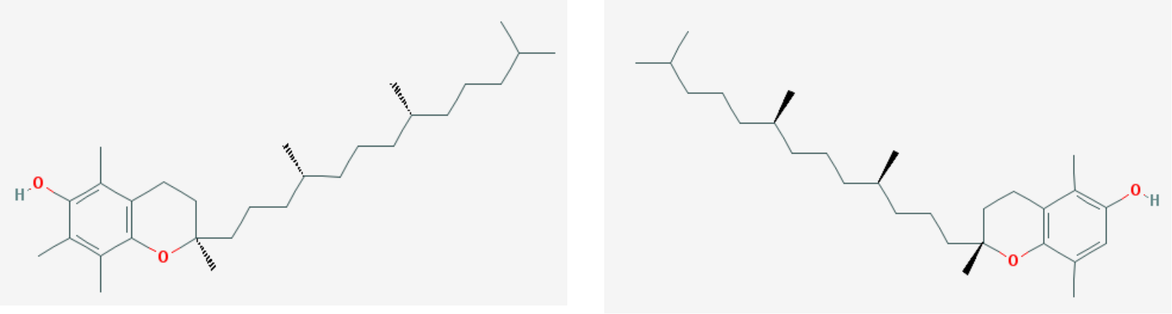


Figure 2.5 – Representation of a glucosylceramide, a sphingolipid. Source National Center for Biotechnology Information (2016k)

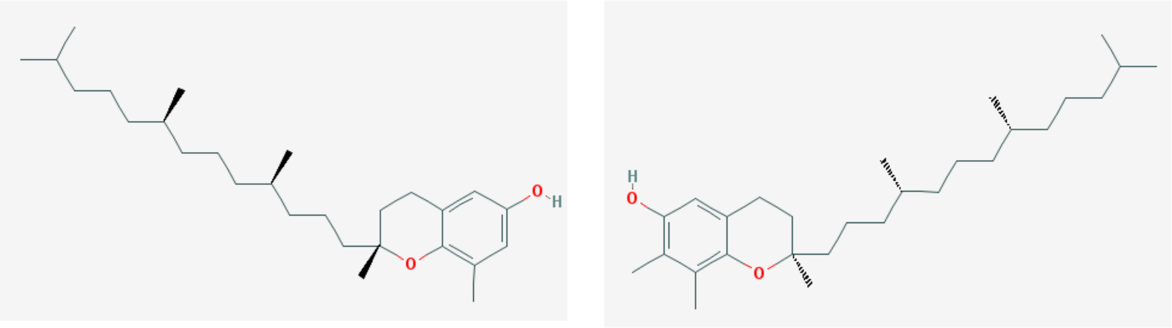
Tocopherols (Figure 2.6) are also found in the refined oil. Their presence in soybean oil is highly desirable, but losses occur during refining, especially at the deodorizer distillation stage. Attempts are made to recover this lost fraction so that it can be returned to the oil, or be sold in a purified form. γ-tocopherol is the most abundant tocopherol present in soybean seed with an average content of 49 ppm of the seed dry weight. In crude soybean oil its content is of ca. 419 ppm. Total tocopherols are present in an average of 241 ppm of seed dry weight and 1577 ppm of the crude oil (Medic et al., 2014). Deodorized oil can present values of about 726 ppm (Johnson et al., 2008). These values represent averages and great variations may occur.

Phytosterols (Figure 2.7a) are sterols in plants, and they are structurally similar to sterols from animal sources. The main phytosterols present in soybean seed are β-sitosterols, followed by campesterol, stigmasterol, Δ5-avenasterol, Δ5-stigmasterol and Δ7-avenasterol. Total phytosterols are present in crude soybean oil in an average of 3780 ppm and in refined oil ca. 2620 ppm (Johnson et al., 2008). Squalene (Figure 2.7b) is a natural lipid belonging to the terpenoid family and is present in crude oil in concentrations around 143 ppm and in refined oil of about 89 ppm (Johnson et al., 2008; Reddy and Couvreur, 2009).

Soybean mature seeds also contains pigments such as chlorophyll (1-2 ppm) and carotenoids (40-50 ppm) (Shahidi, 2005; Johnson et al., 2008).

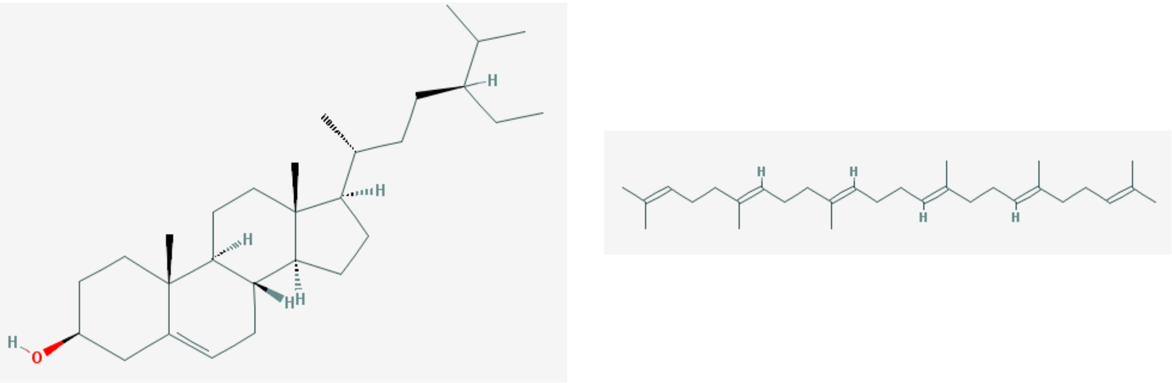


(a) α-tocopherol (b) β-tocopherol



(c) δ-tocopherol (d) γ-tocopherol

Figure 2.6 – Tocopherols. Source: National Center for Biotechnology Information (2016l, 2016m, 2016n, 2016o)



(a) β-sitosterol (b) Squalene

Figure 2.7 – β-sitosterol, one type of the phytosterols present in soybean, and squalene structures. Source: National Center for Biotechnology Information (2016p, 2016q)

2.2.4 Ash

Like other components, minerals content in soybeans are influenced by variety, growing location, and seasons. Major mineral components in soybeans are potassium, phosphorus, magnesium, sulfur, calcium, chloride, and sodium. The minor minerals present in soybeans and soy products include silicon, iron, zinc, manganese, copper, molybdenum, fluorine, chromium, selenium, cobalt, cadmium, lead, arsenic, mercury, and iodine. Sulfates, phosphates, and carbonates are the dominant forms of minerals found in soybean ashes.

During processing, most of minerals present in soybean seed follow the meal portion (composed mostly of protein and carbohydrates), but some portion of calcium, magnesium, and phosphorus can be extracted with the phospholipids and become part of the crude oil. Other minerals, such as copper and iron are not desired to be in the oil fraction because they are strong peroxidants and may negatively influence the quality of soybean oil (Liu, 1997).

2.2.5 Minor components

2.2.5.1 Isoflavones

Isoflavones are flavonoids that are only found in a few plant families. Soybeans contain the highest amount of isoflavones found in seeds, with concentrations ranging from 0.1 to 0.4% (dry weight basis). The structures of these compounds are similar to those of certain human hormones, and they are widely used to alleviate menopause symptoms. Studies also suggest that they have anti-carcinogenic properties (Johnson et al., 2008).

2.2.5.2 Saponins

Soy contains around 0.1-0.3% of saponins. These are alkaloid, steroid, or triterpene compounds linked to sugars, and have surfactant properties. Many studies have shown that saponins are able to decrease blood cholesterol levels and can reduce risks of cancer and heart disease. The binding of bile acids by saponins removes cholesterol metabolites from the colon and hence reduces the risk of colon cancer. In addition, saponins inhibit the proliferation of cancer cells by binding to them (Johnson et al., 2008).

2.2.5.3 Vitamins

Water and oil-soluble vitamins can be found in soybeans. Oil-soluble vitamins were already present in this text in Section 2.2.3. There are α-tocopherol (vitamin E) and carotenoids (pro-vitamin A). The water-soluble vitamin portion is composed of thiamine, riboflavin, niacin, pantothenic acid, and folic acid (Johnson et al., 2008).

2.2.5.4 Phytic acid

Phytic acid can be found in the form of its salts in soybean seeds. They are calcium, magnesium or potassium salt of phytic acid. More than half of the total phosphorus in soybeans is in the form of phytic acid. Because of its chelating power, phytic acid makes many essential minerals in soybeans or in diets unavailable for absorption and utilization for both human and domestic animals; thus phytic acid is known as an anti-nutritional factor (Liu, 1997; Johnson et al., 2008). However, recent reports suggest that phytate may have a positive effect on animal and human health, acting as an anticarcinogen and an antioxidant by complexing iron and decreasing free radical generation and peroxidation of membranes (Medic et al., 2014).

In a soybean crushing facility, the main goal is to separate the lipid (oil) fraction from the proteins and other components and make both fractions suitable for marketing. Section 2.3 explains with more details the steps involved in this process.

2.3 SOYBEAN OIL AND MEAL PRODUCTION

Once soybean seeds have arrived in the crushing facility, its oil content is extracted from the seed. Next, the oil and the solid fraction remaining go through further operations to reach legal and market requirements for their commercialization. Either, oil and meal fraction (how solid fraction is named) have first, the organic solvent removed (when it is used a solvent as an oil extraction method). Following, oil fraction can proceed to the refining step and meal can be dried and grinded or the protein content in the meal can be concentrated in terms of proteins. Figure 2.8 illustrates the most important steps of a soybean crushing and refining facility, as well as the main products and the residues generated. Sections 2.3.1 to 2.3.3 discuss these steps with more details and Section 2.4 deals with the generated residues and their applications possibilities. At this point, it is worth mentioning that no conceptual distinction was made in this text among co-product, by-product or residue, and every output stream that is not one of the main products (oil and meal) was here denominated residue.

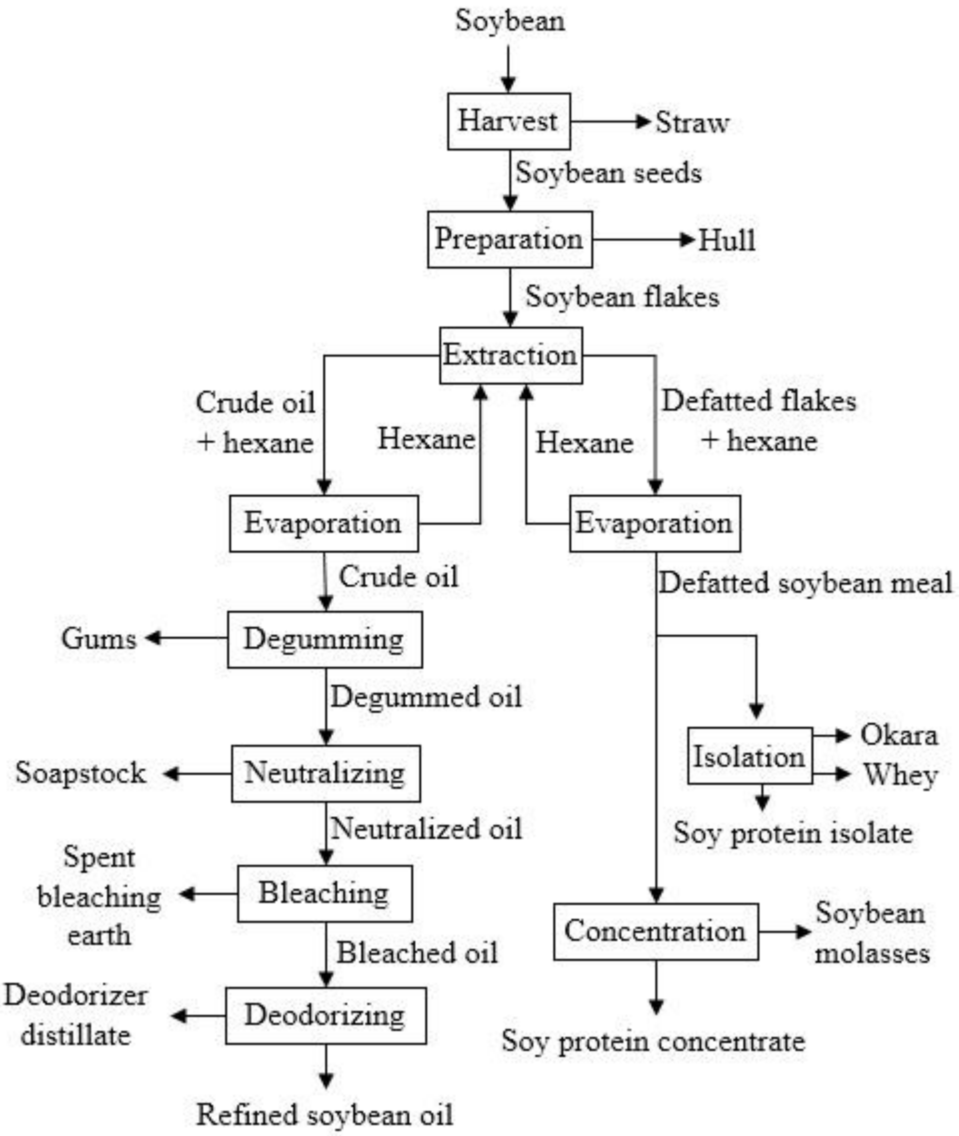


Figure 2.8 – Overview of the typical steps and the residues generated for the production of soybean oil and meal

2.3.1 Soybean oil extraction

The most common method used for extraction of oil from soybean is direct solvent extraction, which currently employs hexane as the solvent. This process essentially consists of three steps: preparation of the seed, extraction of the oil, and desolventizing of the oil and meal (Ng, 2011).

2.3.1.1 Seed preparation

The preparation of the seed aims to maximize the efficiency of the oil extraction process, and involves cleaning, drying and tempering, cracking, dehulling, conditioning, and flaking operations (Singh, 2010). A variation of this conventional system is the introduction of an expander or other method of size reduction (such as grinding) after flaking, in order to increase the yield of oil (Ng, 2011).

The first preparation step is cleaning and it aims to remove foreign materials from the soybeans in order to protect the processing equipment and enable the production of high quality soybean products (Liu, 1997). Soybean graded as US n^o 1 may have a maximum content of foreign material of 1 % and US n^o 2 up to 2 % (Erickson, 1995).

The cleaning apparatus consists of two-deck screen sizer. The top screen allows the soybeans and smaller material to fall through while larger objects are retained and removed, while the second screen retains the soybeans but allows smaller objects to pass through. Next, soybeans are sent through a multiaspirator to remove dust and adhering particles from the bean surface (Liu, 1997).

In order to have the hulls removed more efficiently, moisture content of the beans must be reduced to 10 %. For that, seeds are dried with heated air, usually, by a conventional gas or oil fired drier (Erickson, 1995). The moisture is typically allowed to equilibrate throughout the seed for 1-5 days but for up to 20 days at some plants. This stage is called Tempering.

Once moisture is equilibrated, seeds are sent to be cracked into 4 to 6 pieces in the cracking mills equipment. The mills often consist of two sets of cylindrical corrugated rolls in series that operate with different speeds. The first set of rolls often has a coarser corrugation, and the second set, a finer corrugation to reduce the particle size in two steps (Liu, 1997; Shahidi, 2005).

Once soybeans were dried to 10 % moisture, dehulling after cracking is not difficult, since this practice shrinks the meat away from the hull. Shaker screens, aspirators, and/or gravity tables may be used to separate the hulls from the meats. Hulls should be larger in size, lower in density, and thus are more buoyant in an air stream than the meat and are easily removed by cascade aspirators (Johnson et al., 2008).

Cracked and dehulled soybeans are conditioned by heat and moisture to obtain the optimum plasticity necessary for soybean flake production, prior to oil extraction. The temperature of soybean grits are raised to 65-70 °C and the moisture content to 11 % with steam injection. This operation takes place in pieces of equipment called cookers. There are two types of cookers commonly used – vertical stack cookers and rotary horizontal cookers, the latter being used in larger installations (Erickson, 1995; Liu, 1997; Hamm et al., 2013).

Flaking step distorts the cellular structure of the material and reduces the distance that solvent needs to penetrate to reach the oil in the oleaginous material cells. The flaking mill has two large diameter rolls in parallel, turning in opposing direction at approximately 250 to 300 rpm, and forced together by hydraulic cylinders. The conditioned soybean grits are uniformly fed into the nip of the two rolls, and then, are stretched and flattened reaching typical flakes sizes in the range of 0.3 to 0.4 mm thick and 8 to 18 mm in diameter (Shahidi, 2005). After flacking, soybean seeds are prepared to go to the oil extraction step.

2.3.1.2 Soybean oil extraction

Solvent extraction of soybeans is a diffusion process that can be achieved by immersing the solid in solvent or by percolating solvent through a bed of solids. The most common solvent used is hexane. The liquid fraction obtained, an oil/solvent mixture, is called miscella and the solid fraction, defatted flakes. Example of extractor used in soybean crushing facilities are rotary, horizontal belt, and continuous-loop extractors (Erickson, 1995). In the rotary extractor, a continuous and countercurrent extraction takes place. It consists of a stationary cylinder and a set of compartments that turn around a vertical axis. In the first compartment, the flakes are fed and in the last one, pure solvent. After the solvent percolates the flakes layer, the miscella is collected and pumped to the previous compartment as the extractor rotates (Paraíso, 2001).

Both fractions, miscella and defatted flakes, undergo subsequent steps for solvent removal.

2.3.1.3 Defatted flakes desolventizing

Defatted flakes that leave the extractor contain about 30 % hexane by weight, which is removed by means of a desolventizer-toaster. This process also enhances the nutritional value of the soy protein by inactivating trypsin inhibitors and other naturally occurring toxicants. The flakes are exposed to steam, and the heat of vaporization released from the condensing steam vaporizes the hexane, which is subsequently recovered by condensation (Liu, 1997).

2.3.1.4 Miscella desolventizing

Miscella leaves the extractor containing ~70-78 % (m/m) of hexane and is sent to evaporation and stripping columns to separate the oil from hexane. First, the hexane is evaporated in two stages of evaporators. The first-stage evaporator concentrates the oil to 65-80 % using reclaimed heat from vapors produced in desolventizing meal operation. The second-stage evaporator concentrates the oil to 93-97 % with steam. The concentrated oil is sent to the stripping column in which heat, vacuum, and sparging steam are used to remove the remaining hexane. The hexane is recycled to the extractor to be used again. After the stripping column, crude oil may go to an oil dryer to remove any condensed moisture (O’Brien et al., 2000). The liquid and solid fractions go through further operations in order to achieve the characteristics of the desired final products. The oil obtained after removal of the hexane, known as crude oil, usually passes through a refining step before being marketed (mainly as edible oil) (Section 2.3.2). The solid fraction, after evaporation of hexane, is usually dried and cooled, then ground and graded prior to being marketed as meal for feeding of livestock. Soybean protein concentrate and soy protein isolate can be obtained from the defatted meal (Section 2.3.3).

2.3.2 Chemical refining of soybean oil

Crude soy oil contains many undesirable impurities including free fatty acids (FFAs), phospholipids, volatile/odoriferous compounds, and dark pigments. The refining process aims to remove the unwanted constituents from the oil with the least possible negative effect on triacylglycerols and minimal loss of the desirable constituents. Refining encompasses the operations of degumming, neutralization, bleaching, and deodorization.

2.3.2.1 Degumming

Degumming is a process for the removal of gums (also called phosphatides or phospholipids) from crude soybean oil to improve its physical stability and facilitate further processing (Johnson et al., 2008).

Unless removed, phosphatides can spontaneously hydrate from moisture in the air during storage or in the headspace, making them insoluble in the oil, precipitating, and yielding an unattractive oil with unsightly sludge or gums. They are also prone to degradation, darkening the oil when it is heated as in deodorization step. It is known that consumers prefer lighter refined oils. Furthermore, phosphatides exhibit surfactants properties and, if present in frying oils, can cause dangerous foaming. When hot oil foams up and spills over the rim of a cooking vessel, it may burn the user; if it contacts a flame, it will catch fire (Akoh and Min, 2008).

Degumming may be conducted either as a separate operation or simultaneously with neutralization. However, in case of oils rich in phosphatides, such as soybean and canola oils, it is recommended that degumming takes place as a separate operation (Akoh and Min, 2008).

Direct addition of water to the oil is the most commonly used method of degumming, where the hydrated phosphatides become denser than the triacylglycerols and precipitate, or settle out of the oil (Liu, 1997; Johnson et al., 2008). This step also removes proteinaceous and mucilaginous materials (Johnson et al., 2008). First, water is added to the warm oil arisen from desolventizing step. Usually 1-3 % wt. of water / crude oil is used (~75% of the oil lecithin content). After oil and water achieved sufficient contact time to water attract the (polar) phospholipids, which are, then, partitioned into the water phase, the mixture is sent to centrifugation. If neutralization step is executed in the same facility, degummed oil can follow right to this next step. If the oil is going to be sold as degummed oil, it needs to be dried first to remove the residual water content (Liu, 1997; Shahidi, 2005; Johnson et al., 2008; Akoh and Min, 2008). Usually, about 90% of the phosphatides are removed in this process (Akoh e Min, 2008).

If crude oil is produced from seeds with low quality, a higher amount of nonhydratable phosphatides exists in the oil and this type of gums are unaffected by water degumming and remain in the oil phase. Normal quality soybean oil from the conventional solvent extraction contains about 90% hydratable and 10% nonhydratable phospholipids (Shahidi, 2005). The nonhydratable phosphatides are generally identified as the calcium and magnesium salts of phosphatidic acids that are produced by enzymatic action of phospholipases released by damage to the soybean cellular structure, which occurs with bad handling and/or extraction practices (Johnson et al., 2008). Phosphatidylcholines and phosphatidylinositol are always hydratable while phosphatidylethanolamine and phosphatidic acid are the ones who can complex with divalent metal ions, rendering them nonhydratable (Akoh and Min, 2008).

During soybean seed preparation, some facilities use expanders after flaking. This additional operation almost doubles the usual phosphatide content of soybean oil (Akoh e Min, 2008; Shahidi, 2005). Only about half of the phosphatide content of soybeans is extracted with hexane when preparing soybeans by flaking alone (Akoh e Min, 2008).

After processed, phospholipids or lecithin, its commercial name, can be used in a vast range of foods, feed, pharmaceutical and technical applications, due to its surface-active properties, oftentimes making their recovery economical (van Nieuwenhuyzen and Tomás, 2008). Nevertheless, according to Akoh and Min (2008), the available U.S. supply of soy lecithin is about twice the volume that can be economically sold.

There are other degumming methods, such as acid degumming and enzymatic degumming. For soybean, it is more common water degumming. If acid degumming is used, gums cannot be further exploited as an additional product anymore.

2.3.2.2 Neutralization

Neutralization is also referred to as de-acidification, alkali, or caustic refining. Neutralization removes or reduces free fatty acids by saponification of FFAs using a base (usually NaOH). Saponification refers to the chemical reaction between FFAs or glycerides and sodium hydroxide to form soaps. In this process, non-hydratable gums, trace metals, and saponifiable matter are also reduced or removed. FFAs must be removed as they reduce the smoke point of the oil and increase foaming (Liu, 1997; Akoh and Min, 2008). There are other refining methods, such as physical refining, but in soybean facilities, alkali refining is the most utilized.

Vegetable oil refining plants can operate with one, two or three separation stages, but most plants operate with two separation stages. Three-stage processes are used for some special oils like cottonseed oil and when a single-stage neutralization is used, the residual soaps are removed by filtration using a filter aid. Figure 2.9 presents a three-stage process. If a two-stage process is to be used (the case for soybean oil processing), the second processing stage can be omitted.

Fist, phosphoric acid can be added for conditioning the nonhydratable phosphatides. Next, for neutralization, caustic soda is added directly ahead of the second mixer in excess with respect to the amount required for neutralizing the free fatty acid content and the phosphoric acid added previously. After intensive mixing of oil and caustic soda in a dynamic mixer, the mixture is either conveyed directly to the first disc separator, which separates out the soapstock, or pumped through the hydration tank with agitation. The latter is recommended in case of crude oils with phosphatides content higher than 100 ppm of phosphorous content to improve the hydration and to agglomerate the soap particles. Soybean oil is sent directly to third-stage, where water is added to remove the remaining soaps and other impurities. Finally, the neutralized oil is dried to remove residual water (Zeldenrust, 2012).

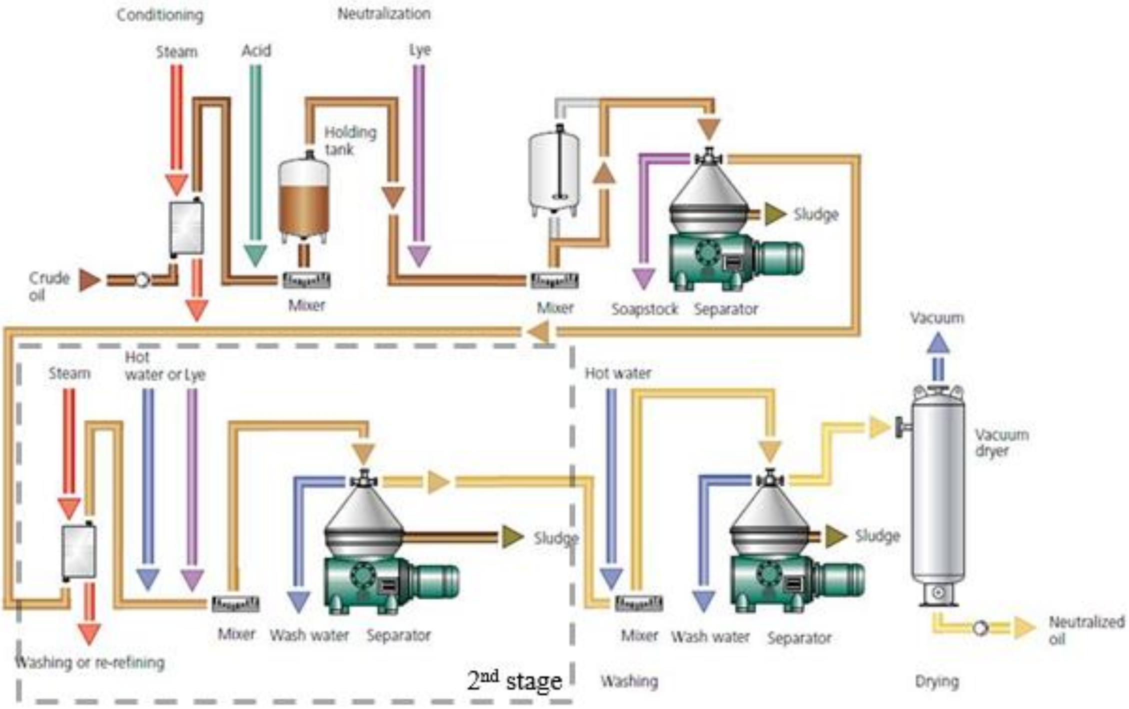


Figure 2.9 – Neutralization stage of vegetable oils refining. Source: adapted from Zeldenrust (2012)

2.3.2.3 Bleaching

Bleaching eliminates or lightens the color of the oil by the adsorption of colored pigments into the micropores of an activated earth, under vacuum and at a suitable temperature. In addition, it also breaks down peroxides (primary oxidation products) into lower molecular weight carbonyl compounds that can be subsequently removed by deodorization. After the appropriate oil and bleaching earth time contact, the mixture is filtrated and bleached oil is sent to deodorizing stage (Liu, 1997; Shahidi, 2005).

Impurities in soybean oil may have various sources. They can be minor ingredients naturally contained in the oil or degradation products induced by bad seed handling or even during processing itself. Impurities include: traces of meal, phosphatides, unsaponifiable matter, trace metals, sulfur, halogens, color bodies (e.g., lutein and chlorophyll), alcohols, esters, ethers, soaps, free fatty acids, peroxides, ketones, aldehydes, trans fatty acids, polycyclic aromatic hydrocarbons (PAH), solvents, pesticides, thermal degradation products, diglycerides, polymers, acids (phosphoric) and water, i.e., fairly everything that is not triacylglycerols (O’Brien et al., 2000).

The major color pigments in edible oils are chlorophyll (green) and carotenoids (orange) and while chlorophyll must be reduced in the bleaching process, carotenoids can be reduced during deodorization. Lutein is the major carotenoid in common soybeans with a yellow seed coat, whereas soybeans with a green seed coat contain xanthophylls in addition to lutein (Shahidi, 2005; Johnson et al., 2008).

The bleaching earth is usually made from naturally occurring minerals belonging to the aluminum silicate family, such as bentonite. Some natural clays already possess the “bleaching activity”, while others become active after a specific treatment. For most of bentonites, the necessary surface area and porosity have to be created. This is usually accomplished by an activation step for montmorillonite, the main component of bentonite, by means of a treatment with acids (O’Brien et al., 2000; Shahidi, 2005). Attempts to develop materials from soybean residues with bleaching capacity to partially or totally substitute bleaching earth have been executed, as shown in Sections 2.4.1 and 2.4.2.

Additionally to adsorption capacity, bleaching earths also present catalytic properties. The most important reaction is the decomposition of hydroperoxides. A number of secondary oxidation products such as aldehydes and ketones may form when the hydroperoxides decompose. Those secondary products are later removed in the deodorization step. Additionally, conjugated fatty acids may develop, which are much more sensitive to oxygen than non-conjugated ones. Therefore, it is very important that contact with air be avoided during bleaching (O’Brien et al., 2000; Shahidi, 2005).

Therefore, as during bleaching not only the adsorptive property of bleaching earth is important, but also the chemical reactions that take place within it, bleaching temperature plays a key role in this operation. Since the speed of both desired and undesired reactions increases with temperature, the optimum temperature depends on the type of oil, the impurities present and the time. Shorter times are recommended when higher bleaching temperatures are used. State-of-the-art for bleaching time and temperature for most oils is in the range of 20-30 min at a temperature of 90-100 ºC (O’Brien et al., 2000).

As for the pressure parameter, because of the recognized detrimental effect of oxygen on the quality and on the oxidative stability of oils, bleaching moved from being performed at atmospheric conditions to vacuum, which should be below 50 mmHg. Most references recommend vacuum levels in the range 20-28 mmHg or even lower (O'Brien et al., 2000; Shahidi, 2005).

After, under vacuum conditions, the oil is agitated in the compartmentalized bleacher for the specified time, it is then delivered to one of two bleaching filters for removal of solid materials. Plate and frame filters or pressure leaf filters can be used. During the filtration cycle, as a filter becomes full, by the indication of an increasing pressure differential between the feed and discharge streams, the filter is taken off-line for cleaning while the alternate filter is brought on-line (Shahidi, 2005).

2.3.2.4 Deodorization

Deodorization is the last step in the refining process. It is a vacuum-stripping process in which neutral oil is treated to remove malodorous and other compounds to obtain fully refined oil. Soybean oil contain not only flavor bodies that must be eliminated to produce a palatable product, but also, during processing, other unit operations can impart a negative flavor and color to the oil that must be removed in the deodorizer. Shelf life and color are also important considerations upon which the deodorizer has a direct impact (O'Brien et al., 2000; Shahidi, 2005; Johnson et al., 2008).

Deodorization is based on the fact that there is a substantial difference between the vapor pressure of the oil and the volatile materials affecting the flavor, color, and the stability of it. After leaving the bleaching plant, bleached oil at about 60 - 90 ºC is sent to be heated. Next, the oil is exposed to surface conditions where volatiles components change to vapor state. Deodorizing conditions normally involve exposing a thin film of oil to a carrier gas at an elevated temperature and low pressure, usually 200-250 °C and 300-400 Pa vacuum. A stripping gas, usually steam, at rate of 0.6-1.2 wt. % of the oil, is introduced to agitate the oil, ensuring oil to be subjected to surface conditions, carrying out the volatiles from the deodorizer to the vapor recovery system. The oil is then cooled (Shahidi, 2005; Johnson et al., 2008; Singh, 2010).

All deodorizers basic principles are essentially the same, but there are several types of systems used to perform deodorization step. These systems can operate at batch, semicontinuous or continuous mode. Some continuous systems are briefly described below (Shahidi, 2005):

- Single-shell vertical unit with several deodorizing compartments fitted with gas-lift pumps (also called mammoth pumps) or sparge rings. As the oil passes through a series of baffles installed in the trays, it overflows through an overflow pipe or weir to the next lower tray.
- Multisectioned tray contained in a horizontal cylindrical vessel, where heat transfer baffles are used as flow baffles, with agitating steam injected between the baffles.
- Vertically stacked horizontal single-shell cylindrical vessel, with agitation steam injected by multiple pipe distributors running the length of the vessel.
- Structured packed column.

Deodorized oils require particular handling and storage conditions to avoid oxidation or other degradation reactions that may affect the quality, such as flavor deterioration and color reversion. If the oil is to be stored in bulk for a long time, saturation of the oil with nitrogen, low-temperature storage and the use of stainless steel tanks, protect the oil against oxidation. Although, nowadays, facilities try to minimize end-products storage, shipping refined oil in bulk or bottled as soon as possible. The addition of a small amount of citric acid (20-50 ppm) to the oil after deodorization is also practiced, because it not only improves the flavor stability but at the same time, acts as a metal chelator. Natural antioxidants can also be added to the refined oil. One example of antioxidant added is tocopherol, nevertheless, as well stated in Shahidi (2005), it seems more logical to prevent the oil from losing too many natural antioxidants during deodorization by using less severe conditions than to add them back later. When refined oil is shipped to industrial consumers, it can be re-deodorized, with less severe process conditions, prior to its final use, to remove small amounts of off-flavors formed during transport and storage (Shahidi, 2005).

2.3.3 Soy protein concentrate and soy protein isolate

By further processing soybean meal, the solid fraction obtained after oil is extracted, the protein content in the meal can become even more concentrated and, when a concentration of 65-72 % dmb is achieved, it can be sold as soy protein concentrate (SPC). Using a different process, the meal can achieve 90-92 % dmb, and be sold as soy protein isolate (SPI).

2.3.3.1 Soy protein concentrate

The protein content of meal can be concentrated to increase its nutritional and market value, and the product is sold as soy protein concentrate (SPC) (Figure 2.10). It is prepared by the removal of soluble carbohydrates from defatted meal by means of three possible processes: (1) acid leaching, using the isoelectric pH of soy proteins, which is 4.5; (2) aqueous ethanol (60-80%) extraction; (3) moist heat water leaching.

Figure 2.10 – A sample of soy protein concentrate

Most commercial soy concentrates are produced by aqueous-alcohol extraction. Soybean molasses or soy solubles (Figure 2.11) is a residue of SPC production by aqueous-alcohol extraction (Liu, 1997).

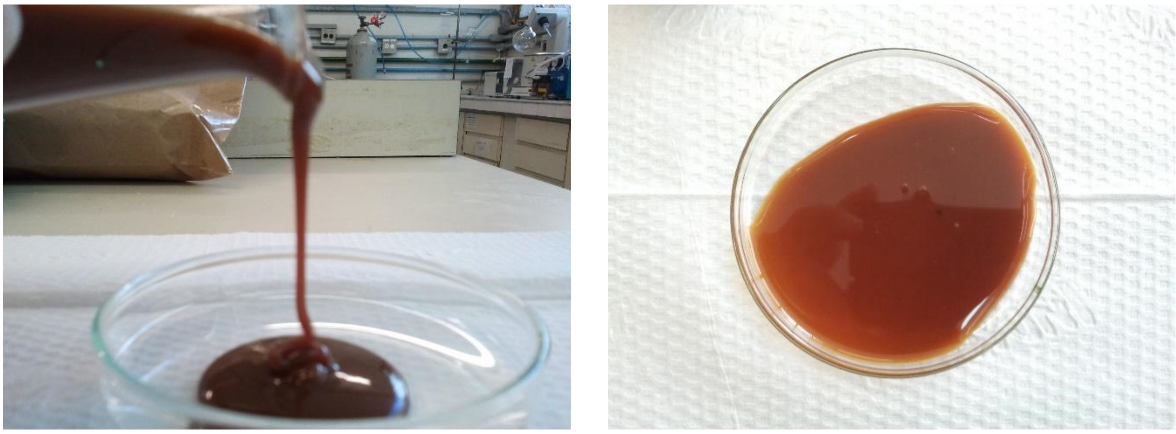


Figure 2.11 – A sample of soybean molasses with a concentration of 75 ºBrix

2.3.3.2 Soy protein isolate

Soy protein isolate (SPI) is traditionally prepared from defatted soybean meal using aqueous or mild alkali extraction (pH 7-10) of proteins and soluble carbohydrates. The insoluble residue, consisting mainly of carbohydrate (soy cotyledon fiber), is removed by centrifugation, followed by precipitation of soy protein at its isoelectric point. The precipitated protein is separated by mechanical decanting, washed, and may be neutralized to a pH about 6.8, and then spray-dried (Liu, 1997; Johnson et al., 2008).

The residues generated during soybean processing have components that may be of commercial value or can be used to provide energy for the biorefinery itself. Based on a survey in academic literature, Section 2.4 describes the composition and possible applications of these residues (illustrated in Figure 2.8).

2.4 SOYBEAN RESIDUES AND ITS APPLICATIONS POSSIBILITIES

This section presents an overview of some applications found in scientific literature for soybean residues.

2.4.1 Soybean straw

About 220 million tons of soybeans and an equivalent amount of straw are produced globally every year (Reddy and Yang, 2009). Soybean straw is composed of stem, leaf, and pod husk (Sruamsiri and Silman, 2008), and its overall composition can vary. Table 2.2 summarizes composition data reported in the literature.

Table 2.2 – Soybean straw composition as reported in the literature

Components	Reddy and Yang (2009)	Xu et al. (2007)	Wan et al. (2011)
Cellulose	44-83%	24.99%	34.09%
Hemicellulose	Remainder, to make up to 100%	11.91%	16.05%, where Xylan: 11.43% Galactan: 1.83% Arabinan: 1.00% Mannan: 1.79%
Lignin	5-14%	17.64%	21.6%
Ash	2-5%	NP	5.16%
Extractives	NP[1]	NP	11.01%
Other[2]	NP	NP	12.09%

[1] NP = values not provided.
[2] Other unidentified compounds (e.g. protein, pectin, acetyl groups, glucuronic acid substitutes).

This material is currently used as feed for livestock, burned, or left in the field to prevent soil erosion (Boateng et al., 2010; Maheri-Sis et al., 2011). Although straw needs to be left on the ground to maintain soil fertility, it has been reported that 30-50% of crop residues can be removed from fields without causing soil erosion or affecting the growth and yield of succeeding crops (Reddy and Yang, 2009).

Several studies have investigated other applications for soybean straw. Possible uses of soy straw include using it as feedstock for the production of polymers, fibers and composite reinforcement, energy and biofuels, and adsorbents. It can also have its cellulose content hydrolyzed to be used as a substrate for fermentation processes.

2.4.1.1 Fibers

Reddy and Yang (2009) developed a technique to produce cellulose fiber from soybean straw. According to the authors, the soy straw fiber showed properties similar to those of other natural cellulose fibers in current use, and could be employed in textiles, composites, and other industrial applications. It has the advantage of not depending on petroleum-based resources (50% of the fibers consumed annually are derived from petroleum), and uses a residue of a crop whose cultivated area is growing. The cultivation of natural fiber crops such as cotton is decreasing, because farmers are shifting to crops such as corn and soybeans, which are easier to grow and provide a better economic return than fiber crops. Furthermore, the price of synthetic fibers, such as polyester, has more than doubled in the last decade (Huda et al., 2007).

Briefly, the process for producing these fibers is to boil soy straw in dilute sodium hydroxide solution for 2 hours, then wash the material with water and neutralize it with dilute acetic acid, and finally dry it under ambient conditions.

Wang and Sain (2007) studied the use of nanofibers made from soybean pods for composite reinforcement. The nanofibers were tested with three different polymers: polyvinyl alcohol (PVA), polypropylene (PP), and polyethylene (PE). The results revealed that the nanofibers enhanced some of the properties of PVA.

2.4.1.2 Polyurethane

Polyurethane (PU) is a polymer used in a wide range of applications, including the production of flexible and rigid foams, coatings, sealants, elastomers, and adhesives. The main feedstocks for production of PU are petroleum-derived, such as polyols. For more sustainable production, research efforts have been concentrated on developing bio-based polyols and polyurethane products from renewable sources. The principal drawback of these techniques is the use of considerable volumes of petroleum-derived solvents to react with biomass to produce polyols (Lee et al., 2000; Hassan and Shukry, 2008; Petrovic, 2008; Chen and Lu, 2009). Hu et al. (2012) developed polyols for the production of PU foams using soy straw and crude glycerol. The great advantage of this method, besides the use of a renewable resource as feedstock, is that the solvent is a residue of soy biodiesel production that has little economic value and is potentially prejudicial to the environment due to the presence of impurities such as methanol, fatty acids, soap, salts, and catalyst residues. This process could improve the sustainability of the PU industry, as well as reduce production costs due to the substitution of petroleum-derived solvents by glycerol, while at the same time alleviating the glut of crude glycerol generated as a biodiesel residue.

2.4.1.3 Adsorbent

Soybean straw can also be used as an adsorbent for pollutants present in industrial wastewaters, such as methyl violet, copper ions, and phenols. Adsorption is widely used in water treatment plants to remove residues from aqueous solutions, because it is simple, effective, and inexpensive.

Methyl violet is a dye that inhibits the photosynthesis of aquatic plants, and repeated or prolonged exposure to it can cause organ damage. Biochars derived from crop residues, including soybean straw, were investigated for the removal of these dyes from wastewater prior to its discharge into water bodies (Xu et al., 2011). Biochar is a carbon-rich residue generated by oxygen-limited pyrolysis of plant-derived biomass in the partial or total absence of oxygen. The study concluded that the biochars investigated, including soy straw biochar, showed high removal efficiency for methyl violet and could be effective adsorbents for removal of the dye from wastewater (Xu et al., 2011).

Adsorbents based on soybean straw have also proved effective for the adsorption of phenol by activated carbon prepared from soybean straw impregnated with $ZnCl_2$, and for the adsorption of copper ions from aqueous solution by soybean straw modified with citric acid (Zhu et al., 2008; Miao et al., 2013).

2.4.1.4 Fermentable sugars for biofuels and other products

Because of its high cellulose content, soybean straw can be used for the production of second generation bioethanol (cellulosic ethanol) and other products obtained by fermentation of sugars, such as lactic acid. For this purpose, cellulose must be degraded to its fundamental unit, which is glucose. This is usually achieved by acid or enzymatic hydrolysis. The advantages of enzymatic hydrolysis are savings in energy costs, due to the relatively mild reaction conditions, and avoidance of the use of toxic and corrosive chemicals. The main drawback is the high cost of enzymes. However, prior to hydrolysis, due to the recalcitrance of lignocellulosic biomass to chemical and enzymatic conversion, a pretreatment process is necessary to enhance cellulose conversion by reducing this recalcitrance and leaving the cellulose more accessible to acid or enzymatic attack (Xu et al., 2007; Wan et al., 2011).

There have been few studies of soybean straw pretreatment for subsequent enzymatic hydrolysis to produce bioethanol or lactic acid. Xu et al. (2007) pretreated soy straw with ammonia, followed by enzymatic hydrolysis. The pretreatment process was evaluated using different ammonia liquor concentrations, pretreatment times, and straw smash size. The factors considered in the hydrolysis were the effects of time, substrate concentration, temperature, and enzyme loading. The best conditions for pretreatment were straw milled to pass through a 140-mesh sieve, a 10% (w/v) concentration of ammonia liquor, and a time of 24 hours. All the experiments were conducted at room temperature, using a solid/liquid ratio of 0.1 g/mL. For the hydrolysis process, the best conditions were 5% (w/v) pretreated soybean straw, hydrolyzed with cellulase (obtained from Wuxi) at a loading of 50 FPU/g of substrate, at 50 ºC, pH 4.8, for 36 hours. Under these conditions, the hydrolysis yield was 51.22%. When comparing to values employed in pretreatment and hydrolysis of lignocellulosic materials performed in the last few years, this solid load is considered low, while the reactions time and enzymatic load are considered too high.

Liquid hot water (LHW) and alkaline pretreatments of soy straw have also been tested for posterior enzymatic hydrolysis of cellulose (Wan et al., 2011). The best results were achieved with the LHW pretreatment, using a temperature of 210 ºC for 10 minutes. Enzymatic hydrolysis was carried out with 2.5% (w/w) solids loading and 20 FPU/g of solid of cellulase (Spezyme CP), for 48 hours at 50 ºC with agitation speed of 130 rpm on a rotary shaker. The glucose yield achieved was 70.76%.

Difficulties encountered in pretreatment techniques include the need for high temperatures and pressures, the high costs of cellulolytic enzymes, and corrosion caused by inorganic acids used for cellulose hydrolysis, which limits their application in industrial production. In order to circumvent these problems, Hu et al. (2013) used an ionic liquid under ultrasound irradiation for the production of reducing sugars from soy straw. According to the authors, ionic liquids (ILs) are environmentally friendly molten salts that have the advantages of low melting points, low volatility, and excellent solvency. They can be used in the design of new materials, because their cations or anions can be introduced into functional groups. Furthermore, the ionic liquid utilized in the study had a low cost of synthesis. The yield of reducing sugars was 266.35 mg/g of soybean straw.

As can be seen, soybean straw contains high quantities of lignocellulosic material, so research has focused on its utilization (especially the cellulose fraction) for the manufacture of fibers and fermentation products of the pretreated and hydrolyzed material. Whole soy straw has also been studied for the production of polyurethane and adsorbents.

2.4.2 Soybean hulls

The soybean hull is the part of the seed that has the highest concentration of carbohydrates. It typically consists of 86% carbohydrate, 9% proteins, 1% lipids, and 1% ash (on a dry mass basis). The hull usually accounts for 8% (dry mass basis) of the seed (Liu, 1997).

Most processed soybeans are dehulled before extraction of the oil and processing of the meal, because the feed industry prefers meals with higher protein content, for which it pays a premium. Removal of the hulls increases the protein content of the meal by about 4 %. The majority of the hulls obtained are, like soy meal, heat-treated to inactivate antinutritional factors and sold as feed. In the case of hulls, the main destination is feed for cattle. A small quantity of hulls is also used in human nutrition. After cleaning and sterilizing, it can be used as a dietary fiber source in bakery products and other foods. Interest in the use of soy hulls for the human diet has increased following research showing that dietary fibers can positively influence human health. Soy hull also has a high iron content (around 32% of seed iron is located in the hull), so it can be used as an iron supplement in foods such as bakery products and breakfast cereals (Liu, 1997; Johnson et al., 2008).

Other applications of soybean hulls that have been studied are their use as adsorbents and for enzyme, pectin, protein, and ethanol production.

2.4.2.1 Adsorbent

Soy hulls can be used as an adsorbent for the removal of soy oil impurities during the refining process. Proctor and Harris (1996) studied the adsorption of FFA, peroxides, phospholipids, and lutein by soy hull carbon. The efficiency of adsorption of these four soy oil components by soy hull carbon, milled soy hull, and boiled soy hull were analysed by Gnanasambandam and Proctor (1997). Gnanasambandam et al. (1998) investigated the influence of temperature on the pyrolysis of soy hull to produce soy hull carbon.

Proctor and Harris (1996) tested soy hull carbon as an alternative to activated bleaching earth adsorbent for the bleaching step of soy oil refining (briefly described above). Soy hull carbon was prepared by combustion of the hulls in a muffle furnace at 440 ºC. One kilogram of soybean released 102 g of hulls, which then yielded 16.5 g of carbon. Bleaching of oil was performed for 30 minutes under magnetic stirring at 100 ºC and a pressure of 2 mm Hg, with variable amounts of carbon added as adsorbent. Before and after adsorption, measurements were made of lutein, peroxide, phospholipids, and FFA. It was found that with larger doses, there was a decrease in adsorption efficiency. This indicated that moderate adsorbate doses could produce oil that was very similar in quality to that obtained with greater weights of carbon. It was also reported that competitive adsorption probably occurred between the oil components, and that for oil pigments such as carotenoids, carbon was not a good adsorbent. The order of affinity of the oil components for soy carbon was phospholipids > peroxides > free fatty acids > lutein. Therefore, possible options would be to use soy hull carbon together with bleaching clay, or as a pretreatment material for the adsorption of phospholipids, peroxides, and free fatty acids, so that bleaching clay could then be used to adsorb soy pigments more efficiently.

In tests of the efficiency of ground soy hull (particles smaller than 100-mesh), boiled soy hull, and soy hull carbon for adsorption of the components of the crude oil, soy hull carbon was shown to be more efficient, compared to the other two materials. The boiling of soy hulls did not result in any improvement of adsorption. It was found that boiling resulted in an open, porous structure, and that carbonization did not affect the particle size. Soy hull carbon showed a random amorphous structure and greater surface polarity, compared to powdered amorphous cellulose (Gnanasambandam and Proctor, 1997). Higher pyrolysis temperatures (500 and 700 ºC) did not influence the adsorption. On the other hand, a lower temperature (300 ºC) decreased the adsorption of the compounds (Gnanasambandam et al., 1998).

The adsorption capacity of modified soy hulls was also tested for wastewater treatment (Marshall and Wartelle, 2004). The hulls were chemically modified with N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride in a strongly alkaline environment in order to convey anion exchange capabilities. The resulting adsorbent was compared to commercial cellulose-based and synthetic anion exchange resins for the removal of anions considered contaminants in drinking water when present in amounts above a certain level. The soy hull resin was more effective for anion removal, compared to the commercial cellulose-based resin, but was not as effective as the commercial synthetic resin.

Gong et al. (2008) used chemically modified soybean hull as a cationic sorbent to adsorb dye residues. The sorption capacities obtained were 238.1 mg/g for acridine orange and 178.57 mg/g for malachite green. The modified soy hull adsorbent proved to be an excellent basic dye sorbent, with sorption that was spontaneous, exothermic, and favored at lower temperatures.

2.4.2.2 Pectin

Pectins find a wide range of uses in food processing, where they are used as gelling agents or stabilizers, and as replacements for fats in confectionary, dairy products, spreads, salad dressings, ice cream, and emulsified meat products. They can also be used as ingredients in pharmaceutical preparations including antidiarrheal, detoxicant, and demulcent formulations (Stephen et al., 2006).

The main commercial sources of pectins are citrus peels and apple pomace. Industrial production involves acid extraction, followed by filtration and precipitation by 2-propanol. Apple pomace and citrus peel contain around 12% and 25% of pectin, respectively, and extraction yields are around 25% (Gnanasambandam and Proctor, 1999).

Gnanasambandam and Proctor (1999) studied the acid extraction of soy hull pectins with nitric acid (0.1 N HNO3, 1:20) at 90 ºC for 40 minutes, with or without previous enzyme pretreatment (mannanase, 0.1% v/v in water, pH 5.5, 50 ºC for 60 minutes). Yields of approximately 15% were obtained for both processes, with purities of 76.7 and 88.3% for acid extraction without and with previous enzyme pretreatment, respectively. The same research group later improved the process for extraction of pectin from soy hull. Under optimal conditions, using 0.05 N HCl followed by precipitation with 2-propanol at pH 3.5, a yield of approximately 26% was obtained, with purity exceeding 70%. These results were similar to those obtained for the extraction of citrus peel (Kalapathy and Proctor, 2001).

An advantage of using soy hulls instead of citrus peel or apple pomace is that soy hulls can be stored without further processing, while the other two materials require drying to prevent deterioration during storage and transportation (Kalapathy and Proctor, 2001).

2.4.2.3 Peroxidase

Phenols can be removed from wastewater by the peroxidase enzyme present in soybean hull, and it has been shown that for this purpose it is not even necessary to extract the peroxidase from the hull (Bassi et al., 2004), and that the presence of Triton X-100 (a surfactant) can improve the phenol removal efficiency (Steevensz et al., 2014). Purified soy hull peroxidases can also be immobilized on macroporous glycidyl methacrylates to perform phenol oxidation or polymer synthesis in organic solvents (Prokopijevic et al., 2014). For the polymerization of phenol, soy hull peroxidase can be immobilized and then used in a fluidized bed to catalyze the reaction (Trivedi et al., 2006).

2.4.2.4 Ethanol

Some of the reported studies concerning the pretreatment of soy hulls for future ethanol production have evaluated the process up to the stage of conversion to glucose, while others have conducted tests up to the fermentation stage.

Lamsal et al. (2010) studied the pretreatment of soybean hulls by grinding and by extrusion. Particle size reduction by grinding does not change the lignocellulosic structure, so its use alone is not sufficient to prepare the lignocellulosic material for further enzymatic hydrolysis. Nonetheless, it does increase the specific surface area of the substrate, making it more susceptible to enzymatic attack. Grinding is therefore usually used as an initial pretreatment step. Extrusion is a thermo-mechanical process that can be applied in combination with chemicals. It uses the shear forces applied by the extrusion screw to remove the softened surface regions of the substrate and expose the interior to thermal and/or chemical action, hence improving the rate of subsequent cellulose conversion. Compared to other traditional pretreatments, this process has the advantage of being continuous, leading to high throughputs, and of being capable of using high solids loads.

The best reducing sugars yields, of around 30%, were obtained using extrusion with 35% moisture content, followed by extensive washing with water. According to Lamsal et al. (2010), the washing step improved the overall process because some of enzymatic inhibitors were washed away prior to the enzymatic hydrolysis. Yields were not improved by the addition of sodium hydroxide with urea and thiourea during the extrusion process, or by calcium chloride treatment after extrusion.

2.4.2.5 Ethanol and protein production

Rojas et al. (2014) studied the production of oligopeptides and ethanol from soybean hulls. Firstly, the proteins in the soy hull were hydrolyzed and solubilized by treatment using a basic medium (pH 9) at 60 ºC for 5 hours, with a solid/liquid ratio (S/L) of 1:10 and 1% ($m_{enzyme}/m_{substrate}$) concentration of proteolytic enzyme. The solid fraction was then pretreated with dilute acid (3% v/v H_2SO_4, 120 ºC, 1 atm, 1:4 (S/L), 40 minutes) for the removal of hemicellulose, followed by enzymatic hydrolysis of cellulose, which was performed for 72 hours using sodium citrate buffer (pH 4.8, 1:10 (S/L), cellulase load of 20 FPU/g, 50 ºC). Finally, fermentation of the saccharified liquor was carried out for 2 hours using *Saccharomyces cerevisiae*. As a result, 60% of the proteins were recovered, most with molecular mass less than 6500 Da. The pretreatment was able to remove 60% of the hemicellulose, and conversion of cellulose to glucose reached 55% during the saccharification process. The fermentation yield was around 90%, relative to the theoretical yield (about 13 g/L of ethanol after 2 hours, leading to a fermentation productivity of 6.5 g/L-h).

In a different approach, Mielenz et al. (2009) produced ethanol using simultaneous saccharification and fermentation, without any prior pretreatment. The aim was to preserve the value of the proteins, so that they could later be used commercially as feed for bovine livestock and monogastric animals, due to the improved quality of the product. Simultaneous saccharification and fermentation was performed for 30 days using enzyme loadings of 11.5 FPU Spezyme CP, 13 U of β-glycosidase, and 2850 U of pectinase per gram of cellulose, and with *Saccharomyces cerevisiae* D5A as the yeast. The conversion of cellulose to glucose reached around 82% of the theoretical yield, and about 31.5 g/L of ethanol was produced, achieving a fermentation productivity of 0.044 g/L-h.

Similar to soy straw, soy hulls are rich in lignocellulosic material, so the literature also reports studies concerning the production of adsorbents and ethanol from soy hulls. Furthermore, hulls also contain considerable amounts of proteins, peroxidase, and pectin, which have their own intrinsic value. Studies involving the production of more than one valuable substance were found in the literature, which is of special interest from a commercial point of view.

2.4.3 Gums

Degumming is a process for removing phospholipids from crude soybean oil, in order to improve its physical stability and facilitate further refining. If not removed, phospholipids can lead to dark-colored oils and act as precursors to off-flavor compounds. The residue generated by the degumming process is called gums and usually, after processed, in industry, it is usual to refer to all the phosphatides present in vegetable oils as lecithin. In biochemistry and medicine, on the other hand, the name lecithin is exclusively given to the sn-3 phosphatidylcholine. Soybean oil is the main commercial source of lecithin (Johnson et al., 2008; van Nieuwenhuyzen and Tomás, 2008).

Lecithin is widely used in the food, cosmetic, and pharmaceutical industries due to its numerous surfactant and bioactive properties. In foods, its main uses are as emulsifier, stabilizer, crystallization control agent, viscosity modifier, antioxidant, and reducer or replacer of fat. Examples of foods that contain lecithin are mayonnaise, salad dressing, margarines, low fat spreads, icings, and frostings (Gunstone, 2008). It is estimated that 25-30 % of the lecithin produced is destined to the production of margarines; 25-30 % to baking chocolate and ice cream, 10-20 % for the manufacture of technical products (e.g. pigment dispersion agent in plastics production or gasoline additive for its inhibition and anticorrosive effects); 3 to 5 % destined to cosmetic industry; and to pharmaceuticals, 3% (Kirk-Othmer, 2001; Wu and Wang, 2003).

2.4.4 Soapstock

Soapstock is a residue of the neutralization of crude or degummed soy oil during the refining process. It corresponds to 6% of the initial volume of the crude oil feed used in the refining, and contains approximately 35% of total fatty acids. Soapstock composition can vary, depending on the seed quality and the process, but it mainly consists of water, free fatty acids, neutral oil, phospholipids, unsaponifiable matter, proteins, and mucilaginous substances (Woerfel, 1981; Shahidi, 2005).

The recovery of soapstock requires an initial treatment, which increases total process costs (Woerfel, 1983). Nonetheless, this residue can be used as feedstock to manufacture other products, resulting in cost reduction and increased process profitability.

According to Woerfel (1981), soapstock can be returned to the meal in the desolventizer-toaster (if the refinery is part of an extraction plant), or it can be saponified and purified to produce industrial soaps. Shahidi (2005) explains that soybean soapstock has high levels of unsaturation and pigmentation, and that its use as soap is restricted to industrial applications, such as powdered hand soaps, metal finishing compounds, laundry and dry cleaning, food plant cleaners, and low-temperature dye washes. It is not suitable for use as toilet soap. Coconut and palm kernel soapstocks are examples of oil refining residues that can be used as toilet soap feedstocks. According to Shahidi (2005), most of the soapstock produced is used as a feed ingredient, contributing to metabolizable energy. Studies of the addition of soapstock to the feed of dairy cows, laying hens, and broilers have shown positive results. On the other hand, decreased amino acid digestibility was observed for pigs and roasters, with subsequent problems such as poor growth performance, when soybean soapstock was added to the feed (Abel-Caines et al., 1998; Pardio et al., 2001, 2005; Bruce et al., 2006; Zinn and Jorquera, 2007).

Most of the available literature about possible uses of soapstock concerns the conversion of fatty acids (FAs) into fatty acid alkyl esters (FAAEs) for use in biodiesel production. One way to achieve this is by an alkaline hydrolysis followed by an acid-catalyzed esterification of fatty acids. This sequence of reactions can result in 99% conversion. The disadvantage of the method is that when the acid is added to the soapstock alkaline solution, large amounts of sodium sulfate are produced, generating a residue with potentially high disposal costs. In addition, in order to remove free fatty acids from the remaining solution, subsequent washes with $NaC\ell$, $NaHCO_3$, and $Ca(OH)_2$ are required (Haas et al., 2000, 2001, 2003). Haas et al. (2003) circumvented this problem by using a strong acid to separate the soapstock into two layers. The organic layer, composed mainly of FAs, acylglycerols, pigments, and other lipophilic materials, was submitted to an esterification step, resulting in only 0.2% of residual FAs.

Soapstock can also be used for the production of biosurfactants. Rhamnolipids have been successfully produced using soybean soapstock, with a yield of 75% (Nitschke et al., 2005).

Other than its utilization as feed and for industrial soap manufacture, the high free fatty acid content of soapstock has mainly resulted in research concerning its use for biodiesel production.

2.4.5 Spent bleaching earth

Originally, bleaching was used as a color reducing process, removing compounds such as carotenoids and chlorophyll. Nowadays, bleaching is also important for the removal of residual soaps, phosphatides, and oxidizing bodies. It also breaks down peroxides into lower molecular weight carbonyl compounds, so that they can be further removed during deodorization operations (Johnson et al., 2008; Bergeron et al., 2012).

The agents normally used as adsorbents are natural clays (of the aluminum silicate family), activated earths (natural clays treated with sulfuric or hydrochloric acids), activated carbon, and synthetic silicates. Synthetic silicates are typically used together with earth clays for the adsorption of secondary oxidation products such as aldehydes and ketones, phosphatidic and sulfur compounds, trace metals, and soaps, leaving the clay free to adsorb carotenoids and chlorophyll, hence improving the efficiency of the process (Johnson et al., 2008). Many studies can be found in the literature concerning possible new materials that could be used as bleaching agents (such as soy hull carbon, as presented in Section 2.4.2.1).

The usual dosage of clay earth used in this process is between 0.3 and 0.5% (w/w), depending on the quality of the oil, and on press effects. The latter is a phenomenon that occurs during the filtration stage (to separate the clay and adsorbed oil compounds), when there is still adsorption of the components, and can increase the overall efficiency of the bleaching process (Johnson et al., 2008).

The residue generated by the bleaching step during the soybean oil refining process is called spent bleaching earth (SBE), and is usually consigned to landfill. Around 1.2-1.6 kg of SBE is typically generated per metric ton of edible oil produced. As this material is prone to spontaneous combustion, it needs to be covered with soil or sand immediately after discarding (Johnson et al., 2008; Huang and Chang, 2010).

Studies reporting on possible uses of SBE can be divided into two main categories: those that focus on the regeneration and reuse of the clay, and those that focus on the use of the oil recovered from the clay. The amount of oil retained in the clay can vary from 25 to 75% of the weight of the earth, and can be recovered using steam, aqueous, solvent, or pressure extraction treatments (Johnson et al., 2008; Singh, 2010). According to Singh (2010), this residue can be used as a feed supplement, pellet binder, and metabolizable energy source in poultry diets. Johnson et al. (2008) described a process of recovering the oil from bleaching earth using water and lye, where the oil recovered could be used for technical purposes or as cattle feed (due to its low quality). Since the clay residue did not ignite spontaneously, it could be used to cover other waste, instead of needing to be covered.

The oil recovered from the spent bleaching earth was also successfully utilized for the production of coating systems that demand good mechanical properties and mild chemical resistance. The performance obtained was similar to that of conventional water-based alkyd (polyester modified by the addition of fatty acids and other components) coatings used for industrial finishes that require these characteristics (Toliwal et al., 2008).

Pizarro and Park (2003) and Huang and Chang (2010) evaluated the production of biodiesel from the oil recovered from spent bleaching earth. In the first of these studies, the oil was recovered from spent bleaching clay employed in palm, rapeseed, and soy oil refining processes. The oil was recovered from the spent bleaching earth using double extraction with n-hexane (1:1 w/w) and concentration under vacuum with a rotary evaporator. Methanolysis was performed for 72 hours using an enzymatic solution with 200 IU/mL of lipase from *Rhizopus oryzae*, a 1:1 molar ratio of oil to methanol (30:1 in mass terms), in a shaker at 37 ºC and 175 rpm. The enzymatic solution was prepared in such a way that water mass percentage was 75 % of the oil mass to be transesterified. The recovered soy oil exhibited the worst conversion to fatty acid methyl ester. Under the same conditions, the conversions achieved (mass of FAME produced/initial mass of oil) for the extracted oils were 55% (palm oil), 30% (rapeseed oil), and 25% (soybean oil). The authors suggested that the high viscosity of the extracted soybean oil could have been a possible cause of the low conversion value.

Huang and Chang (2010) also studied the production of biodiesel from spent bleaching clay from soy oil refining. In this case, the samples had already passed through a primary recovery in the plant, using steam at 294 kPa. The extraction was performed with n-hexane (1:4, w/w) in a Soxhlet extractor, and was continued for 6 hours, until the hexane extractant became colorless. The hexane was then removed in a rotary vacuum evaporator. A two-step esterification was performed. Firstly, water was removed from the oil by evaporation at 105 ºC. Esterification was then performed using 100 g of oil with 29 g of methanol and 1 g of sulfuric acid, for 1 hour at 60 ºC. The excess of water was again removed as a preparation for the subsequent transesterification step, in which 90% conversion was achieved under optimized conditions, using 100 g of oil, a 1:6 oil/methanol molar ratio, and 1 g of sodium hydroxide, with 90 minutes of reaction at 80 ºC. It was found that the properties of the resulting biodiesel were in reasonable agreement with the EN 14214 and ASTM D6751 standards.

Huang and Chang (2010) conducted a preliminary financial analysis for a 1,000 tonne/year biodiesel production unit, and reported a production cost of 0.37 US$/L. This was lower than the local (Taiwan) pre-tax petroleum diesel price of 0.71 US$/L (assuming a crude oil price of 100 US$/L). It was also lower than the estimated prices of biodiesel produced from soybean, rapeseed, and waste cooking oils in Taiwan (0.8-1.5 US$/L), as well as production costs of 0.80-0.95 US$/L in Europe. Typically, the feedstock accounts for the largest fraction of the cost, but in this case, as the feedstock was a cheap residue, chemicals were the inputs that had greatest impact on production costs.

Techniques that have been reported for the recovery and reuse of clay involve treatments such as heat provided by an air stream, solvent extraction of the oil followed by calcination of the clay, and supercritical carbon dioxide extraction. Although regenerated clay does not provide the same efficiency as the original material, it has nevertheless been shown that it can be reused (King et al., 1992; Foletto et al., 2002; Ma and Lin, 2004; Lin and Lin, 2005). These results considered only one regeneration cycle, so no information is available concerning the total possible number of cycles in which regenerated clays could be used.

2.4.6 Deodorizer distillate

Deodorizer distillate (DD) is the residue of the deodorization step of the oil refining process. The main goal of this step is the removal of aldehydes, ketones, and other volatile substances that might affect the flavor and odor of the refined oil. These substances include fatty acids, tocopherols (also known as vitamin E), sterols, and squalene, all of which have commercial value. Table 2.3 presents the composition of DD reported by Gunawan et al. (2008).

Table 2.3 – Composition of deodorizer distillate

Compounds	Composition (% (m/m))
Free fatty acids	45.38 ± 2.13
Triacylglycerols	18.45 ± 2.20
Diacylglycerols	4.85 ± 1.21
Squalene	1.83 ± 0.05
Fatty acid steryl esters	3.91 ± 0.39
Tocopherols	6.40 ± 0.85
Free sterols	5.36 ± 0.19
Others (hydrocarbons, aldehydes, ketones, pesticides, herbicides, and the breakdown products of tocopherols and free phytosterols)	15.23 ± 0.16

Source: Gunawan et al. (2008).

In order to be marketed as vitamin E, tocopherols must have purity of at least 60% and be free from fatty acids. Squalene may be found in tocopherol mixtures, but squalene itself has economic value, because it is widely used as a moisturizer in the cosmetics industry. Sterols are known health promoters (Dumont and Narine, 2007).

Phytosterols are also known health promoters. They can be found in margarines, tablets and even in eye creams to enhance health benefits such as lowering cholesterol or soothing irritation (Dumont and Narine, 2007).

One way of extracting sterols from deodorizer distillates is by solvent extraction and crystallization. The main advantage of this method is that it does not cause oxidation of tocopherol, which can therefore also be recovered. The main drawbacks are that the amounts of solvents required are high, the technique requires laborious manipulations, and recovery and purity are low (Lin and Koseoglu, 2003).

Lin and Koseoglu (2003) studied the separation of sterols by crystallization without pretreatment. The best results were obtained by crystallization at -20 ºC for 24 hours using a mixture of acetone and methanol, followed by centrifugation, filtration, and washing steps. As a result, over 90% of the tocopherols and squalene were recovered in the filtrate fraction, and 80% of the total sterols were retained in the cake fraction.

Gunawan et al. (2008) used a modified Soxhlet extraction and silica gel column chromatography to separate squalene, tocopherols, free phytosterols, TAGs, FFAs, and fatty acid steryl esters (FASEs). FASEs are conjugated phytosterols in which the OH group of the free phytosterol is ester-linked with a fatty acid (Gunawan et al., 2010). The modified Soxhlet extraction separated FASEs and squalene into one fraction, and tocopherols, free phytosterols, TAGs, and FFAs into another fraction. The composition of the fraction containing FASEs and squalene included 12.19% of FASEs and 6.29% of squalene, corresponding to recoveries of 94.32% and 100%, respectively. In the other fraction, the contents and recoveries of the components, respectively, were 35.05% and 20.41% (FFAs), 3.49% and 5.89% (TAGs), 2.39% and 9.83% (tocopherols), and 0.41% and 2.09% (free phytosterols).

After the fraction containing FASEs and squalene had been subjected to silica gel column chromatography, with elution using 10.96 L of hexane at 23 ºC, it was possible to obtain a solution with 95.90% purity and 93.09% recovery of squalene. It was found that although this process required large amounts of flammable and environmentally unfriendly organic solvents, the compounds could be easily recovered without the use of highly sophisticated techniques such as molecular distillation, under atmospheric pressure and at lower temperature.

The production of biodiesel from DD has been studied using enzymatic or counter-current probe ultrasonic enhanced transesterification (CCPUE). Biodiesel production using lipase, tert-butanol as reaction medium, and 3A molecular sieve as adsorbent achieved 97% conversion of FFAs and TAGs to biodiesel (Li Wang et al., 2006). After 120 cycles, the lipase showed no significant loss of activity. The use of tert-butanol was able to eliminate the negative effects of excessive methanol and glycerol, and the molecular sieve controlled the water concentration in the medium during the reaction. Using CCPUE (Yin et al., 2015), almost the same conversion (96.1%) was obtained under the best conditions: initial temperature of 25 ºC, 10:1 methanol to triglyceride molar ratio, flow rate of 200 mL/min, catalyst (NaOH) content of 1.8%, ultrasound on-time of 4 s and off-time of 2 s, and a total time of 50 minutes. To achieve this yield, prior to the CCPUE procedure, the DD was pre-esterified with sulfuric acid and methanol, after which the phytosterols were removed by centrifugation at different temperatures. The resulting liquid was then submitted to CCPUE.

2.4.7 Soybean meal

Most of the soybean meal produced is destined for use as animal feed, although the demand for soy proteins for human consumption has grown since the late 1950s (Endres, 2001). In addition, a small quantity of meal is used for industrial purposes (Liu, 1997).

Flours derived from oil extraction processes, known generally as defatted flours, are usually divided into three main categories: defatted flours, soy protein concentrates, and soy protein isolates. The first is the flour that results after removal of the hulls and oil, and contains around 53% protein. The second is defatted flour from which, besides hulls and oil, sugars have also been removed, resulting in a protein concentration of around 66-70%. The third is defatted soy flour from which sugars, other water-soluble materials, and cotyledon fibers have been removed, resulting in 92-96% protein content (Bressani, 1981; Endres, 2001; Singh et al., 2008).

Soy products are not only valued as animal feed or for the human diet because of their high protein content, but also for their nutritional quality. Two factors are important for the nutritional value of a protein: its amino acid composition and its digestibility. Soy contains sufficient quantities of almost all amino acids (especially lysine), with the exception of those that include sulfur in the molecule (cysteine and methionine). Most cereals contain limited amounts of lysine, but generally large amounts of sulfur-containing amino acids. Thus, soy protein sources are good complements for products based on cereal protein. In terms of protein digestibility, which is a measure of the bioavailability of the amino acids, defatted soy proteins also score well. Digestibility is a function of intrinsic factors, such as protein structure and levels of antinutritional factors, and external factors, such as heat treatments and purification processes (Wolf, 1970; Liu, 1997).

Soy proteins are also widely used as functional ingredients in food systems. Depending on the type of flour (defatted, concentrated, or isolated) and the quantity used, they can modify a broad range of food properties. These include solubility, emulsification (dispersion of oil droplets in a continuous aqueous matrix, or vice-versa), stabilization (by proteins that act as surfactants, decreasing interfacial tension between the phases), and foaming (dispersions of gases in liquids stabilized by these proteins, which form flexible, cohesive films around the gas bubbles). They also promote gelation, resulting from the capacity of the proteins to form networks, through protein-protein interactions, that immobilize a large amount of water. The gels formed exhibit relatively high non-Newtonian viscosity, elasticity, and plasticity, together with water-binding and water-holding capacity, where water is bound to the protein surface by hydrogen bonding. A good water-holding capacity is important for the production of meat analog soy products, because it improves texture, juiciness, and taste (Kinsella, 1979; Altschul and Wilcke, 1985; Liu, 1997; Belitz et al., 2009).

Another way to improve the desired functional property is to modify soy proteins by means of physical, chemical, or enzymatic methods. The modification of proteins can also alter their nutritional value. There has been much research in this field, and the partial hydrolysis of soy proteins, especially, has been extensively studied.

Proteins can be hydrolyzed by acids, alkalis, or enzymes. Although the use of chemicals for hydrolysis has the advantage of being cheaper and faster, enzymatic hydrolysis can usually be performed under milder conditions. Furthermore, the color and odor of the products obtained are often better than achieved by chemical hydrolysis. This is because the specificity of enzymatic catalysis prevents or reduces side reactions, hence providing better control of processes, and the amounts of chlorohydrins and salts in enzymatic hydrolysates are smaller than in hydrolysates produced by acid hydrolysis (Klostermeyer et al., 2000).

Studies have shown that the metabolic transformation of protein hydrolysates, especially in the form of di- and tripeptides, is a more energy-efficient process than for intact proteins or an equivalent mixture of free amino acids. Intact proteins can cause allergic effects in some organisms, and it has been reported that free amino acids in excess can induce osmotic diarrhea. The effects of hydrolyzed proteins have been tested for human use in sports nutrition, malnutrition, post-surgical recovery, burn recovery, gastric repair, muscle damage recovery, infant formulas, and allergic individuals. Aquaculture is another field where there have been many studies concerning the effects of these hydrolysates, because aquatic animals are very sensitive to intact proteins, while at the same time the substitution of live food diets is desirable due to their high costs (Siemensma et al., 1993; Infante et al., 1997; Maldonado et al., 1998; Boza et al., 2000; Clemente, 2000; Stranz and Kastango, 2002; Carvalho et al., 2004; Manninen, 2009; Nankervis and Southgate, 2009; Thomson and Buckley, 2011).

In industry, possible uses of soy proteins include the production of adhesives, plastics, and textile fibers (Kumar et al., 2002; Lodha and Netravali, 2005; Li et al., 2009; Ng, 2011).

2.4.8 Soybean molasses

Soybean molasses is a residue of the concentration of protein present in defatted soybean flakes using aqueous alcohol extraction. After the defatted soy flakes have been washed with the aqueous alcohol solution, the liquid fraction passes through steps in which alcohol and excess water are removed, leaving a brown viscous syrup with around 25% of moisture and a characteristic bittersweet flavor (Liu, 2004; Siqueira et al., 2008; Soccol et al., 2013).

The composition of soybean molasses can vary according to the soybean variety, growing conditions, location, and year. However, regardless of these factors, the main constituents of soybean molasses are carbohydrates such as oligosaccharides (stachyose and raffinose) and disaccharides (including sucrose), plus smaller amounts of monosaccharides (fructose and glucose), which together account for around 57% of the total dry weight (Siqueira et al., 2008), or 30% w/v (Solaiman et al., 2007). Soybean molasses also contain proteins, lipids, minerals, and substances known as phytochemicals (plant compounds that might affect human health), such as isoflavones and saponins (Liu, 2004; Soccol et al., 2013).

2.4.8.1 Fermentation medium

Due to its high concentration of carbohydrates, soybean molasses can be a good medium for fermentation. Depending on market conditions, soybean molasses may be available at a cost as low as 20% of that of the commonly used glucose substrate. Its use can therefore result in substantial savings, given that the cost of the feedstock contributes up to 75% of the price of bioproducts (Lynd et al., 1999; Solaiman et al., 2007). A wide range of products can be obtained using soybean molasses as fermentation medium, including proteins, lipids, and fuels.

Single cell proteins are the dried cells of microorganisms such as algae, yeasts, molds, and bacteria. As a large fraction of the microbial cell consists of proteins, single cell proteins can be considered a source of protein concentrate, and they are used as protein supplements in human nutrition and in animal feeds (Nasseri et al., 2011). As the global demand for proteins is increasing, single cell proteins are a valuable resource; an advantage is that the possible fermentation media used for these microbes include agro-industrial wastes, which can help to reduce the costs of protein production.

Gao et al. (2012) produced single cell proteins using soybean molasses as the fermentation medium, due to its high fermentable sugar content. Eight different microorganisms were tested, of which *Candida tropicalis* gave the best results. It was also found that addition of yeast extract and $CaCl_2$ improved microorganism growth. After 30 hours of fermentation in a 10 L bioreactor, a yield of 10.83 g/L was obtained under optimized conditions, with a total protein concentration of 6.11 g/L and a 56.41% protein content of the dry cells. The range of amino acids present included all those essential for animals. The nucleic acids content was lower, compared to the findings of other similar studies reported in the literature. High amounts of nucleic acids are not desired, due to their limited nutritional value and possible toxic effects following consumption by animals and humans. When metabolized, nucleic acids yield uric acid, which at high concentrations can cause gout or renal stones (Nasseri et al., 2011).

Sophorolipids are glycolipids that possess a hydrophobic fatty acid tail and a hydrophilic carbohydrate head (sophorose, a glucose disaccharide). They are produced extracellularly by several Candida yeast species. Sophorolipids have potential uses as surfactants, emulsifiers, antimicrobials, and as a source of specialty chemicals such as sophorose and hydroxylated fatty acids. Soybean molasses was tested as a source of nitrogen and carbon for the production of sophorolipids by *Candida bombicola*, with and without the inclusion of yeast extract and urea in the fermentation medium (Solaiman et al., 2007). The production of sophorolipids using soybean molasses alone was nearly 71% of the yield obtained when urea and yeast extract were included. Although the yield was somewhat lower in the absence of the additional ingredients, it was argued that this was compensated by avoidance of the high costs of the other components.

Soybean molasses was also evaluated as a fermentation medium for the production of fuels. Qureshi et al. (2001) carried out the production of butanol by *Clostridium beijerinckii* BA 101 using spray dried soybean molasses as fermentation medium. Butanol is considered a superior fuel, with a calorific value greater than that of ethanol, and can be used in plastics manufacturing and in the extraction of food flavorings. It was found that a yield of 10.7 g/L of butanol was achieved when the medium was complemented with another sugar source and 80 g/L of spray dried soybean molasses. This yield was lower than when glucose was used in place of soybean molasses, which produced 23.8 g/L after 72 hours. Increasing the amount of soybean molasses decreased butanol production. This was attributed to an inhibitory effect of the salts present in molasses (salts are added to assist the spray drying operation). Tests showed that the two salts tri-calcium phosphate and sodium chloride influenced the butanol yield in opposite ways, with tri-calcium phosphate acting to increase butanol production from 23.8 to 31 g/L, while sodium chloride inhibited butanol production. It was also found that *Clostridium beijerinckii* BA 101 utilized glucose, fructose, sucrose, and galactose as carbon source, but not raffinose, stachyose, pinitol (a cyclic polyol), and melibiose (a reducing disaccharide, D-galactose-α(1,6)-D-glucose), which are all present in soybean molasses.

Saccharomyces cerevisiae is another organism that does not utilize complex sugars such as raffinose and stachyose as carbon source. The hydrolysis of these sugars prior to fermentation could therefore improve fuel production yields. For bioethanol production, soybean molasses have been used without previous hydrolysis, with acid or enzymatic hydrolysis, and with simultaneous hydrolysis and fermentation.

Siqueira et al. (2008) studied the production of bioethanol from *Saccharomyces cerevisiae* using soybean molasses alone as the fermentation medium, without pH adjustment or previous hydrolysis. Use of a soluble solids concentration of 30% (w/v) and a yeast concentration of 3 x 10^8 cells/mL resulted in an ethanol yield of 45.4%, relative to the total concentration of sugar consumed after 6 hours of fermentation. Scaling-up this process, yields of 163.6 and 162.7 L of anhydrous ethanol per tonne of dry molasses were achieved at pilot and industrial scales, respectively. These production yields were slightly smaller than the yield of 169.8 L/tonne achieved at the laboratory scale.

Romão et al. (2012) submitted soybean molasses to a previous acid hydrolysis before fermentation using *Saccharomyces cerevisiae*. The amount of acid and other conditions were varied, and the best results were achieved using 1:4 dilution of molasses, 20 minutes of hydrolysis with nitric acid at pH 4.0 and absolute pressure of 1.5 atm, and a subsequent fermentation time of 14 hours. Ethanol production was 50.1 g/L, corresponding to a 60% yield of ethanol relative to the initial total sugar concentration, and to a 78% yield of ethanol relative to the total concentration of sugar consumed. Acid hydrolysis increased the ethanol yield by 13.3%, compared to direct fermentation with soybean molasses.

The same experiments developed by Romão et al. (2012) were performed using enzymatic hydrolysis instead of acid hydrolysis for pretreatment of soybean molasses, followed by fermentation. Simultaneous enzymatic hydrolysis and fermentation was also tested (Silva et al., 2012). For the hydrolysis followed by fermentation, the best conditions were hydrolysis for 10 hours at 55 ºC, pH 4.5, 0.050% ($m_{enzyme}/m_{substrate}$), 230 rpm, and 250 g/L of soybean molasses. The fermentation was performed for 4 hours at 35 ºC, pH 4.5, 35 g/L of inoculum, and 230 rpm. The ethanol yield was 80.3%, relative to the total sugars consumed, and 67.1%, relative to the initial total sugars. For simultaneous hydrolysis and fermentation, the ethanol yield was 81%, relative to the total sugars consumed, and 61.5%, relative to the initial total sugars, using a soybean molasses concentration of 250 g/L, 12 hours at 35 ºC and 230 rpm, 35 g/L of S. cerevisiae, and 0.050% of enzyme.

After the fermentation performed by Siqueira et al. (2008), it was observed that the residue generated, called soybean vinasse, could also be used. Evaluation was made of the production of α-galactosidase and lactic acid using soybean vinasse as the medium and strains of *Lactobacillus agilis*, as this yeast can metabolize complex oligosaccharides.

For the production of α-galactosidase by *Lactobacillus agilis*, soybean vinasse was used as inoculum and fermentation medium, with yeast extract to adjust the C:N ratio. Under optimized conditions, enzymatic activity of 11.07 U/mL was achieved after 144 hours of fermentation (Sanada et al., 2009). For the production of lactic acid, fermentation of soybean vinasse with *Lactobacillus agilis* LPB 56 was performed without supplementation with an inorganic nitrogen source or yeast extract, achieving a yield of 85% (stachyose and raffinose converted into lactic acid) (Karp et al., 2011).

2.4.8.2 Enhancement of carbohydrates quality

Reis et al. (2010) studied the hydrolysis of galacto-oligosaccharides present in soybean molasses by two types of α-galactosidases and invertase produced by *Aspergillus terreus*. Galacto-oligosaccharides, such as raffinose and stachyose, are the main substances responsible for flatulence and intestinal disturbances in humans and monogastric animals after the ingestion of soybeans and other legumes. Enzymatic hydrolysis could provide a way of improving the nutritional value of products containing these components. Total hydrolysis of raffinose and stachyose was achieved by hydrolysis using a 1:10 (w/v) soybean molasses to water ratio, with 10 g incubated with an enzyme preparation containing 8 U of α-galactosidases and 10 U of invertase, at 40 °C for 240 minutes. According to the authors, a drawback of this process is that the enzymes used do not have GRAS (generally recognized as safe) status. It was suggested that a possible way of overcoming this problem would be to clone and overexpress the genes encoding these enzymes in suitable organisms. This would enable production of the enzymes at low cost, benefiting from the advantages that fungal enzymes offer, including their ease of manufacture and suitability for a wide range of technological applications, due to their extracellular location, optimal performance at acidic pH, and broad stability profile.

2.4.8.3 Purification of phytochemicals

Most of the purification processes that have been described for soybean molasses phytochemicals, such as isoflavones and saponins, are in the form of patents. Other publications mainly focus on the development of analytical methods for the identification or quantification of these compounds. Few academic studies were found in this area.

Song et al. (2009) used a poly glycidyl methacrylete–zirconium dioxide-β-cyclodextrin (PGMA–ZrO2-β-CD) composite matrix as the adsorbent in an expanded bed adsorption process for the isolation and purification of isoflavones present in soybean molasses. The process achieved up to 90% recovery of the isoflavones, with a purity of 75.4%. Advantages of the expanded bed adsorption technique were high efficiency and its integrated nature, resulting in large reductions in operation time and cost, compared to traditional purification processes.

As observed in the reported studies, soybean molasses contain large quantities of carbohydrates that can be used as fermentation media to produce a wide range of products. Some of the carbohydrates present in molasses can be difficult to digest by monogastric animals, but can be easily converted to digestible sugars by hydrolysis. The molasses also contains phytochemicals such as isoflavones and saponins, which when isolated have high commercial values.

2.4.9 Soy protein isolate residues

The manufacturing process of soybean protein isolate generates two residue streams with components that can be exploited. The first one is the solid fraction resulting from the addition of aqueous sodium hydroxide followed by centrifugation, which is called by some authors as soy cotyledon fiber, by others as okara or even as spent flakes. To the clarified extract (liquid fraction), hydrochloric acid is added and then, again the mixture is centrifuged. The liquid fraction obtained is called whey and is the second residue stream that can be exploited.

When searching in academic literature studies dealing with uses for these residues, it was found that the stream residues names are also used for streams of other soybean processes – soy cotyledon fiber and spent flakes can also refer to the meal obtained after dehulling and defatting. Okara and whey are also named as residues from soy milk and tofu production, and soy soluble polysaccharides may also refer to all soluble saccharides present in the whole soybean.

2.4.9.1 Soy cotyledon fiber, spent flakes or okara

Johnson et al. (2008) called the insoluble fraction residue generated after alkali extraction and centrifugation as soy cotyledon fiber and they described that this residue may be used as a source of dietary fiber ingredients.

Jong (2005, 2007) called this residue as spent flakes and analysed it as filler (Jong, 2005) or co-filler in rubber composites (Jong, 2007). In the first study, soy spent flakes were incorporated as a filler into carboxylated styrene-butadiene latex and compared with when it was filled with soy protein isolate. The experiments showed that rubber composites filled with spent flakes were more rigid and brittle than the ones filled with SPI, presenting a good alternative in terms of composite strength and also of cost, since spent flakes have lower commercial value than SPI. In the second study, soy spent flakes were used as a co-filler together with carbon black in an attempt to increase the modulus recovery value after consecutive deformation cycles when compared to soy spent flakes as the only filler. The author concluded that the use of soy spent flakes to partially substitute carbon black as the reinforcement co-filler produces rubber composites with good viscoelastic properties at lower costs as, again, soy spent flakes have low economic value.

A search in Scopus using strings soy* and okara presented 169 articles but only one was about an application of the residue obtained from SPI production. The large majority was about the residue generated from soymilk and tofu processing, in which soybean is not usually defatted. Nevertheless, it was found that some studies analysed the application of what was called soybean soluble polysaccharides and a portion of these studies explained that these saccharides were obtained after extracting and processing them from okara, the solid residue from soy protein isolate production. The main application for this residue is as a stabilizer agent in emulsions systems, followed by the utilization of it for the production of films for food packaging.

Soy soluble polysaccharides (SSPS) are mainly composed of rhamnogalacturonan backbone branched with β-1,4-galactan and α-1,3 or α-1,5-arabinan chains, and homogalacturonan covalently bound to a protein moiety (Zhao et al., 2015). SSPS were widely used in studies dealing with emulsions. Yin et al. (2015) used SSPS to stabilize emulsions with pea proteins to avoid its precipitation under acidic conditions. Zhao et al. (2015) analysed the influence of SSPS on the physicochemical properties of lactoferrin-coated orange oil emulsion and concluded that the presence of SSPS increased the stability of the emulsion during the storage of 4 weeks at 55 ºC. In another example, Wu et al. (2014), used SSPS to stabilize an emulsion with thyme oil to form an essential oil emulsion that could act as an antimicrobial delivery system to enhance microbiological safety of food products.

SSPS were also used to produce a biodegradable edible film as in Tajik et al. (2013). In this study, the authors developed a biodegradable edible film based on SSPS and using glycerol as a plasticizer. According to the authors, with the best glycerol concentration of 20%, the formed film exhibited commercial potential for food-packaging applications.

In an attempt to produce bioethanol, Long and Gibbons (2013) used SSPS as a culture medium. Ethanol production of 40 g/L was obtained using 50% soy solubles as the medium and *Saccharomyces cerevisiae* as yeast. As mentioned before, *Saccharomyces cerevisiae* is unable to metabolize complex sugars present in soybean molasses. These complex sugars are also present in soy solubles, so a large fraction of the carbohydrates remained unfermented.

2.4.9.2 Soybean whey

As informed beforehand, the liquid fraction obtained after extraction with HCl and centrifugation of soy curd during SPI production is called soy whey. Most studies related to this residue focuses on isolation of the proteins contained in soybean whey. During SPI process production, about 20 tonnes of soy whey wastewater are produced per tonne of SPI, with protein concentration at about 3 g/L (Wang et al., 2013). Li et al. (2014) made a pilot study about the separation of soy whey proteins from soy whey wastewater using foam fractionation followed by thermal sterilization and spray-drying of the fraction of soluble proteins. As a result, they obtained a recovery of 30.6 ± 1.5% of proteins, constituted of Kunitz trypsin inhibitor (the major ingredient), lipoxidase, β-amylase and lectin. They also observed that the functional properties of proteins decreased and that the up-scaling caused a slightly decreasing in recovery and an increase in protein denaturation.

In Liu et al. (2015), a two-stage batch foam fractionation was performed to separate the soy proteins from the isoflavones. In the first stage, soy whey wastewater was concentrated and next the concentrated solution was again submitted to foam fractionation with adjusting temperature and pH, dissociating the isoflavones from proteins, achieving a recovery percentage of proteins of 89.43% and a retention percentage of isoflavones in the residual solution of 90.02%.

Emulsions stabilization ability of whey proteins with SSPS was also studied. Ray and Rousseau (2013) discovered that mixtures of denatured soy whey proteins with SSPS could stabilize oil-in-water emulsions against coalescence and phase separation for more than 60 days at pH 3 and 21 days at pH 8.

Soy whey was also used as a substrate to culture *Lactobacillus plantarum* B1-6 to produce a potential fermented soy beverage with health and nutritional improvements (Xiao et al., 2015) and for the production of nisin (Mitra et al., 2010), an antibacterial peptide produced by *Lactococcus lactis*. In both cases, the results obtained were promising.

2.5 CHAPTER CONCLUSION

Soybean processing involves several operations and produces, besides its main products, large amount of residues. These residues may find applications that result in products with commercial value or in producing energy for the process itself. However, before studying possible applications for the residues generated during soybean processing, it is interesting to quantify the amount of residue generated and the thermal and electrical energy demand of the process. Chapter 3 analyses residues generated during the production of refined oil, SPC, SPI and biodiesel from degummed oil, when a fraction of the degummed oil produced during the refining stage is diverted to biodiesel production process. It also assesses the amount of some utilities required for the process.

3 SIMULATION AND ANALYSIS OF A SOYBEAN BIOREFINERY FOR THE PRODUCTION OF REFINED OIL, BIODIESEL AND DIFFERENT TYPES OF FLOURS

3.1 INTRODUCTION

Nowadays, there has been an effort from enterprises to maximize the use of their raw material and to make their process flexible so they can fulfil market needs. As an example, several sugarcane factories in Brazil can be cited, as they have a degree of flexibility in shifting between ethanol and/or sugar production, depending on the market demand. A soybean crushing and refining facility can also benefit from different possible paths for its raw material depending on the market needs.

In a soybean facility, the oil is first separated from the meal. The meal has as a major component, protein, with concentrations varying from 56 to 59% on dry matter basis (dmb). By further processing, the protein content in the meal can become even more concentrate and when a concentration of 65-72% dmb is achieved, it can be sold as soy protein concentrate (SPC). Using a different process, the meal can achieve 90-92% dmb, and be sold as soy protein isolate (SPI). The oil fraction, in its turn, can be processed to produce biodiesel or refined oil. As can be seen, from both, meal and oil fraction, there is more than one process that the material can be subjected. Studies dealing with the modeling of soybean processing can already be found in academic literature, but these studies deal with one or, at most, two products, usually crude oil and soybean meal or biodiesel from degummed soybean oil (not account the process of oil extraction and degumming). To the best of the authors knowledge, a study aiming to simulate a flexible process with the possibility of producing four products derived from soybean seeds and divert the process flow to a product that is more attractive according to the market needs has never been conducted. Therefore, the aim of this part of the work is to simulate and analyse a soybean crushing, refining and biodiesel production facility so the mass and energy demands can be depicted and better understood.

3.2 PROCESS SIMULATION

For modeling and simulation of oil extraction and refining, biodiesel, SPC and SPI production, SuperPro Designer v. 9.0 was used. Data for process simulation was obtained from academic literature and technical reports. A biorefinery with capacity for processing 2500 MT/day of dehulled soybean seed was considered. It is important to explain that the mass balance for the process was obtained from the literature while the amount of utilities required were obtained from SuperPro Designer and compared to data from literature whenever available.

3.2.1 Components properties

The insertion of pure components properties in SuperPro Designer v. 9.0 is better explained in this section. For the simulations to be performed, the simulator requires some properties that are constant and others that are temperature dependent. The constant properties are molecular weight, enthalpy of formation, normal boiling point, normal freezing point (although this is not used in the current version - the program does not make distinction between liquid and solid phases), critical temperature, critical pressure, compressibility factor, acentric factor (omega), Henry's constant, particle size and default volumetric coefficient. The necessary temperature dependent properties are the liquid/solid density, liquid/solid heat capacity, gaseous heat capacity, saturated vapor pressure and heat of vaporization.

To represent each class of component, substances were chosen according to the component’s distribution in the soybean seed and to the availability of data in the academic literature. In the case of fatty acids, three of them were chosen because chemical reactions during the process generated one of these three chosen ones.

3.2.1.1 Triacylglycerols

Triacylglycerols present in soybean were represented by the pure component named "Soybean oil", which was already available at SuperPro Designer v. 9.0 database. Based on the molecular formula and molecular weight informed, it was probably based on the triolein triacylglycerol properties.

3.2.1.2 Free fatty acids

To represent the free fatty acids (FFA) in soybean, three different FFA were chosen: linoleic acid, oleic acid and stearic acid. Their properties were obtained from Aspen Plus database v. 28.0 available in the university where this work was developed. To estimate the vapor pressure parameters, Aspen uses extended Antoine equation, shown in Equation 3.1, where P_v is the vapor pressure in Pa at temperature T in K and A to G are parameters for a given compound.

$$\ln(P_v) = \frac{A+B}{T+C} + D*T + E*\ln(T) + F*T^G \tag{3.1}$$

Liquid density is calculated by Aspen using Rackett equation (Equation 3.2), where ρ_L is the liquid density in kmol/m^3, T is the temperature in K and A to D are the parameters.

$$\rho_L = \frac{A}{B^{1+(1-\frac{T}{C})^D}} \tag{3.2}$$

The gas heat capacity is calculated using Aly-Lee equation (Equation 3.3), where ${c_p}^{id}$ is the gas heat capacity in (J/kmol-K), T is the temperature in K and A to E are the parameters.

$$c_p^{id} = A + B*\left(\frac{\frac{C}{T}}{\sinh\left(\frac{C}{T}\right)}\right)^2 + D*\left(\frac{\frac{E}{T}}{\cosh\left(\frac{E}{T}\right)}\right)^2 \tag{3.3}$$

The liquid heat capacity is calculated by a polynomial equation of order 3 (Equation 3.4) and the heat capacity is measured in (J/kmol-K) and the temperature in K.

$$c_p^L = A + B*T + C*T^2 + D*T^3 \tag{3.4}$$

Finally, the heat of vaporization is calculated using the extended Watson equation (Equation 3.5), where Δh_v is the heat of vaporization in J/kmol, T_r is the reduced temperature ($T_r = T/T_c$; T and T_c are in K) and A to E are the parameters.

$$\Delta h_v = A*(1-T_r)^{B+CT_r+DT_r^2+ET_r^3} \tag{3.5}$$

3.2.1.3 Phospholipids

Phospholipids from soybean were represented by a phosphatidylethanolamine whose most of constant properties were available in Díaz-Tovar (2011). Based on the molecular weight and on the number of carbons informed, it matched with a phosphatidylethanolamine in which the glycerol residue is also linked to two stearic acids. The acentric factor and the temperature dependent properties were not available. Therefore, those were estimated.

Vapor pressure (in Pa) was estimated using the Hoffmann-Florin equation (Eq. 3.6) and the points to adjust the parameters were the critical temperature and pressure (in K and Pa, respectively) and the normal boiling point (in K), which were available in Díaz-Tovar (2011). P_0 was set as 101325 Pa.

$$ln\frac{P^s}{P_0} = \alpha + \beta * f(T) \tag{3.6a}$$

$$f(T) = \frac{1}{T/_K} - 7{,}9151 * 10^{-3} + 2{,}6726 * 10^{-3} * log\frac{T}{K} - 0{,}8625 * 10^{-6} * \frac{T}{K} \tag{3.6b}$$

$$\alpha = ln\frac{P_1^s}{P_0} - ln\frac{P_1^s}{P_2^s} * \frac{f(T_1)}{f(T_1) - f(T_2)} \tag{3.6c}$$

$$\beta = \frac{ln\frac{P_1^s}{P_2^s}}{f(T_1) - f(T_2)} \tag{3.6d}$$

SuperPro Designer needs the vapor pressure (in Pa) in terms of Antoine or extended Antoine parameters (A to G). The conversion of the parameters obtained from Hoffmann-Florin equation to the extended Antoine parameters was done using Equations 3.7 (Gmehling et al., 2012).

$$A = \alpha - 7.9151 \times 10^{-3}\beta \tag{3.7a}$$

$$B = \beta \tag{3.7b}$$

$$D = -0.8625 \times 10^{-6}\beta \tag{3.7c}$$

$$E = \frac{2.6726 \times 10^{-3}}{ln10}\beta \tag{3.7d}$$

$$C = F = G = 0 \tag{3.7e}$$

The acentric factor was estimated using Equation 3.8 (Gmehling et al., 2012). The vapor pressure (in Pa) of $T/Tc = 0.7$ ($T = 605.801$ K) was calculated using Equation 3.1a.

$$\omega = -1 - log\left(\frac{P^s}{P_c}\right)_{\frac{T}{T_c}=0,7} \tag{3.8}$$

Liquid/Solid density (kmol/m^3) was estimated using COSTALD method and then adjusting a polynomial curve to the results obtained in the range of $0.25 < T_r < 1$, because SuperPro requires a linear or a polynomial equation as input. The coefficients of the polynomial were used as input for the simulator. The coefficients for Equations 3.9 were obtained from Gmehling et al. (2012).

$$v_s = (\rho^L)^{-1} = v_c \times V_R^{(0)} \times (1 - \omega \times V_R^{(\delta)}) \tag{3.9a}$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \tag{3.9b}$$

$$V_R^{(\delta)} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \tag{3.9c}$$

Gas heat capacity was estimated using Joback group contribution method (Equation 3.10, units shown within the equation). Values for each group were obtained from Harrison and Seaton (1988) and Gmehling et al. (2012). Harrison and Seaton (1988) provided a method to estimate group contributions that were not available in Joback method and then added this particular contribution to Joback equation. It was used to estimate the contribution of the group with phosphorous. Next, a polynomial equation was adjusted to the results obtained and the new parameters units were converted in such a way that the heat capacity unit was J/kmol-K.

$$\begin{aligned} \frac{c_p^{id}}{J/_{mol \cdot K}} &= \left(\sum \Delta_A - 37.93\right) + \left(\sum \Delta_B + 0.21\right) \cdot \left(\frac{T}{K}\right) + \\ &+ \left(\sum \Delta_C - 3.91 \cdot 10^{-4}\right) \cdot \left(\frac{T}{K}\right)^2 + \left(\sum \Delta_D + 2.06 \cdot 10^{-7}\right) \cdot \left(\frac{T}{K}\right)^3 \end{aligned} \tag{3.10}$$

Liquid heat capacity was estimated using Rowlinson / Bond equation (Equation 3.11) and then fitting a polynomial curve to the obtained results. Again, first the value was obtained in J/mol-K and then converted to J/kmol-K.

$$c_P^L = c_P^{id} + 1.45R + 0.45R(1-T_r)^{-1} + \\ +0.25\omega R[17.11 + 25.2(1-T_r)^{\frac{1}{3}}T_r^{-1} + 1.742(1-T_r)^{-1} \tag{3.11}$$

The heat of vaporization (in J/kmol) is calculated in SuperPro Designer by the empirical Equation 3.12. Parameter a was calculated using Equation 3.12b and b using 3.12c (generalized Watson correlation). ΔH^{0}_{vap} (the enthalpy of vaporization at the normal boiling point) was calculated using Chen's correlation (Eq. 3.12d), where $T_{br} = T_{boiling} / T_c$. All temperatures units are in K and pressure in Pa.

$$\Delta H_{vap} = a \times (1 - T_r)^b \tag{3.12a}$$

$$a = \frac{\Delta H_{vap}^{o}}{(1 - T_{br})^b} \tag{3.12b}$$

$$b = \left[0.00264 \times \frac{\Delta H_{vap}^{o}}{R \times T_b} + 0.8794\right]^{10} \tag{3.12c}$$

$$\Delta H_{vap}^{o} = \frac{R \times T_b}{(1.07 - T_{br})} \times (3.978 \times T_{br} - 3.958 + 1.555 \times \log(P_c)) \tag{3.12d}$$

3.2.1.4 Squalene

The constant properties of squalene were obtained from Díaz-Tovar (2011). The acentric factor and the temperature dependent parameters were estimated the same way described in Section 3.2.1.3.

3.2.1.5 Phytosterols

The phytosterols group were represented by β-sitosterol. The properties for β-sitosterol were obtained from Aspen Plus database as presented in Section 3.2.1.2.

3.2.1.6 Tocopherols

Tocopherols properties in SuperPro Designer were represented by the properties of α-tocopherol obtained from Aspen Plus database as presented in Section 3.2.1.2.

3.2.1.7 Proteins and carbohydrates

Proteins in soybean meal were represented by two groups: soluble and insoluble. The properties for each one were taken from a set of studies from the Joint BioEnergy Institute, (available at http://econ.jbei.org or at Intelligen site: http://www.intelligen.com/literature.html), which made the SuperPro files used in their studies available. The same procedure was done for carbohydrates.

3.2.1.8 Ash and other substances

SuperPro Designer v. 9.0 database have a pure component named "Ash", which was used to represent the ashes. For other substances necessary for the simulations, pure substances from SuperPro Designer v.9.0 database were also used.

3.2.2 Oil Extraction

For the production of crude oil and defatted meal, after hulls are removed, the seeds are fed to a solvent extraction operation to separate the oil fraction from the meal. Afterwards, both solid and liquid fractions go through a series of operations so the hexane can be removed. Hexane and water used during the process are recovered and reused. For the process modeled in this work, data for mass and energy balances were obtained from Paraíso (2001). A diagram for this step is presented in Figure 3.1. The process scheme obtained from SuperPro Designer is presented in Figure 3.2. Soybean prepared seeds and hexane in the proportion of 1.2 L (60 ºC) of hexane to 1 kg of soybean seeds (60 ºC) enter the extractor and a cycle is completed at every 45 min. After leaving the extractor with a concentration of 26 wt. % oil and 49 ºC, the miscella is sent to the first stage evaporator. This evaporator uses the saturated vapors from desolventizer-toaster (DT), at 71 ºC, to change heat with miscella and therefore, evaporate a fraction of the hexane content. To do this, an utility was created in SuperPro composed of hexane and water and with heat properties provided by Paraíso (2001). Leaving the first evaporator, with a mass percentage of 65 % of oil and 50 ºC, miscella is heated to 59 ºC with saturated steam at 152 ºC and follows to the second evaporator, where saturated steam at 152 ºC was also used and, with a concentration of 98 % of oil, miscella enters the stripper to evaporate practically all hexane present (ca. 2 wt. %). The stripper operates at 800 mbar and consumes 0.13 kg of superheated steam at 180 ºC and 4 bar per kilogram of oil entering the stripper.

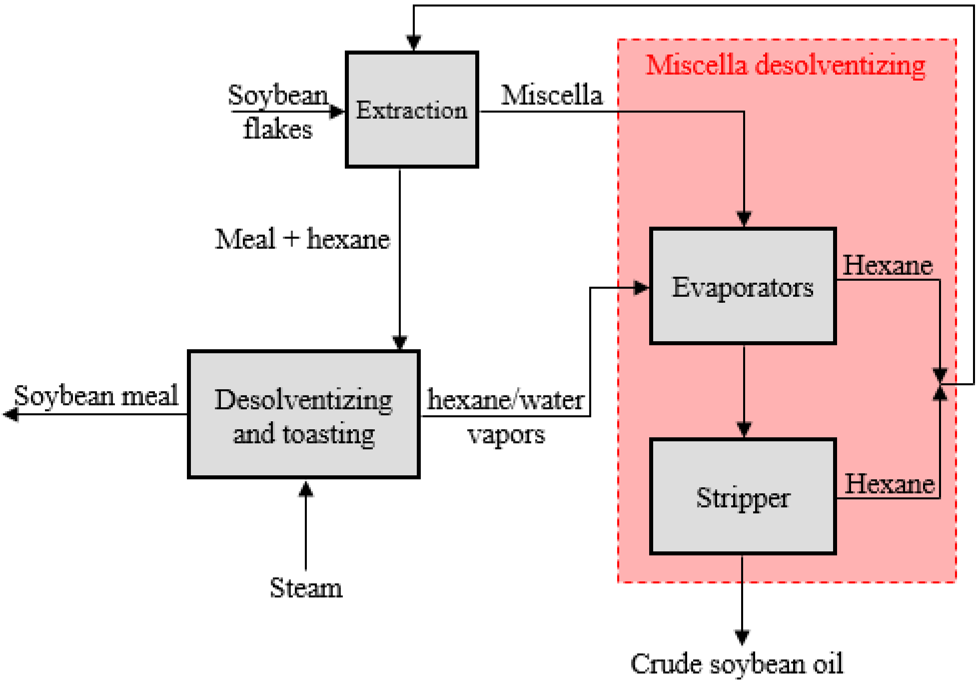
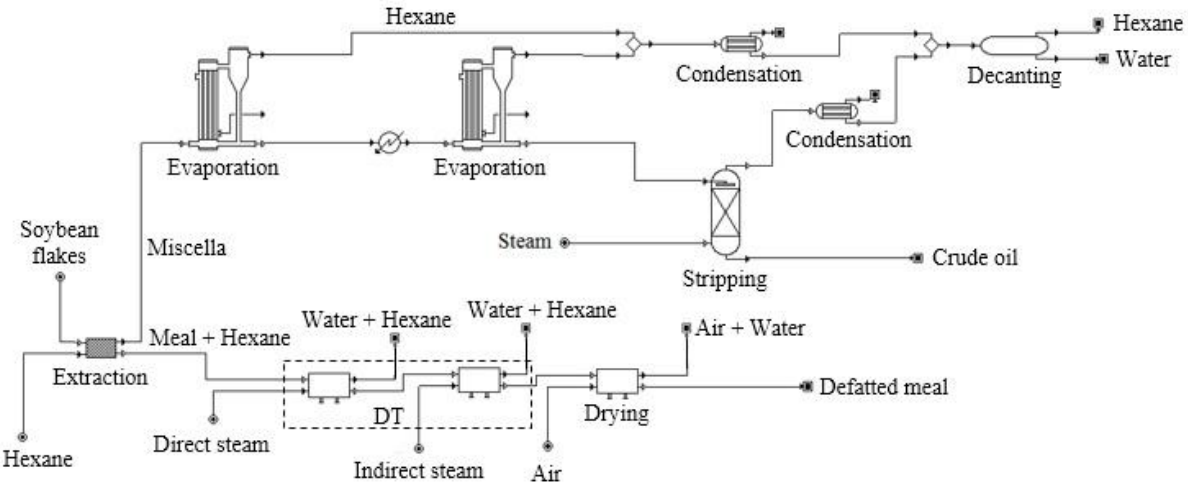


Figure 3.1 – Diagram for soybean oil extraction step

Soybean meal and hexane, the solid fraction, is sent to the desolventizer-toaster (DT). DT was represented in SuperPro Designer by two rotary dryers, where the first represented the direct steam (180 ºC and 2.45 bar) inject at the meal and the second the indirect steam used to evaporate hexane and water from the meal (180 ºC and 10.03 bar). The third rotary drier was used to remove residual water of meal, with air injection, until it reaches 7 % moisture.



Main data:
Extraction operation: $P = P_{atm}$, $T = 60\ °C$, $t_{cicle} = 45\ min$, $V_{hexane}/m_{flakes} = 1{,}2\ L/kg$.
Soybean flakes stream: $\dot{m}_{flakes} = 92.27\ MT/h$.
Miscella stream: $T = 49\ °C$, $m_{oil}/m_{total} = 26\ \%$.
Meal + Hexane stream: $T = 49\ °C$, $m_{meal}/m_{total} = 76\ \%$.

Figure 3.2 – Oil and defatted meal production process

The defatted meal can be further processed into SPC or SPI and crude oil goes to degumming step and then can be processed into biodiesel or refined oil.

3.2.3 Oil Refining

To make soybean refined oil, crude oil must be refined, a purification process which encompasses 4 steps: degumming, neutralizing, bleaching and deodorizing. For all steps saturated steam at 152 ºC, saturated steam at 242 ºC and cooling water entering at 25 ºC and leaving at 30 ºC the heat exchanger were used as utilities. Data for these steps were obtained from Erickson (1995), Shahidi (2005) and Johnson *et al*. (2008).

The refining process starts with degumming, in which the phospholipids (gums) are removed from the oil stream by the addition of water (2 wt. %). Phospholipids solubilize into the water phase and are then separated by centrifugation. A diagram for degumming is presented in Figure 3.3.

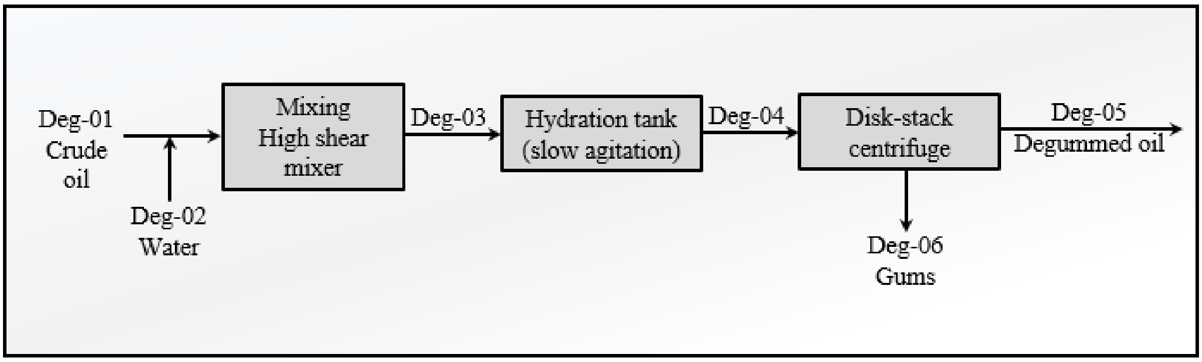


Figure 3.3 – Diagram of the water degumming step of crude soybean oil

At this point, degummed oil can be diverted to biodiesel production and/or continue the refining process.

The next step for refining the oil is the neutralization, in which free fatty acids present in the oil are removed. To degummed oil heated to 80 °C phosphoric acid is added to remove the remaining non-hydratable phospholipids. Next, 1.2 wt. % sodium hydroxide is added to the oil. Free fatty acids present in the oil react with the base to form soap, as presented in Equation 3.9.

$$Linoleic\ acid + sodium\ hydroxide \rightarrow Water + Sodium\ linoleate \qquad (3.9a)$$

$$C_{18}H_{32}O_2 + NaOH \rightarrow H_2O + C_{18}H_{31}NaO_2 \qquad (3.9b)$$

Soaps move to the water layer and are separated from the oil layer by centrifugation. Oil layer is washed with ¼ of oil mass with water to remove excess of soaps. Next, neutralized oil needs to be dried to remove residual water, since during the following bleaching step water may promote undesirable reactions. A block diagram for neutralization step is presented in Figure 3.4.

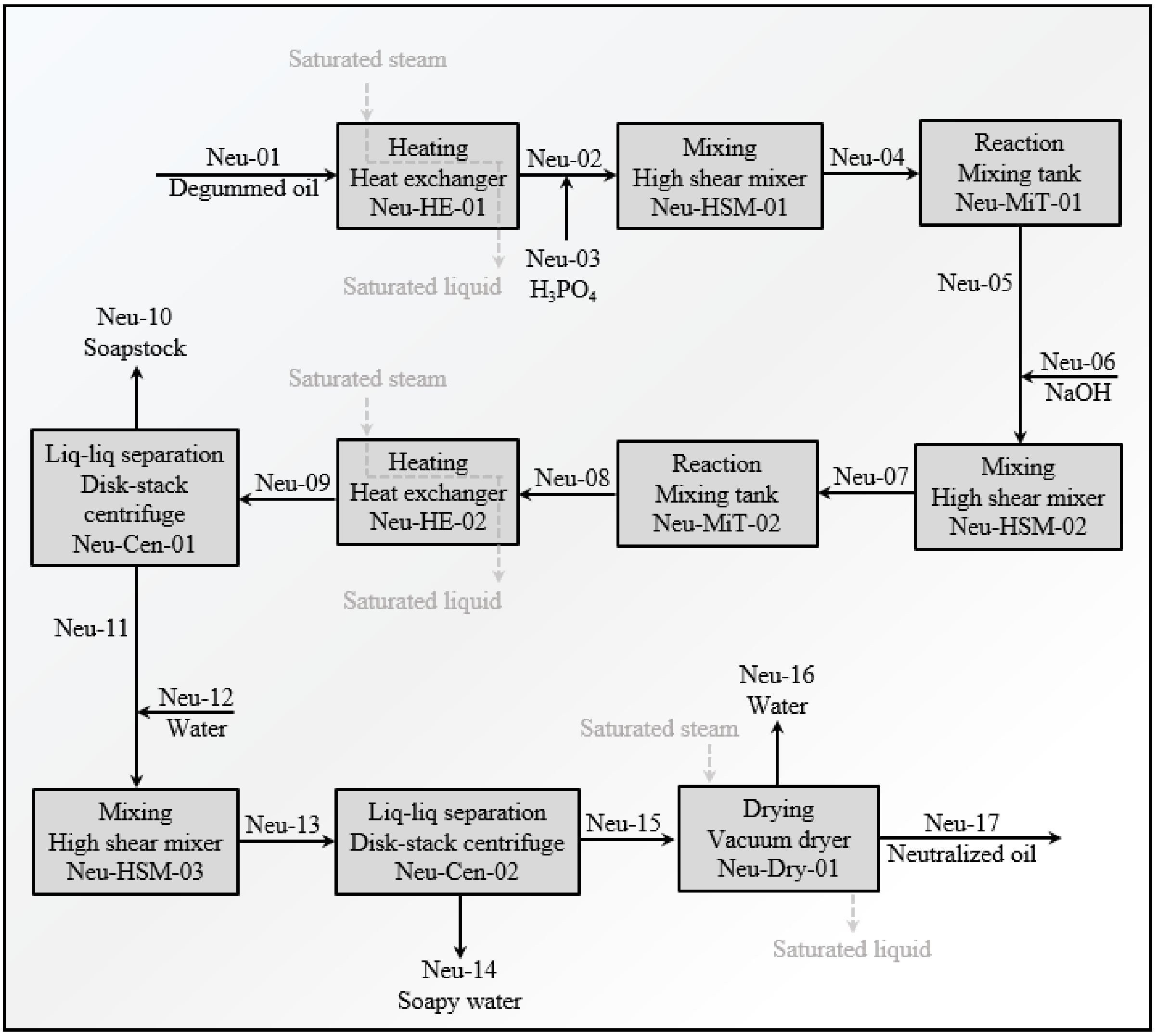


Figure 3.4 – Block diagram representing neutralization step

Next, pigments like chlorophyll and carotenoids and other impurities are separated during the bleaching step. To neutralized oil at 100 °C, 1 wt. % of bleaching earth is added and mixed under 28 mmHg vacuum for 30 min. Next, the mixture is sent to be filtrated. Figure 3.5 shows a block diagram representing the bleaching step.

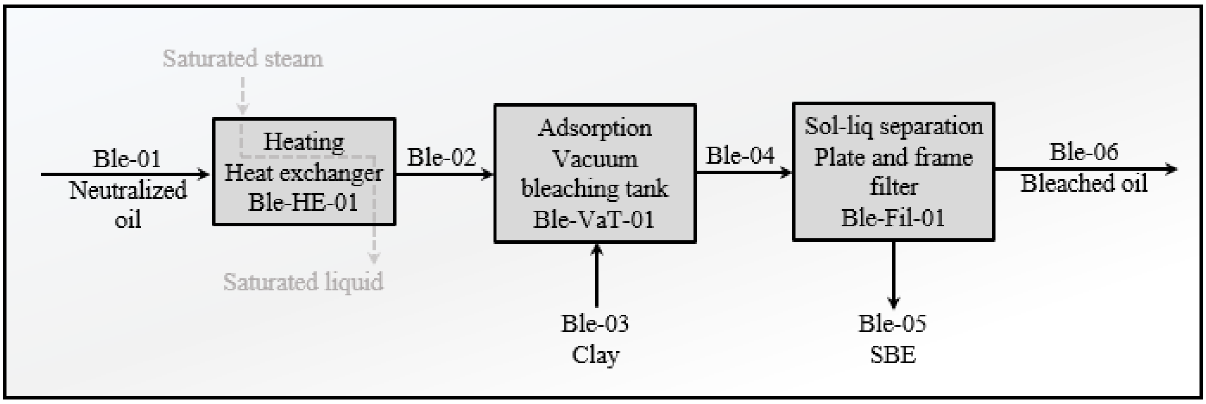


Figure 3.5 – Diagram for the bleaching step of refining process of soybean oil

Finally, odor and flavor components are removed in the deodorization step (Figure 3.6), which consists mainly in a steam stripping operation where superheated sparge steam at 240 ºC removes these volatiles compounds. Figure 3.7 shows the oil refining process scheme obtained from SuperPro Designer v. 9.0.

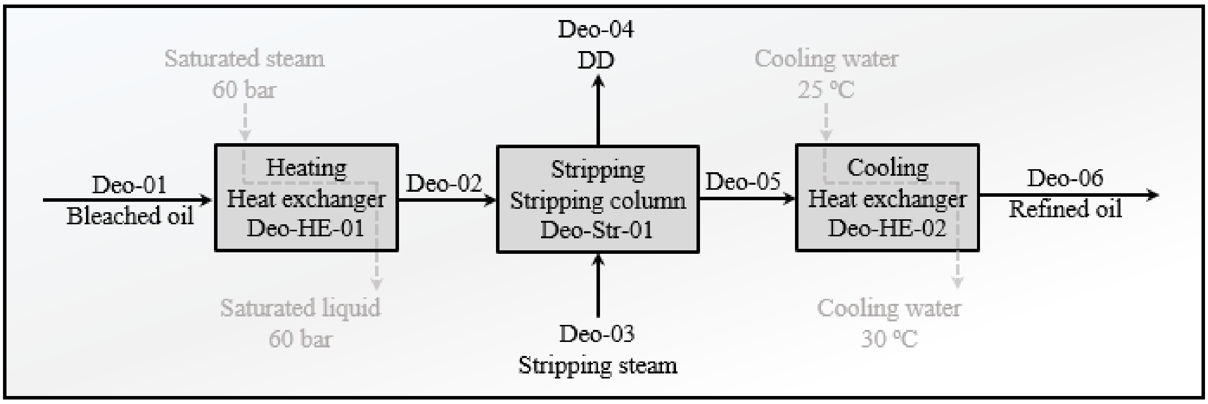
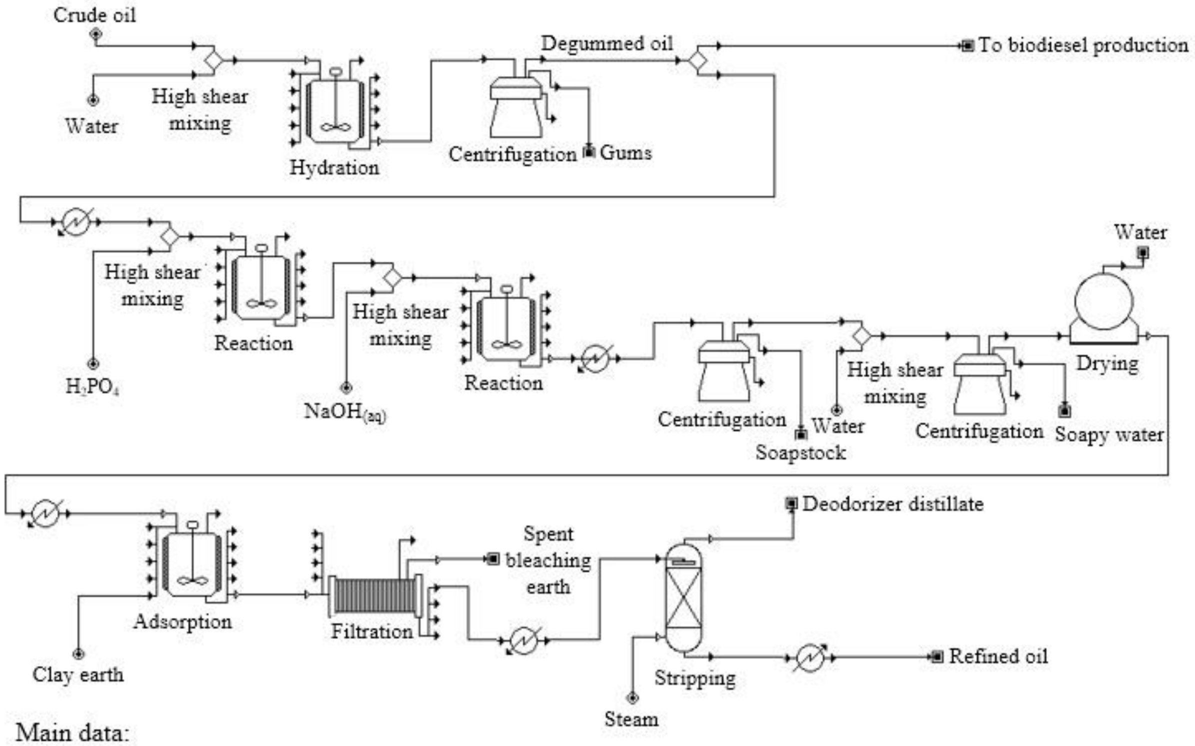


Figure 3.6 – Block diagram for deodorization step simulated in this work



Main data:
Crude oil stream: $\dot{m}_{\text{crude oil}} = 17.99$ MT/h.
Degumming step: $m_{\text{water}}/m_{\text{degummed oil}} = 0.02$.
Neutralizing step: $m_{H_3PO_4}/m_{\text{degummed oil}} = 0.003$, $m_{NaOH(aq)}/m_{\text{degummed oil}} = 0.015$.
Bleaching step: $m_{\text{clay earth}}/m_{\text{degummed oil}} = 0.01$, T = 100 °C, P = 28 mmHg, t = 30 min.
Deodorization step: $m_{\text{sparge steam}}/m_{\text{degummed oil}} = 0.011$, T = 240 °C.

Figure 3.7 – Refining process of soybean oil

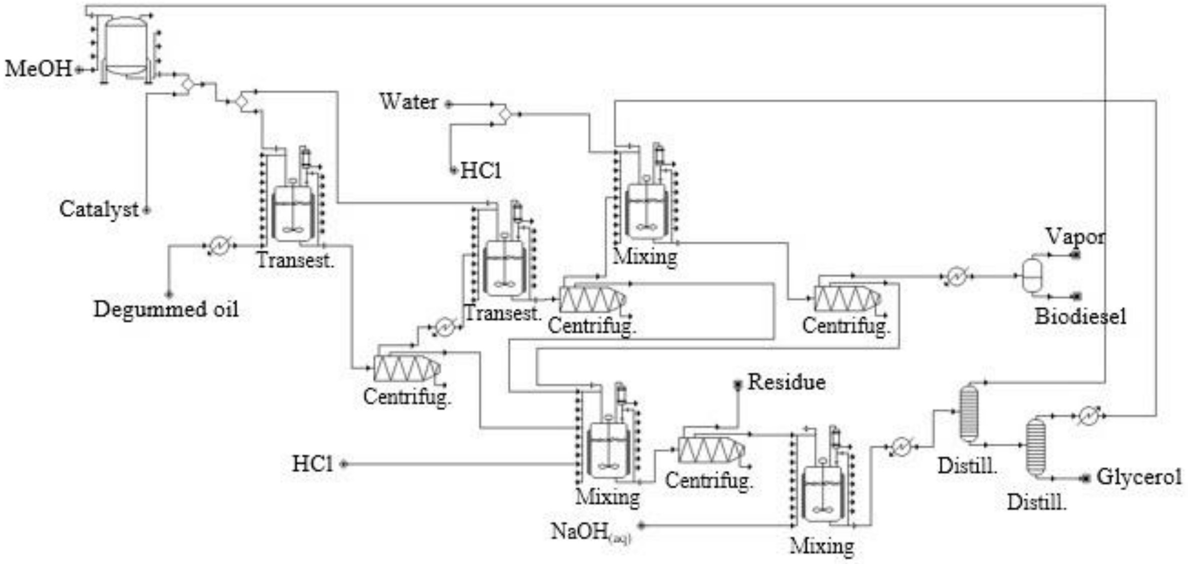
3.2.4 Biodiesel production

The amount of degummed oil diverted to biodiesel production reacts with methanol catalyzed by $NaOCH_3$. The process was based on the study of Haas et al. (2006). SuperPro Designer v. 9.0 already comes with an example for this process. Figure 3.8 presents a summarized version of the flowsheet from SuperPro Designer. The transesterification reaction proceeds in two sequential reactions both at 60 ºC and for 1 hour. The first reactor is fed with 16.95 kg of methanol and 0.28 kg of sodium methoxide for each 100 kg of degummed soybean oil. Next, the mixture is sent to a centrifuge, where the glycerol-rich layer is separated from the oil layer. The oil layer follows to the second reactor, where unreacted degummed oil reacts again with methanol. Methanol and sodium methoxide are added in the same proportion again. A transesterification (Equation 3.10) efficiency of 90% was considered. The mixture of methyl esters, glycerol, unreacted substrates and catalyst exiting the second reactor was sent to a continuous centrifuge.

$$Triolein + 3\ methanol \xrightarrow{NaOCH_3} Glycerol + 3\ FAME \quad (3.10a)$$

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3\ CH_3OH \xrightarrow{NaOCH_3} C_3H_8O_3 + 3\ C_{18}H_{33}O_2CH_3 \quad (3.10b)$$

The crude methyl ester stream was washed with water at pH 4.5 to neutralize the catalyst and convert any soaps to free fatty acids and then centrifuged. The centrifuged stream still contained more water than the allowed. So, it was sent to a vacuum drier where the water content was reduced. The glycerol-rich aqueous streams from the three centrifuges were sent to the glycerol purification section, where glycerol at a concentration of 80 wt. % was obtained. The mixture was treated with a 35 wt. % solution of hydrochloric acid (1.8 wt. % $m_{HCl\text{-}sol}$ / $m_{glycerol\text{-}stream}$) to convert contaminating soaps to free acids, allowing removal by centrifugation. Glycerol stream was then neutralized with 0.1 wt. % NaOH. Next, methanol was recovered from this stream by distillation and recycled into the transesterification operation. At last, glycerol stream was distilled to reduce its water content.



Main data:
Transesterification section: $m_{MeOH}/m_{degummed\ oil} = 0.099$, $m_{catalyst}/m_{degummed\ oil} = 0.0125$. For each reactor: T = 60 °C, t = 1 h, η = 90 %.
Biodiesel purification section: $m_{water}/m_{degummed\ oil} = 0.04$, $m_{HCl}/m_{degummed\ oil} = 0.0017$.
Glycerol purification section: $m_{HCl}/m_{degummed\ oil} = 0.0055$, $m_{NaOH}/m_{degummed\ oil} = 0.0004$

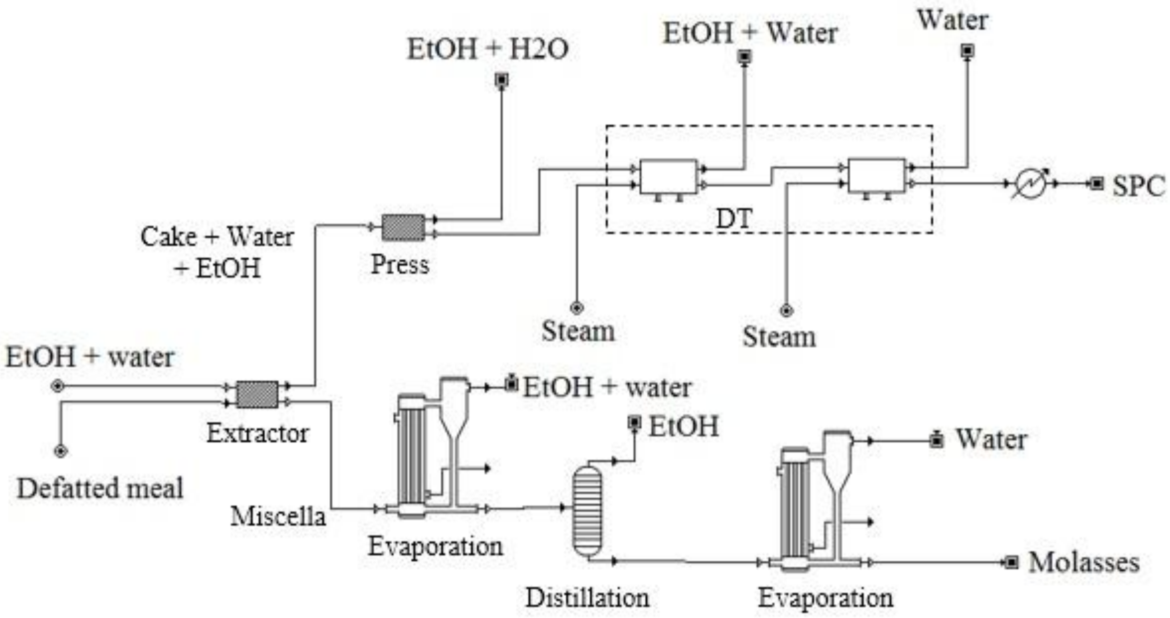
Figure 3.8 – Summarized biodiesel production process

There are different ways to perform energy recovery in SuperPro Designer. In this case, the energy was recovered by the use of a tool provided by the simulator. To do so, the process was first designed with no integration between hot and cold process streams, next an option called “Energy recovery opportunities” can be accessed and the program present matching opportunities for integration. In this case, bottom liquid hot stream from the first distillation operation was used to heat the degummed oil and the stream entering the first distillation operation (composed of water, glycerol and methanol) was heated by the bottom liquid hot stream from the second distillation operation.

3.2.5 SPC production

For the production of soy protein concentrate, defatted soybean meal enters an extractor similar to that used during oil extraction, but instead of hexane, a solution of ethanol and water is used, with 60 % wt. ethanol for 1 hour. A liquid and a solid fraction leaves this extractor. The liquid fraction, as in oil extraction, is also called miscella, but in this case, it is rich in soluble carbohydrates, water and ethanol. The solid fraction has the meal with its protein content concentrated, water and ethanol (Johnson et al., 2008). Figure 3.9 presents the flowsheet for SPC production process developed using SuperPro Designer.

The solid fraction is sent to a press where its moisture can be reduced by 30 percent units. Next, it is desolventized and dried also using similar pieces of equipment as the defatted meal. Ethanol is also recovered and sent back to the process. The protein final concentration is 66 wt. % dmb.



Main data:
Extraction operation : $V_{solvent}/m_{defatted\ meal} = 4.5$ L/kg, $m_{EtOH}/m_{solvent} = 0.6$.
Miscella stream leaving extractor: $m_{solvent}/m_{total} = 0.94$.
Cake + Water + EtOH stream after extractor: $m_{solvent}/m_{total} = 0.6$.
Cake + Water + EtOH stream after press: $m_{solvent}/m_{total} = 0.3$.
Miscella stream leaving extractor: $m_{solvent}/m_{total} = 0.94$.

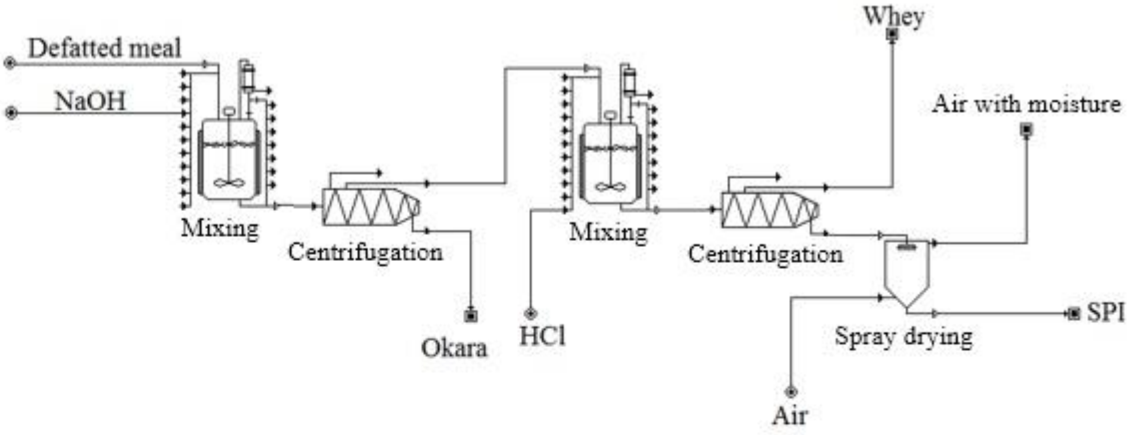
Figure 3.9 – SPC production process

The miscella is first sent to a two stage evaporator. It enters the evaporator with an initial concentration of 5 ºBrix and leaves with 11 ºBrix. Next, miscella is sent to a distillation column were all the alcohol is evaporated and a concentration of 30 ºBrix is achieved. Now, free from solvent, this residue is called soybean molasses. Next, it is sent to another evaporator with four stages in series and its final concentration of 75º Brix is achieved (Johnson *et al.,* 2008; Soccol *et al.*, 2013).

3.2.6 SPI production

The production of soy protein isolates starts with the proteins of the defatted meal being solubilized in a 2 M NaOH solution in the proportion with defatted meal of 1:10. The mixture is kept agitated during 1 hour at 60 ºC. The insoluble fiber, called Okara, is then separated by centrifugation. In this process, 80 % of the proteins are solubilized and okara leaves the centrifuge with 80 % of moisture. Next, the proteins are precipitated using a solution of $HC\ell$ 2 M (30 % (wt/wt)). The residue generated is called whey and contains mainly soluble sugar and some small proteins. The solids concentration of soybean whey is 2 wt. %. Finally, soybean protein isolates are sent to spray drier where air at 157 ºC is used to remove the moisture excess until it reaches a final water concentration of 5 wt. % and 90 wt. % of protein.

Data for this process was obtained from Smith *et al.* (1962), Mitra *et al.* (2010) and Li *et al.* (2014). Figure 3.10 shows the production process of SPI obtained from SuperPro Designer.



Main data:
First mixing: $m_{NaOH\ 2M}/m_{defatted\ meal} = 9.3$.
Second mixing: $m_{HCl}/m_{defatted\ meal} = 2.8$.

Figure 3.10 – SPI production process

3.3 RESULTS AND DISCUSSION

Table 3.1 presents the amount of the starting material required to produce a specific product and the amount of residue generated to produce this product, e.g., it is necessary 1 tonne (1,000 kg) of degummed oil to produce 970 kg of refined oil and this process also generates 70 kg of residues for every tonne of refined oil produced. Residues do not take into account those streams that are reused in the process (e.g. hexane). For each tonne of seed processed, 170 kg of crude oil and 750 kg of meal are obtained. If half of this amount of oil is used to produce biodiesel, the process yields ca. 83.3 kg of biodiesel (0.5 kg degummed oil diverted to biodiesel production / kg degummed oil produced x 170 kg crude oil produced x 0.98 kg degummed oil produced / kg crude oil processed x 1.00 kg biodiesel produced / kg degummed oil processed). On the other hand, if the other half is processed into refined oil, about 80.80 kg of refined oil is produced. The biodiesel process achieves a little higher yield, but it also produces a higher amount of residues, including glycerol into the account. For the production of biodiesel, 108 kg of methanol and 3 kg of catalyst are necessary for every tonne of biodiesel obtained. To produce one tonne of refined oil, 2 kg of NaOH and 10 kg of bleaching earth are necessary. To produce one tonne of SPC, about 1.34 tonne of defatted meal and 5,960 kg of ethanol 60% are necessary, whilst to obtain a tonne of SPI, 77.6% more defatted meal is necessary and for each tonne of SPC and SPI produced, 390 and 26,010 kg of residues are generated respectively. The SPI production process achieves lower yields and requires 22,120 kg of NaOH (0.02 mol/L) and 6,770 kg of HCℓ (0.02 mol/L), producing much more residues, but it also has a higher market value that makes the process viable, although environmental aspect must be taken into account with much more emphasis.

For the production of each tonne of defatted soybean meal it is necessary ca. 30 kg of direct superheated steam at 180 ºC and 0.98 bar, 119 kg of direct superheated steam at 180 ºC and 2.45 bar and 12 kg of indirect saturated steam at 180 ºC. These values agree with the ones obtained from (Paraíso, 2001). Table 3.2 presents the utilities demanded for the production of biodiesel or refined oil. It can be seen that the production process of biodiesel consumes both more cooling water and steam than the refining one. To produce 1 kg of biodiesel, 51.97 kg of cooling water and 0.38 kg of steam are necessary, whereas 15.58 kg of cooling water and 0.20 kg of steam are required to produce 1 kg of refined oil.

Table 3.1 – Amount of products and residues generated during soybean processing

(Product / Start material) or (Residue / product)	Ratio (kg / kg)
Defatted meal / Dehulled seed	0.75
Crude oil / Dehulled seed	0.17
Degummed oil / Crude oil	0.98
Gums / Degummed oil	0.04
Biodiesel / Degummed oil	1.00
Glycerol / Biodiesel	0.11
Residues (not included glycerol) / Biodiesel	0.04
Refined oil / Degummed oil	0.97
Residues / Refined oil	0.07
SPC / Defatted meal	0.75
Molasses / SPC	0.39
SPI / Defatted meal	0.42
Residues / SPI	26.01

Table 3.2 – Utilities demanded for the production of biodiesel and refined oil

Cooling water (kg of utility / kg product)		Saturated steam (152 ºC) (kg of utility / kg product)		Saturated steam (242 ºC) (kg of utility / kg product)	
Biodiesel	Refined oil	Biodiesel	Refined oil	Biodiesel	Refined oil
51.97	15.58	0.11	0.03	0.27	0.16

3.4 CONCLUSIONS

Soybean processing facilities have more than one alternative for processing the material into a product. The choice on which and how much of each one of the products should be made need to be based both in market demand and in process (which turns out to be economic) measures. The aim of this chapter was to model a soybean crushing, refining and biodiesel production facility and analyse mass and energy demands for each possible alternative of production (biodiesel or refined oil, soy protein concentrate or soy protein isolate). It was possible to observe that the yields of producing biodiesel and refined oil were not much different, but biodiesel production generates much more residues. As for the meals, SPI production generates higher amounts of residues and yields lower quantities of the final product when compared to SPC. Moreover, this model can be the first step of a tool for helping processing decisions, making possible to vary the amount of raw material that can be diverted for the production of different products, giving the flexible enterprise the advantage to better adapt to changes in demands that occur in the market. Additional analysis, such as the degree of flexibility that this facility should have and an economic analysis could make this tool more precise and complete. Furthermore, a sensitivity analysis on main process parameters could be conducted. Bearing the exposed in mind, Chapter 4 is dedicated to analyse the influence of the variation of degummed oil diverted to biodiesel or refined oil production and assess the possibility of using some residues generated during process or the biodiesel produced as fuel in a coupled cogeneration system to generate the thermal and electrical energy required for the whole process.

4 ASSESSING ENERGETIC AND AVAILABLE FUELS DEMANDS OF A SOYBEAN BIOREFINERY PRODUCING REFINED OIL, BIODIESEL, DEFATTED MEAL AND POWER

4.1 INTRODUCTION

In this chapter, a soybean processing facility producing soybean defatted meal, refined oil and biodiesel from degummed oil is simulated varying the amount of degummed oil diverted to biodiesel production sector. The fraction of degummed oil diverted to biodiesel production process has impact both on thermal and electrical energy demands of the entire process, and this influence in analysed in details here. To fulfill these energetic demands, different cogeneration systems and fuels are considered and different scenarios are evaluated.

It is worth mentioning that, as cogeneration systems were studied in this part of the work, steam of different characteristics is used as hot utility here in Chapter 4 and differs from that of previous chapter. Instead of using a low pressure saturated steam at 152 ºC (standard value at SuperPro Designer v. 9.0), a low pressure steam at 2.5 bar and 127.41 ºC was used, so steam energy could be better utilized by the turbine and still fulfill the process requirements, and high pressure saturated steam at 60 bar and 278.58 ºC was used instead of 242 ºC and 34.67 bar.

4.2 DEVELOPMENT

The used methodology and the conducted analyses are presented in the form of an article.

Assessing energetic and available fuel demands from a soybean biorefinery producing refined oil, biodiesel, defatted meal and power

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Abstract

Soybean processing facilities can produce various products, readily fitting in a biorefinery concept. In addition, they can also produce their own energetic needs by using their own residues and/or products. The aim of this study was to assess the relationship among the availability of fuel, process energetic demands and different market situations in a soybean processing facility. It was observed that soybean straw or a combination of straw, hulls and biodiesel could supply all the thermal and electricity demands of the process and even produce electricity surplus. Using an extraction-condenser turbine operating at 60 bar and 480 ºC to fulfill energetic demands from the whole process using only one type of fuel, 18.33% to 19.41% of the total straw brought from the field would be necessary, depending on the amount of degummed oil diverted to biodiesel production. Furthermore, the maximum electricity surplus this facility could produce is 0.95 kWh/kg of processed soybeans.

Keywords: soybean, biorefinery, cogeneration, bioenergy

4.2.1 Introduction

Soybean processing facilities, besides producing crude oil and defatted meal, can also further process these products to generate other products with increased commercial value. Furthermore, it is also possible to make use of the residues generated during the process as new products for further operations. Therefore, these facilities are good candidates for a biorefinery concept application – the straw, often left in the field, can be partially brought to the industrial site and used to generate energy to supply the process needs and, possibly, a surplus of electrical energy, that can be sold to the grid, if a cogeneration system is coupled to the process. The same destination can be given to the hulls, removed from the seeds during the oil extraction process. Furthermore, from the degummed oil obtained after extraction and degumming soybean oil, there is the possibility of producing refined oil or biodiesel.

Furnaces and boilers used to provide energy in industrial processes generally use petroleum-derived fuels. However, if residues are used as fuel in the furnaces and boilers, this could lower, or even, release the need to import energy from external sources, such as petroleum-derived fuels or electricity from the grid. Moreover, cogeneration systems reduce greenhouse gas emissions and increase thermal efficiency when compared with separated production of electrical and thermal energies (typically 49% for separated energy production and 75% for cogeneration systems) (Siirola and Edgar, 2012). Furthermore, if an excess of electrical energy is produced, the surplus could be sold to the grid, inverting the role of the industry with respect to the grid, from a consumer to a supplier. This could not only reduce costs, but increase profits and eliminate the dependence on external sources and its variations on offer, as what happened worldwide in the 1970’s petroleum crisis and in the electrical energy crisis in Brazil in 2001 and 2015, when the electrical energy supply became scarce and costs increased significantly.

A good and consolidated example of self-sufficiency in energetic terms is the sugarcane industry. Much research deals with the production of bioethanol, alone or coupled with sugar, in a sugarcane crushing facility, where bagasse, a residue generated during the process, is burned in a boiler, producing enough thermal and electrical energy to meet the whole energetic demand process and, depending on the cogeneration system characteristics, an electricity surplus can be obtained and sold to the grid (to cite just a few: Arshad and Ahmed, 2016; Dias et al., 2013, 2011; Ensinas et al., 2007). Moreover, sugarcane facilities that produce sugar coupled with ethanol have the advantage of being flexible to a certain degree as, in addition to having one more product, the amount of sugarcane juice diverted to each production sector can be varied. This makes the enterprise less susceptible to crises in a given market, as these products belong to different markets. Thus, depending on demand for each product at a certain period, a larger amount of one product can be produced at the expense of a reduction in the other.

Concerning soybean processing, the use of straw, hulls and degummed oil for energy production, either in the form of liquid fuel or to be directly burned can be found in the literature. Boateng et al. (2010) studied the thermochemical conversion by fast pyrolysis of soybean straw to produce bio-oil, biochar and combustible gas at the same time. Chen et al. (2010) produced hydrocarbon oil by co-deoxy-liquefaction of soybean straw mixed with sunflower oil. Biohydrogen production from soybean straw using anaerobic mixed bacteria after biomass pretreatment was studied by Han et al. (2012). Mladenović et al. (2009) used soybean straw bales for combustion to produce thermal energy for greenhouse and office heating. Research concerning the utilization of soybean hulls for energy production purposes (fuels included) is concentrated on using this residue for bioethanol production (Hickert et al., 2014; Long and Gibbons, 2013; Mielenz et al., 2009; Rojas et al., 2014; Schirmer-Michel et al., 2008). As for biodiesel production from soybean oil, various papers can be found in the academic literature (Anitescu et al., 2008; Deshpande et al., 2010; Du et al., 2004; Go et al., 2012; Granjo et al., 2015; Haas et al., 2006; Lin and Lin, 2006).

Most of this research studies isolated processes, outside the context of a biorefinery (with the exception of Granjo et al. (2015)). Few consider the energy demand required for the process under study and/or a way to provide this energy. Granjo et al. (2015) and Haas et al. (2006) are the ones that consider the energetic demand for the production of biodiesel, but Granjo et al. (2015) consider the energetic demand from the seed preparation step to biodiesel production, while Haas et al. (2006) consider the energetic demand starting from the degummed oil as feedstock. However, they do not consider a way to provide this energy. Boateng et al. (2010) and Deshpande et al. (2010) use part of the product to provide energy for the studied process. Boateng et al. (2010) use all the combustible gas and part of bio-oil produced to generate the required energy for the process. Deshpande et al. (2010) consider the possibility of using part of the biodiesel produced as a fuel to supply the energy required for the supercritical transesterification of soybean oil to biodiesel.

This work aims to assess the relationship among fuel availability, process energetic demands and different market situations in a soybean plant facility in which refined oil, defatted meal, biodiesel and electrical energy are produced. The coupled cogeneration system uses residues and/or one product from the process as fuel. Furthermore, the process is flexible in the sense that it allows a variable amount of feedstock to be diverted to the refined oil or to the biodiesel production, according to the market needs. Different scenarios are analysed in order to evaluate if the energetic demands of the plant could be supplied by the proposed fuels and even if a surplus of electricity generation is available, bringing to the soybean industry reality a flexible and energetic self-sufficient process which is very well established in the sugarcane industry. To the best of the authors' knowledge, no previous study with these characteristics has been previously conducted in the literature.

4.2.2 Methodology

For modeling and simulation of oil extraction and refining, biodiesel, meal and energy production, the commercial software SuperPro Designer v. 9.0 was used. Data for process modeling was obtained from the academic literature and technical reports and is better described throughout the text.

For the process simulation, it was assumed a soybean crushing facility with a capacity of processing 2,500 metric tons (MT) of raw seed per day. An overall view of the process simulated is presented in Figure 4.1, where only the main streams are presented. Soybean straw is usually left in the field, and it is estimated that the amount generated is equivalent to the amount of soybean seeds produced (Reddy and Yang, 2009). The process can be divided into three main stages – oil extraction and degumming, oil refining and biodiesel production. Usually, technical texts concerning soybean oil extraction and refining allocate the degumming operation as part of the refining process. However, in this paper, it was chosen to include the degumming step into the set of operations called oil extraction, because from the degummed oil two products can be produced: refined oil and biodiesel. In addition to the soybean main process, there is a cogeneration system with the main purpose of supplying steam and electricity to the process.

The aim of the rest of this section is to better explain each one of these steps.

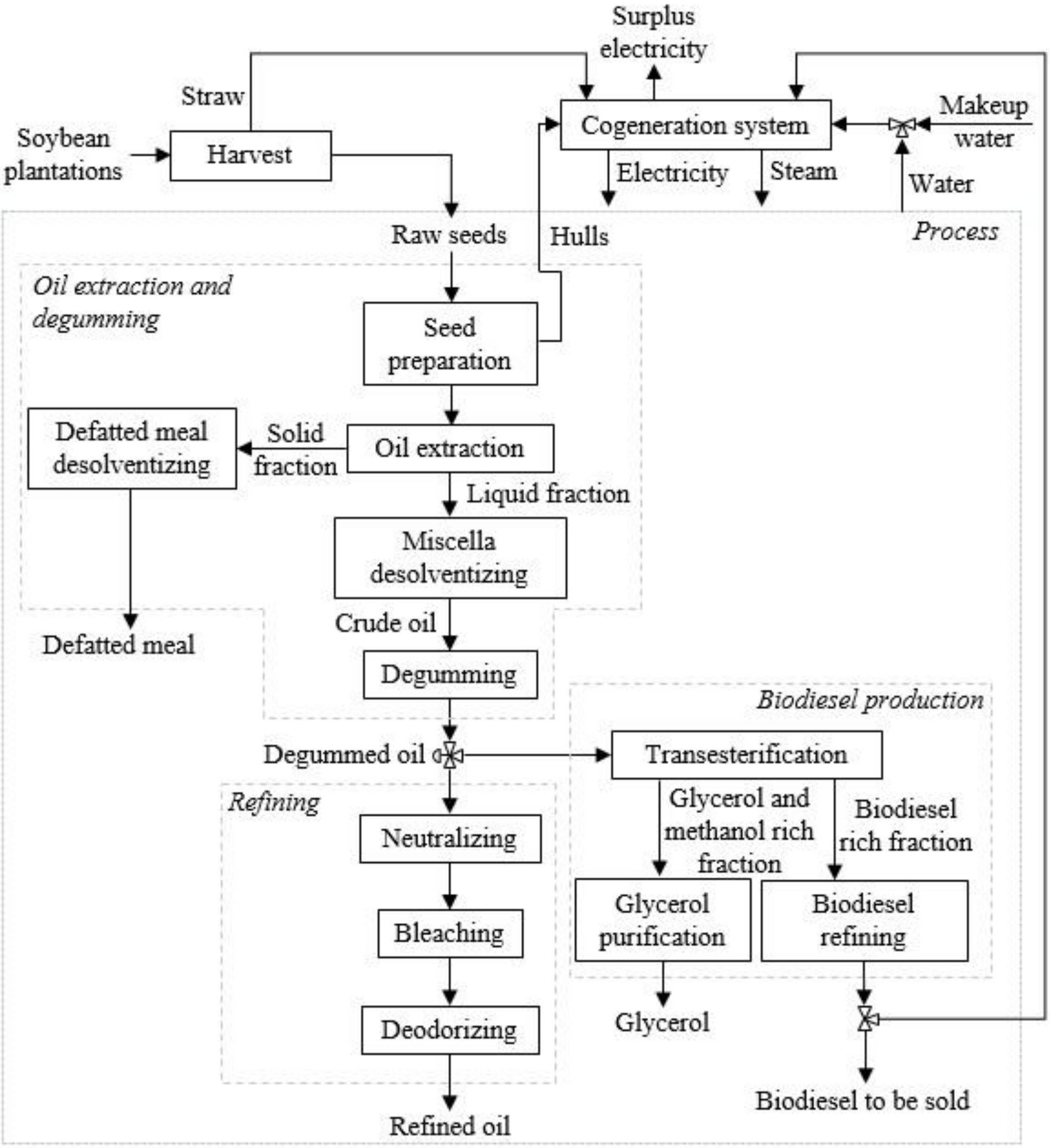

Figure 4.1 – Overall view of the soybean processing plant presenting only the main streams

4.2.2.1 Soybean degummed oil and meal production

The method for oil extraction used in this work was direct solvent extraction using hexane as a solvent, the most common method used in industry nowadays. Data for oil extraction and defatted meal production was obtained mainly from Erickson (1995) and Paraíso (2001). Soybean seed, hulls, crude oil and defatted meal composition and some mass flow information were obtained from Medic et al. (2014), Erickson (1995) and Liu (1997).

The production of crude soybean oil and defatted meal can be divided into four main stages: (1) Seed preparation. (2) Oil extraction. (3) Miscella desolventizing and (4) Meal desolventizing.

Seed is properly prepared for extraction by means of scalping, drying, tempering, cleaning, cracking, dehulling, conditioning and flaking the seeds (Erickson, 1995). This set of operations allows the oil to get more available during the extraction operation and results in higher yields. The drying operation requires a considerable amount of heat to raise the airflow temperature used to carry part of the humidity presented in the seeds, which is usually at 13 % (m/m) and needs to reach ca. 10 % (m/m). The equipment usually used to accomplish this is a conventional gas or oil fired drier.

In this work, the scalping operation was removed from the preparation process and the cleaning step was placed before drying, in an attempt to save energy, since with the previous removal of trash less mass goes to the dryer (as done by (Granjo et al., 2015)). Figure 4.2 presents the flowsheet created in SuperPro Designer v.9.0 for the simulation of the seed preparation sector of the soybean plant.

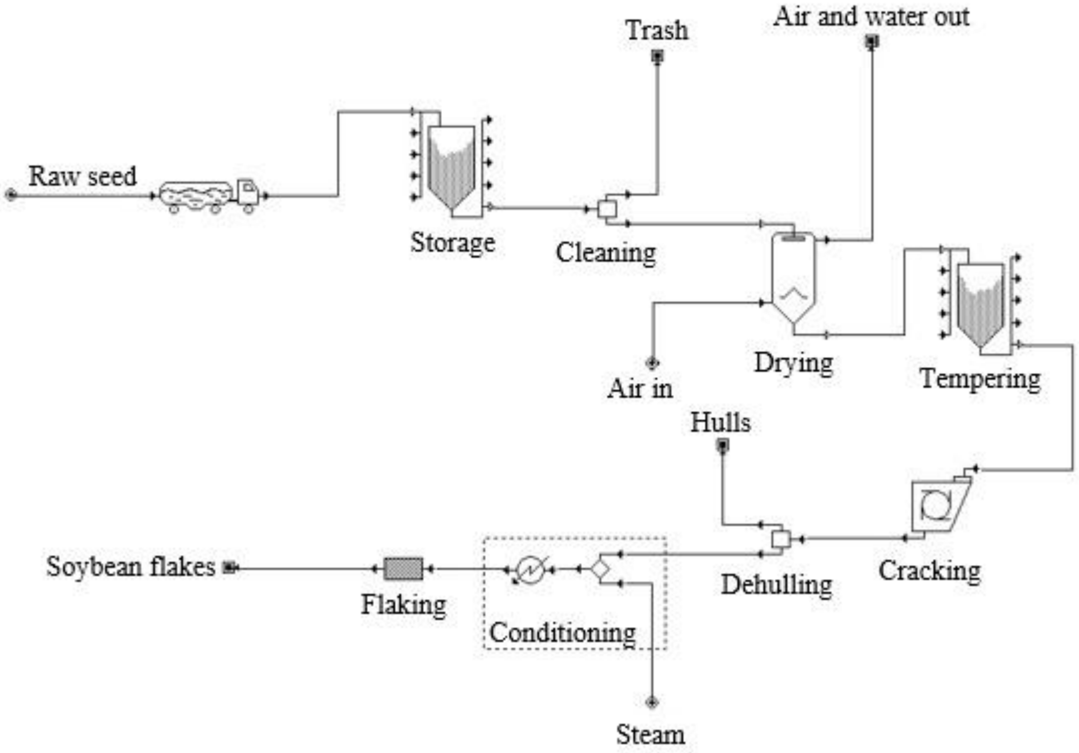

Figure 4.2 – Flowchart diagram for the soybean seed preparation step

Afterwards, soybean flakes and hexane are put into the extractor for the extraction process at a proportion of 1.2 L of hexane per kilogram of soybean (Figure 4.3).

The operation generates two output streams: one liquid rich in oil called miscella, and a solid one rich in proteins called meal. These streams then pass through a series of operations for desolventizing and recovery of hexane, which is further reused in the process.

In order to obtain crude soybean oil with a residual hexane concentration of ca. 1300 ppm (maximum), miscella leaves the extractor with 25% in mass of oil and at 49 ºC and goes through a 2-stage evaporation and stripping operation.

Meal with 20-35 % (m/m) of hexane is placed into a piece of equipment called a desolventizer-toaster where direct and indirect steam is injected to evaporate the solvent and inhibit antinutritional factors found in soybean meal. Afterwards, the meal passes through a dryer where it leaves with approximately 7 (m/m) % of moisture.

Once more, in order to save energy, some heat integration is present in the oil extraction stage: the miscella in the first evaporator is evaporated using vapors at about 71 ºC which leave the desolventizer-toaster (water + hexane) and the inlet stream of the second evaporator is heated with crude soybean oil that leaves the stripping operation.

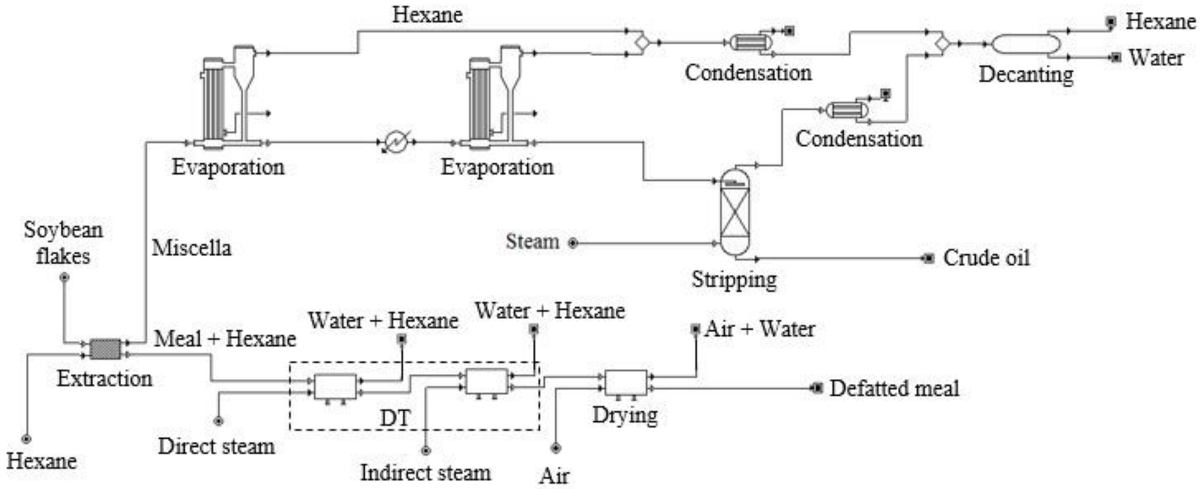

Figure 4.3 – Flowchart diagram for crude oil and meal production

4.2.2.2 Soybean oil refining

Crude soybean oil contains many undesirable impurities including free fatty acids (FFAs), phospholipids, volatile/odoriferous compounds and dark pigments, which are removed in the refining process. Refining encompasses the operations of degumming, neutralization, bleaching and deodorizing. The degumming step aims to remove phosphatides (also known as gums) using hydration and centrifugation processes. Removing these components from crude soybean oil is important to improve its physical stability and facilitate further refining (Shahidi, 2005; Singh, 2010). Neutralization removes FFAs by chemical reaction between the FFAs and sodium hydroxide. Phosphoric acid can also be added to remove the non-hydratable phosphatides that were not removed in the degumming operation. If phosphatides removed during degumming are not used to produce commercial lecithin, H_2PO_4 can also be added to the degumming step. During the neutralization step, trace metals and saponifiable matter are removed too. This step ends by vacuum drying the oil, eliminating any residual water left in the oil. Bleaching eliminates pigments by adsorption into the micropores of an activated earth, under vacuum. Deodorizing removes or reduces odoriferous volatile compounds by vacuum steam distillation at an elevated temperature of 200-250 °C and 400 Pa vacuum (Singh, 2010). The hot refined oil that leaves the vacuum steam distillation is used to heat the bleached oil entering the same operation.

Crude oil refining was modeled (Figure 4.4) using data from Erickson (1995), Sahidi (2005) and AOCS Lipid Library site.

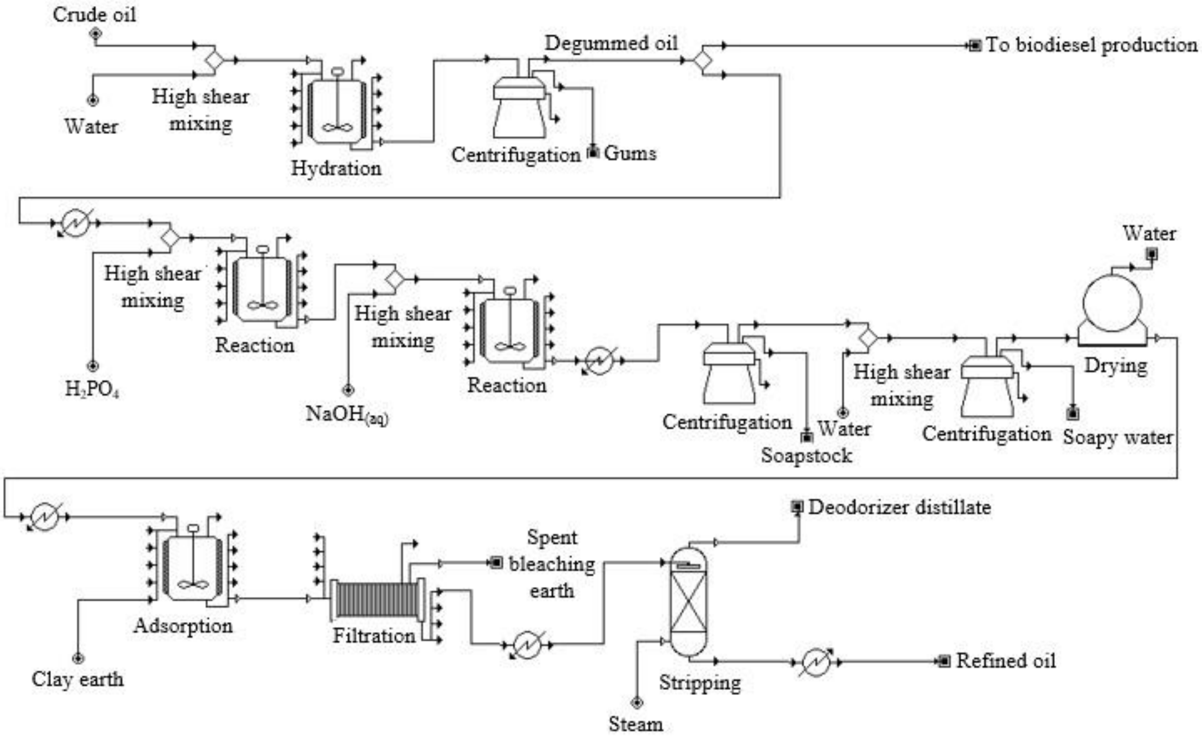

Figure 4.4 – Flowchart diagram for refined oil production

4.2.2.3 Biodiesel production

A few routes can be chosen for biodiesel production. In this work, biodiesel was produced from degummed oil using methanol and sodium methoxide as catalyst. First, degummed soybean oil undergoes transesterification with an excess of methanol in the presence of $NaOCH_3$. Two streams are obtained after centrifugation: one rich in fatty acid methyl esters (biodiesel) and the other rich in glycerol. Then, biodiesel is further refined and glycerol purified. SuperPro Designer v.9.0 already comes with an example of biodiesel production from degummed soybean oil with data based on Haas et al. (2006). The process also takes into account energy integration opportunities. Energy integration can be done adding heat exchange operations directly to the flowsheet or, as was done in this case, from a heat recovery network the simulator provides. In this case, the process is designed with no integration between hot and cold process streams. Afterwards, an option called “Energy recovery opportunities” can be accessed and the program presents matching opportunities for integration. In this study, modeled process (Figure 4.5) was based on the cited example, with modifications in mass flows.

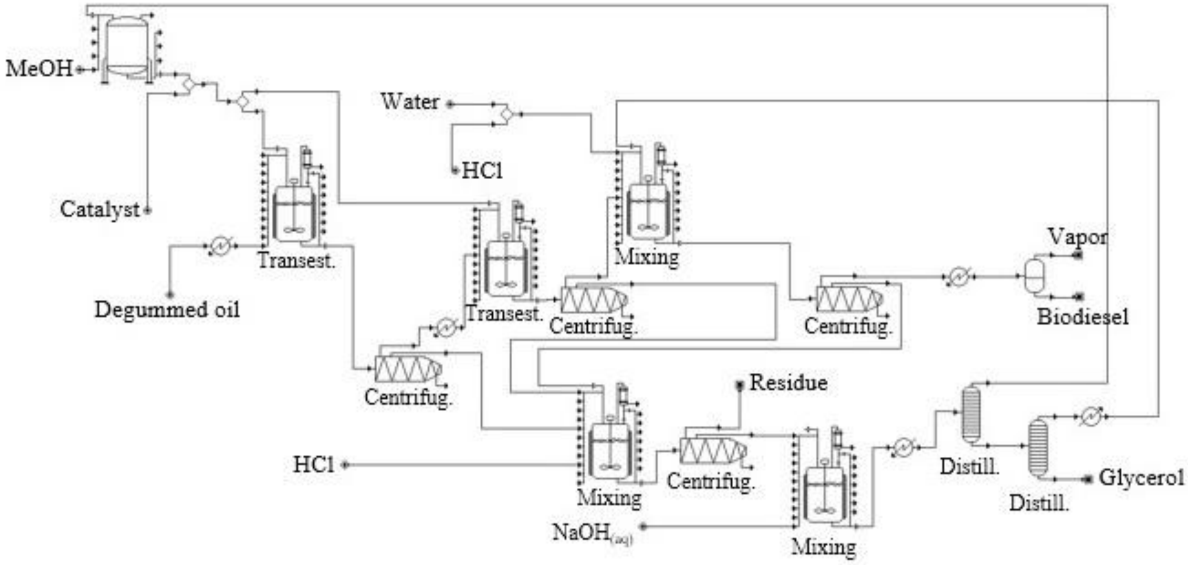

Figure 4.5 – Main operations for the production of biodiesel from soybean degummed oil

4.2.2.4 Influence of degummed oil division on integrated process energetic demand

In the process modeled, a variable amount of degummed oil can be diverted to biodiesel production and the rest is processed to refined oil, according to the market needs. Different fractions of degummed oil diverted to biodiesel production were simulated (cases studies 1-5, Table 4.1) in order to assess its influence on the energetic demand of the process.

Table 4.1 – Division of degummed oil in the different case studies

Case study	Percentage of degummed oil diverted to refining operations
Bio-0	100% (no biodiesel production)
Bio-25	75%
Bio-50	50%
Bio-75	25%
Bio-100	0% (no refined oil production)

4.2.2.5 Fuel composition

Soybean straw, soybean hulls and soybean biodiesel were evaluated as boiler fuels. Table 4.2 presents the elemental composition of these fuels. Based on this composition, SuperPro Designer v. 9.0 estimated the fuel lower heating value (LHV).

Table 4.2 – Elemental composition of the fuels used in this work

Element / % (m/m)	Fuel		
	Soybean straw [a]	Soybean hull [b]	Soybean biodiesel [c]
C	44.53	39.86	76.960
H	5.18	5.88	11.850
N	0.87	0.79	1.697
S	0.00	0.08	0.017
O	38.89	41.17	9.410
Ash	3.26	4.72	0.040
Water	7.27	7.50	0.026

(a) Data from Boateng et al. (2010).

(b) Data from ECN Phyllis2 database (2012).

(c) Data from Lin and Lin (2006). As the total was not equal to 100%, the difference was assumed to be nitrogen, an element not reported by Lin and Lin (2006). Moreover, ash was equal to zero and carbon residue equal to 0.04. Here, this number was accounted as ash.

4.2.2.6 Estimation of furnace fuel demand

The drier used in the drying operation of the seed preparation step usually uses a furnace fueled with gas or oil derived from petroleum. The possibility of using a furnace fueled with soybean straw, soybean hulls or biodiesel was analysed. To calculate the amount of fuel required to evaporate the water, Equations 4.1 and 4.2 were used (Maier and Bakker-Arkema, 2002).

$$Fuel\ consumption = \frac{100 * Burner\ capacity}{AE * E_{ff}} \tag{4.1}$$

Where, fuel consumption is expressed in kg/h; AE is the available energy for the particular fuel in BTU/kg and E_{ff} is the combustion efficiency in %.

$$Burner\ capacity = 1.1 * AV * (T_f - T_0) \tag{4.2}$$

Where Burner capacity is the amount of energy needed from a burner to raise the air temperature to a certain level and is given in BTU/h; AV is the total airflow rate in cubic feet per minute; T_f is the final air temperature after the burner in ° F; T_0 is the initial air temperature before the burner in ° F.

Using air density value at 25 ºC, the total airflow rate was assumed to be 396,619.29 cfm (221.63 kg_{air} / h = 2.16 kg_{air} / MT_{seed} – values adapted from Granjo et al., 2015). T_f and T_0 were considered 140 ºF (60 ºC) and 77 ºF (25 ºC) (Erickson, 1995). The combustion efficiency was assumed as 70% for all the fuels analysed. The available energy value used was the lower heating value of each fuel (LHV). LHV for soybean biodiesel was found in the literature with value of 37.68 MJ/kg (Mehta and Anand, 2009). To calculate the LHV of soybean straw and hulls, the elemental composition presented in Table 2 and the Equations 4.3 to 4.6 obtained from the U.S. Department of Energy – Biomass Energy Data Book were used (U.S. Department of Energy, 2011), where LHVp,w is the low heating value at constant pressure for wet biomass in MJ/kg, HHVp is the high heating value at constant pressure for dry biomass, M is the moisture content of the biomass in decimal wet mass fraction, HHV is the high heating value at constant volume for wet biomass, HHVd is the high heating value at constant volume for dry biomass, X is the mass fractions (mass percent in dry basis) for Carbon (C), Hydrogen (H), Sulfur (S), Nitrogen (N), Oxygen (O), and ash content (ash).

$$LHV_{p,w} = HHV_p * (1.0 - M) - 2.443 * \mathrm{M} \tag{4.3}$$

$$HHV_p = \mathrm{HHV} - 0.212 * X_H - 0.0008 * (X_O - X_N) \tag{4.4}$$

$$HHV = HHV_d * (1 - \mathrm{M}) \tag{4.5}$$

$$HHV_d = 0.35\, X_C + 1.18\ X_H + 0.10\ X_S - 0.02\ X_N - 0.10\ X_O - 0.02\ X_{ash} \tag{4.6}$$

4.2.2.7 Cogeneration systems

In order to evaluate if the process modeled could be energetically self-sufficient, two main cogeneration systems were studied, one using two coupled backpressure steam turbines (BP) (Figure 4.6) and other using an extraction-condenser steam turbine (EC)

(Figure 4.7). Soybean hulls, soybean straw and biodiesel were evaluated as combustible matter to feed the boiler. For the soybean straw, it was considered that half of the mass generated would be brought to the facility and half left in the field for soil conservation.

The boiler was assumed to generate steam at 480 ºC and 60 bar. As some operations of the process require steam with high temperatures and pressures, part of the high-pressure steam produced in the boiler was directly sent to the process. The process also requires saturated steam at 10.03 bar and 2.5 bar. Therefore, in the backpressure turbines configuration (Figure 4.6), steam leaving the first turbine is at 10.03 bar and the amount required by the process is then diverted to it. Remaining steam is sent to the second turbine, from which exhaust steam at 2.5 bar is removed. Part of this steam is used in the process and the remaining is condensed. Analogous configuration is made in the extraction-condenser steam turbine configuration (Figure 4.7). Table 4.3 shows equipment efficiencies adopted for the cogeneration systems and Figures 4.8 and 4.9 present the scheme obtained from the SuperPro Designer for these cogeneration systems, respectively.

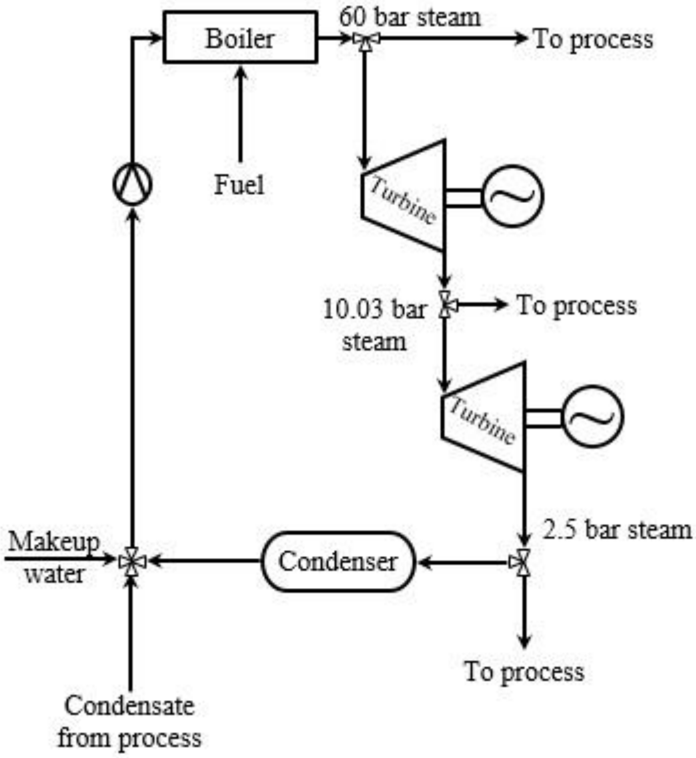

Figure 4.6 – Schematic representation of the cogeneration system where two backpressure steam turbines are used

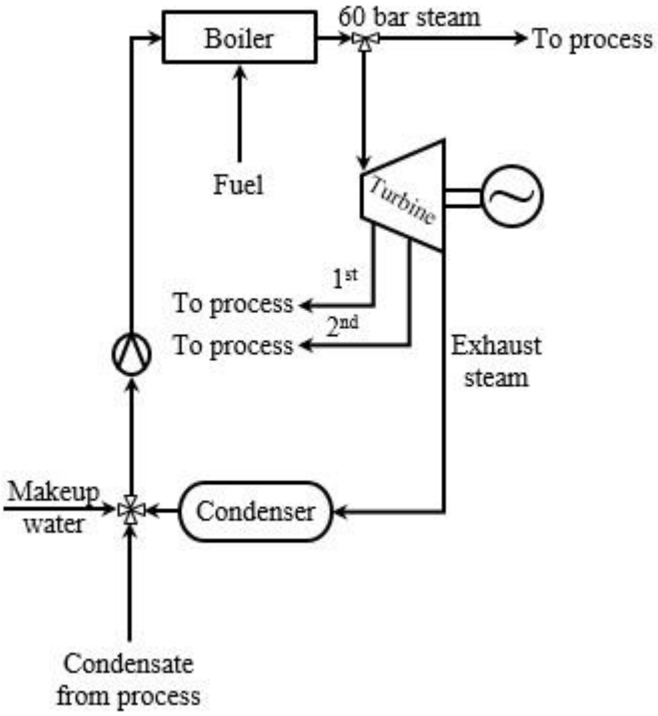

Figure 4.7 – Schematic representation of the cogeneration system where an extraction-condenser steam turbine is used. The first extraction is steam at 10.03 bar, the second one is at 2.5 bar and the exhaust steam is at 0.085 bar

Table 4.3 – Equipment efficiencies adopted for the cogeneration systems

Piece of equipment	Value
Pump isentropic efficiency (%)	80
Boiler thermal efficiency (%)	85
Turbine isentropic efficiency (%)	80
Electric generator efficiency (%)	96

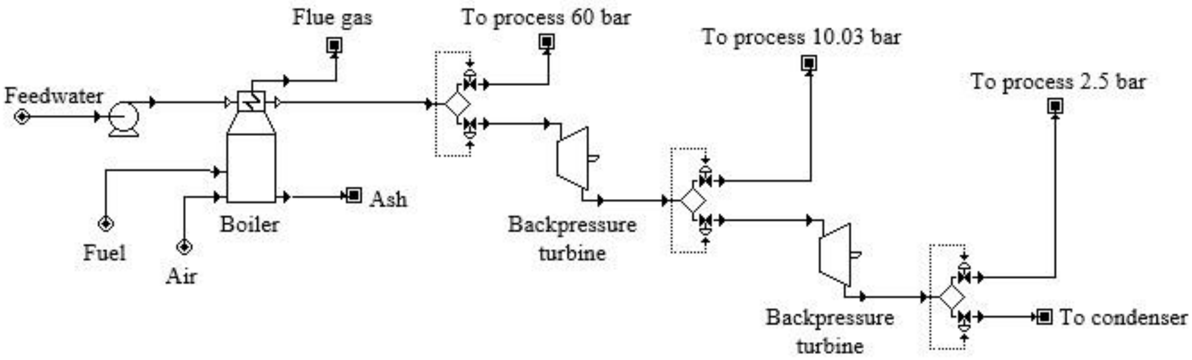

Figure 4.8 – Scheme obtained from the SuperPro Designer for the cogeneration system consisting of two backpressure steam turbines

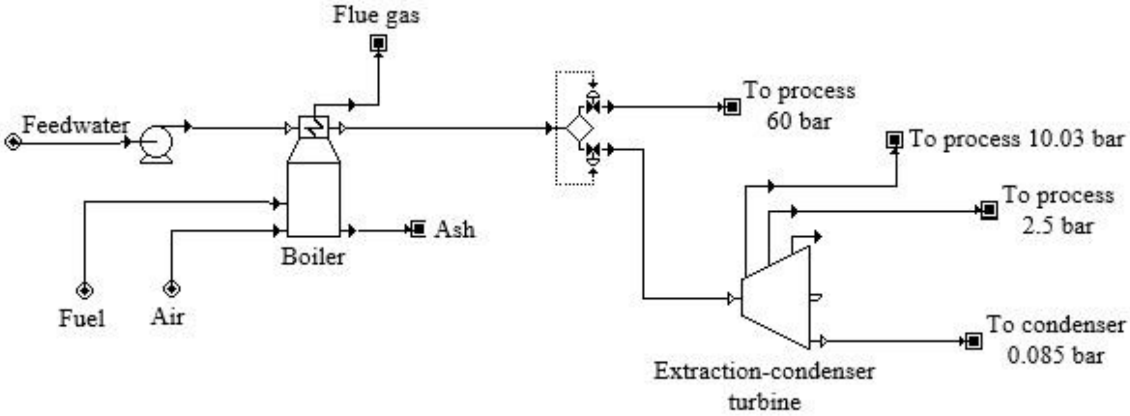

Figure 4.9 – Scheme obtained from the SuperPro Designer for the cogeneration system consisting of an extraction-condenser steam turbine

4.2.2.8 Evaluation scenarios concerning available fuels

For each cogeneration system and each case study (Table 4.1), different evaluation scenarios, were specified, as shown in Table 4.4. In each scenario, given the process specifications, one or two fundamental questions should be answered by analysing the process energetic demands. As will be discussed in the results, the thermal demand of the process (in any case study) is entirely fulfilled by the burning of any of the available fuels, but the same is not true for electrical energy demand. Taking this into account, the formulated questions are focused on electricity demand satisfaction in the different evaluation scenarios or in the amount of electricity surplus produced. Evaluation scenario 3 assumes that it is not desired to bring straw from the field, so it is not available as fuel in the plant facility. Furthermore, in evaluation scenarios 3 and 4, hulls are supposed to be used in the furnace coupled to the drier used in the drying operation during seed preparation step. Hence, the amount of hulls accounted for is the remaining after the necessary amount to supply the seed preparation furnace was subtracted. In scenarios 1 and 2, this assumption is not necessary because, as only one type of fuel is destined to the boiler, another fuel considered here could be used in the furnace.

Table 4.4 – Specified evaluation scenarios conceived for getting complete and accurate information about integrated process energetic fulfillment with different available fuels.

Evaluation Scenario	Questions to be answered (process specifications in premises)
1	How much electricity surplus is produced if only one fuel type is burned in the boiler and all available fuel is used?
2	What is the fuel surplus, if it is desired to just fulfill both thermal and electrical energy demands of the process and only a single type of fuel is burned in the boiler?
3	(a) If available soybean hulls and all produced biodiesel are burned in the boiler, how much electricity surplus is produced? (b) What is the biodiesel surplus, if it is desired to just fulfill both thermal and electrical energy demands of the process and the boiler is fed with biodiesel and the available soybean hulls?
4	(a) Supposing a market situation in which it is very attractive to sell both electricity and biodiesel, how much electrical energy surplus could hulls and all straw provide? (b) Supposing a market situation in which it is attractive to sell electricity but not biodiesel, how much electrical energy surplus could hulls, all straw and biodiesel provide?

4.2.3 Results and discussion

First of all, the process can be evaluated in terms of yield of each process step, or set of operations, which is presented in Table 4.5. In this table, the yield of each set of operations is translated in terms of mass ratio of output to input. Taking this into account, it can be observed that 66.2% of all seeds fed to the soybean plant facility give rise to defatted meal, while only around 17% of this seeds mass are transformed into degummed oil. It is interesting to observe that the mass of soybean hulls available in the facility is actually not large (7.4% of seed mass), which, as demonstrated further on this section, make this potential fuel alone unable to make the soybean biorefinery independent from the electricity supply from the grid.

Table 4.5 – Ratios relating process outputs to inputs in different parts of the integrated process

Output / Input	Ratio ($kg_{output\text{-}stream}/MT_{input\text{-}stream}$)
Defatted meal / Seeds	662.1
Hulls / Seeds	74.1
Degummed oil / Seeds	169.9
Refined oil / Degummed oil	967.5
Biodiesel / Degummed oil	1,004.7

Table 4.6 – Process thermal demand of the different case studies

Case study	2.5 bar saturated steam		10.03 bar saturated steam		60 bar saturated steam		Total	
	kg_{steam} / $MT_{deg\text{-}oil}$	MJ_{steam} / $MT_{deg\text{-}oil}$	kg_{steam} / $MT_{deg\text{-}oil}$	MJ_{steam} / $MT_{deg\text{-}oil}$	kg_{steam} / $MT_{deg\text{-}oil}$	MJ_{steam} / $MT_{deg\text{-}oil}$	kg_{steam} / $MT_{deg\text{-}oil}$	MJ_{steam} / $MT_{deg\text{-}oil}$
Bio-0	312	681	870	1752	176	276	1358	2710
Bio-25	332	724	870	1752	206	324	1408	2801
Bio-50	352	767	870	1752	237	372	1459	2892
Bio-75	371	810	870	1752	268	421	1509	2982
Bio-100	387	844	870	1752	298	469	1555	3065

Table 4.7 – Electrical energy demand of the different case studies

Case study	Total electricity requirement (MW)	kWh / $MT_{deg\text{-}oil}$
Bio-0	7.83	442.38
Bio-25	7.82	441.65
Bio-50	7.80	440.93
Bio-75	7.79	440.21
Bio-100	7.78	439.49

The thermal demand of the process in each case study is presented in Table 4.6. For the current work, electrical energy demanded by the process was estimated taking into account data found in studies by Hamm et al. (2013) and Sheehan et al. (1998). Table 4.7 presents the electricity demand for each case study analysed.

As can be observed in Tables 4.6 and 4.7, the refining set of operations requires less steam and more electricity than the biodiesel production ones. Therefore, as the amount of degummed oil diverted to biodiesel production increases, the steam requirements also increase and the electricity decreases. Steam at 10.3 bar is only required in oil the extraction operation and, therefore its demand remains constant with changes in the amount of degummed oil diverted to refining operations or biodiesel production. Steam at 60 bar is required in the refining sector, in the stripping operation, and in biodiesel production sector, in the operations of biodiesel vacuum drying and distillation for glycerol purification.

From seed preparation to the degumming step, the total steam demand is 401 MJ of steam per metric ton of seed processed. This result is a bit lower than that reported by Granjo et al. (2015) and much lower than the demand reported by Sheehan et al. (1998), which were 420.30 and 920.56 MJ of steam per metric ton of seed processed, respectively. In this work, the refining operation demanded ca. 216 kg of steam per metric ton of refined oil. Dorsa (2000) estimated a steam requirement of 209 kg of steam/ MT of refined oil, while 185 kg of steam / MT of refined oil were estimated by Hamm et al. (2013). In the biodiesel production sector, steam demand of 709.3 MJ / MT of biodiesel was obtained while in the studies carried out by Granjo et al. (2015) and Sheehan et al. (1998) amounts of 831.46 and 1,390.86 MJ / MT of biodiesel were required, respectively. It is important to draw attention to the fact that these studies only reported the total steam amount required, but they did not specify the thermodynamic state of steam used.

Sheehan et al. (1998) surveyed available data for steam demand in industrial plants for biodiesel commercial production and found values varying from 401.75 to 2,585.4 MJ of steam / MT of biodiesel. This difference in steam demand can be assigned to different process conditions used.

As for electricity demand, different values were also found. From seed preparation to the degumming step, Sheehan et al. (1998), Granjo et al. (2015) and Dorsa (2000) found 69.47 (used as the basis for this work), 65.04 and 30.00 kWh of electricity required/MT of seed processed, respectively. During oil refining, Granjo et al. (2015) found 41.92 kWh/MT of refined oil while Dorsa (2000) achieved the value of 12.55 and Hamm et al. (2013), 33.00 kWh/MT of refined oil (used as the basis for this work). Biodiesel production was the process sector where electrical energy requirement data available in the literature were more close to each other. Sheehan et al. (1998) found an electricity requirement of 28.90 kWh/MT of biodiesel (used as the basis for this work), while Granjo et al. (2015) found 28.87 and Haas et al. (2006), 26.63 kWh/MT of biodiesel.

Table 4.8 – Lower heating values (LHVs) and necessary mass flow of fuel for the drying operation in the seed preparation step

Residue / Product	LHV (MJ/kg)	Mass flowrate (kg/s)
Soybean straw	16.42	0.70
Soybean hull	15.21	0.76
Soybean biodiesel	37.68	0.31

Lower heating values of the different fuels were used to calculate the amount of fuel needed in the drying operation during seed preparation step (Table 4.8). If soybean hulls are used for this operation, it will consume ca. 35 wt. % of this resource. As for straw, it will be 4.8 wt. %. The percentage of available biodiesel needed in the drying operation naturally depends on the amount produced during the process (i.e. it depends on the case study).

The process thermal demand in each case study could always be satisfied, regardless of the coupled cogeneration system or the fuel used in the boiler. The questions regarding electricity demand fulfillment or its surplus amount (Table 4.4) are answered by the data found in Tables 4.9 to 4.12. In these tables, it can be observed that, at least from the technical point of view, in this study, the EC steam turbine generates better results than the two BP coupled steam turbines, whether generating more electricity or fuel surplus. The reason lies in adding a last stage extraction with pressure below the atmospheric, improving the energy conversion of the available enthalpy in the steam inlet.

As can be seen in Table 4.9, using only soybean hulls generated from the dehulling operation as the boiler fuel is not an option in the operation of the integrated process, because it does not fulfill the electricity need for the process, if either two BP turbines or the EC one is used. In case study Bio-25, in which only 25% of degummed oil is diverted to biodiesel production, the biodiesel amount produced is not enough to supply the electrical demand of the process either. As the amount of degummed oil diverted to biodiesel production increases, the surplus of electricity also increases. If half of the straw generated in the field were brought to the facility (an amount here called available straw), it would be enough to supply the electrical energy demand of the process and even provide surplus of electricity for all case studies.

In the context of a biorefinery, if straw is used to supply the exact energetic needs of the process, with no electricity surplus, other destinations could be given for the straw surplus (Table 4.10), e.g., for bioethanol, adsorbents, polymers, fibers or composites reinforcement production, just to cite a few. Naturally, the new process steps (to produce bioethanol, adsorbents, etc.) would have their own energy demands, and, therefore not all straw surplus shown in Table 4.10 could be processed into these new products, because part of this straw amount would be burned to fulfill the larger energy demand. As can be observed in Table 4.10, not all biodiesel produced would be consumed when it is used as fuel in the cogeneration system.

Table 4.9 – Electricity surplus produced in evaluation scenario 1 with different cogeneration systems coupled to the process

Case study	Electricity surplus (MW), only one fuel type is burned in the boiler					
	Cogeneration system provided with two BP turbines			Cogeneration system provided with one EC turbine		
	Hulls	Straw	Biodiesel	Hulls	Straw	Biodiesel
Bio-0	-3.70	29.65	-	-2.57	53.08	-
Bio-25	-3.77	29.58	-3.37	-2.75	52.91	-2.07
Bio-50	-3.85	29.51	2.61	-2.93	52.73	7.84
Bio-75	-3.93	29.42	8.53	-3.10	52.56	17.70
Bio-100	-4.00	29.35	14.66	-3.27	52.39	27.62

Table 4.10 – Fuel surplus in evaluation scenario 2 with different cogeneration systems coupled to the process

Case study	Fuel surplus (kg/s), only one fuel type is burned in the boiler			
	Cogeneration system provided with two BP turbines		Cogeneration system provided with one EC turbine	
	Straw	Biodiesel[1]	Straw	Biodiesel[1]
Bio-0	11.02	-	11.82	-
Bio-25	10.99	-	11.78	-
Bio-50	10.96	0.53 (22%)	11.74	0.96 (39%)
Bio-75	10.93	1.75 (47%)	11.70	2.18 (59%)
Bio-100	10.90	2.97 (60%)	11.66	3.39 (69%)

[1] Values shown between parentheses correspond to the percentages of straw or biodiesel available/produced that exceeds the amount needed to be burned in the boiler.

Table 4.11 presents the results for evaluation scenario 3 for both cogeneration system configurations. As can be seen, with only hulls, in case study Bio-0, with no biodiesel production, cogeneration system cannot operate, since the amount of soybean hulls are not sufficient to fulfill electrical energy requirements. From case 2 onwards, all energetic demands can be fulfilled. When electricity surplus is desired (situation (a)), with the increase in the amount of biodiesel produced (due to the higher amount of degummed oil diverted to these process steps), the surplus electricity also increases. On the other hand, when it is desired to just fulfill both thermal and electrical energy demands (case (b)), the surplus of biodiesel increases with the increase of degummed oil converted into biodiesel. Concerning the different configurations, better results are obtained when using EC turbine configuration.

Table 4.11 – Surplus electricity (a) and surplus biodiesel (b) in evaluation scenario 3 with different cogeneration systems coupled to the process

Case study	Cogeneration system provided with two BP turbines		Cogeneration system provided with one EC turbine	
	(a) Electricity surplus (MW)	(b) Biodiesel surplus (kg/s)[2]	(a) Electricity surplus (MW)	(b) Biodiesel surplus (kg/s)[2]
Bio-0	-	-	-	-
Bio-25	0.27	0.06 (5%)	4.00	0.49 (40%)
Bio-50	6.24	1.28 (52%)	13.91	1.71 (69%)
Bio-75	12.16	2.50 (67%)	23.75	2.92 (79%)
Bio-100	18.14	3.72 (75%)	33.68	4.14 (84%)

[1] Soybean hulls flowrate fed to the boiler is 1.39 kg/s, which is the exceeding amount to that necessary in the furnace of seed preparation sector.

[2] Values shown between parentheses correspond to the percentages of biodiesel produced that exceeds the amount needed to be burned in the boiler.

In a market situation in which selling electricity to the grid is very profitable, with EC turbine and using all fuels available, electricity surplus could achieve 98.68 MW, with all degummed oil diverted to biodiesel production (Table 4.12), representing an increase of ca. 69 % of electricity surplus when compared to when no biodiesel is used as boiler fuel. If this comparison is made in case study Bio-25, in which 25 % of degummed oil is diverted to biodiesel production, the increase in electricity surplus is of 17%, i.e., 17% more electrical energy is produced if the produced biodiesel is also burned in the boiler. Analogous comparisons in case studies 3 and 4 lead to ca. 34% and 51%, respectively. When comparing the BP system to the EC system, it is possible to produce an average of 1.76 times more surplus electricity with the EC system.

Table 4.12 – Electricity surplus burning hulls[1] and all straw (a) and burning hulls, all straw and biodiesel (b) in evaluation scenario 4 with different cogeneration systems coupled to the process

Case study	Electricity surplus (MW)			
	Cogeneration system provided with two BP turbines		Cogeneration system provided with one EC turbine	
	(a) Hulls[1] and all straw burned	(b) Hulls[1], all straw and biodiesel burned	(a) Hulls[1] and all straw burned	(b) Hulls[1], all straw and biodiesel burned
Bio-0	33.29	-	59.16	-
Bio-25	33.22	39.22	58.98	68.99
Bio-50	33.15	45.19	58.80	78.91
Bio-75	33.06	51.11	58.63	88.75
Bio-100	32.99	57.08	58.46	98.68

[1] Soybean hulls flowrate fed to the boiler is 1.39 kg/s, which is the exceeding amount to that necessary in the furnace of seed preparation sector.

4.2.4 Conclusions

Soybean crushing and refining facilities can produce their own energy needs, besides refined oil, biodiesel and defatted meal. The process has thermal and electrical energy needs and these needs could be supplied by using as fuel, materials obtained during the seed processing. By the simulation of the process using a commercial software, it was possible to evaluate the energy requirements for the process and verify that both thermal and electrical energy demand could be fulfilled using straw as the fuel or a combination of hulls and biodiesel using cogeneration systems coupled to two backpressure turbines or an extraction-condenser steam turbine and inlet steam at 60 bar and 480 ºC. Using a cogeneration system with an extraction-condenser steam turbine could provide better technical yields for all scenarios evaluated. With a 2,500 MT/day soybean seeds processing facility, to produce only the thermal and electrical energy necessary to fulfill the process requirements, using EC steam turbine, only soybean straw, among all available fuels, could accomplish the task. For different fractions of degummed oil being converted into biodiesel, the amount of straw surplus varies between 11.66 and 11.82 kg/s (respectively 80.59% and 81.70% of the total straw brought from the field). In a scenario in which the production of electricity is interesting, the system could provide 98.68 MW of electricity surplus (0.95 kWh/kg of processed soybean), in the best case, using all fuels available and using all degummed oil to produce biodiesel.

Acknowledgements

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4.3 CONCLUSIONS

This chapter presented, in the form of an article, analysis on the capacity of different cogeneration systems submitted to different scenarios, with fuels provided only by the process itself, to produce thermal and electrical energy fulfill process, comprising operations of soybean crushing, oil extraction, defatting meal, and refining and biodiesel production from soybean oil. However, during these processing steps, several residues are generated. These residues may be converted into products of commercial value. Next chapter is dedicated to analyse applications for these residues, as well for residues of SPC production.

5 RESIDUES EXPLOITATION EXTENDING THE SOYBEAN BIOREFINERY PROCESSES

5.1 INTRODUCTION

During the refining of crude soybean oil, four residues are generated: gums, soapstock, spent bleaching earth and deodorizer distillate. In addition, if defatted meal has its proteins concentrated, this concentration process generates a residue called soybean molasses. Each of these residues possesses components that can result in another product with commercial value after further processing. Several options were exposed in Chapter 2. In this chapter, for each one of these residues, an application, based on the academic literature, was chosen to be simulated and an assessment of the results and of the integration to the soybean biorefinery was provided.

From gums, lecithin is the product manufactured. Biodiesel was the chosen product to be obtained both from soapstock and spent bleaching earth. Tocopherols concentration was the target for exploiting deodorizer distillate and, finally, from soybean molasses thermal and electrical energy was produced. The mass balance for each residue exploitation was based on literature data, while the energy balance was provided by SuperPro Designer.

This chapter is organized so as each residue exploitation is entirely discussed separately.

5.2 LECITHIN PRODUCTION FROM THE GUMS RESIDUE

In fact, it cannot be said that gums are a residue from soybean processing since its use as soybean lecithin is already well established in industry. Lecithin as product can be presented in the form of standard liquid lecithin, de-oiled lecithin powder and phosphatidylcholine (PC) enriched fraction. Standard lecithin is obtained when gums resulted from the degumming process are only dried to achieve a maximum of 1 % of water content. In de-oiled lecithin powder, besides water, neutral oil is also removed from the product. PC-enriched fraction presents a higher content of phosphatidylcholine (van Nieuwenhuyzen and Tomás, 2008). Table 5.1 presents typical composition of lecithin products.

Table 5.1 – Typical composition of soybean lecithin (mass percentage)

Component	Standard liquid lecithin	De-oiled lecithin powder	PC-enriched fraction
Phospholipids			
Phosphatidylcholine	15	24	38
Phosphatidylethanolamine	11	17	8
Phosphatidylinositol	10	16	3
Phosphatidic acid	4	6	1
Others	7	11	1
Glycolipids			
Sterolglycoside	7	11	6
Galactodiacylglycerol	4	6	3
Complex carbohydrates			
Sucrose	1	1.5	1
Raffinose	0.5	1	0.5
Stachyose	2	3	1
Neutral oil	37	3	37
Water	1	1	1
Total	99.5	100.5	100.5

Source: adapted from van Nieuwenhuyzen and Tomás (2008).

The process for the production of standard liquid lecithin is presented here based on data from Van Nieuwenhuyzen (1976) and van Nieuwenhuyzen and Tomás (2008).

5.2.1 Process description

The process for the production of standard liquid lecithin requires basically drying the gums derived from the degumming process and cooling the obtained product. Water removal to less than one percent is performed in a drying film evaporator. The evaporator operates at 90 ºC and 270 mbar.

The pure components used in SuperPro Designer v. 9.0 to represent the components in the gums were the same as the ones presented in Chapter 3. Therefore, no distinction between the different types of phospholipids was made during the simulation.

5.2.2 Results and discussion

Figure 5.1 presents the scheme assembled in SuperPro Designer v.9.0.

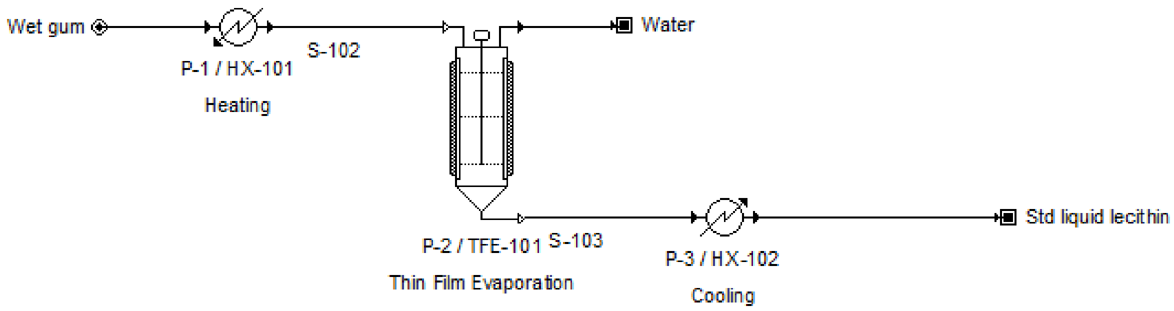


Figure 5.1- Gums drying for standard liquid lecithin production

The production of standard liquid lecithin does not require many operations. If it is to be used for food purposes, a bleaching step prior to drying is required, normally using hydrogen peroxide (van Nieuwenhuyzen and Tomás, 2008). This operation was not performed here because it was not found in literature the amount of hydrogen peroxide required. To remove the water content to less than 1.00 wt. %, 0.64 kg of saturated steam at 127.41 °C is required per kilogram of wet gums processed. Table 5.2 present the mass balance obtained for this operation.

Table 5.2 – Mass balance for lecithin production

Stream	Gums		Standard liquid lecithin	
Component	Mass flow (kg/h)	Component percentage (%)	Mass flow (kg/h)	Component percentage (%)
Triacylglycerols	98.28	15.15	98.28	30.03
Free fatty acids	18.07	2.79	18.07	5.52
Phospholipids	195.56	30.15	195.56	59.75
Phytosterols	0.59	0.09	0.59	0.18
Tocopherols	0.39	0.06	0.39	0.12
Squalene	0.01	0.00	0.01	0.00
Carotenoids	0.08	0.01	0.08	0.02
Chlorophyl/pheophytins	< 0.00	< 0.00	< 0.00	< 0.00
Others	11.36	1.75	11.36	3.47
Water	324.33	50.00	2.95	0.90
TOTAL	648.67	100.00	327.28	100.00

5.3 BIODIESEL PRODUCTION FROM SOAPSTOCK

The process presented here was based on the studies from Haas and Scott (1996), Haas et al. (2000, 2001), Haas (2005) and Haas et al. (2006). From Haas and Scott (1996), only the soapstock composition was used to compare with the one obtained in this work. In that first cited study of Haas' group, the production of biodiesel from soapstock used a combined non-enzymatic-enzymatic method. The method showed to be less promising than the next method they have analysed, which used only non-enzymatic reactions (Haas et al., 2000), on which the process simulated in this section was based.

In Haas et al. (2000), the method was developed in bench scale and some process parameters were optimized. Haas et al. (2001) produced biodiesel from soapstock using basically the same process described in the previous study, but few alterations were done and in a large scale of production. The performance of biodiesel obtained was also tested in engines. Haas (2005) provided a review from the methods tested by his group for the production of biodiesel from soapstock and also suggested that in an industrial scale of production, instead of using freeze-drying for drying saponified soapstock, falling film evaporator would perform this operation more effectively. Therefore, falling film evaporator was used to simulate this operation in this work. Finally, the pieces of equipment and operations more appropriate for this type of process in an industrial scale was based on Haas et al. (2006), where the focus was on producing biodiesel from degummed soybean oil, but in a very similar way.

5.3.1 Process description

The amount of soapstock and soapy water leaving the neutralization process are gathered together and, from now on, this mixture is called soapstock. Besides free fatty acids (now in the form of sodium soaps), the residue also contains other two components that can be esterified to produce biodiesel: phospholipids that were not removed during degumming and triacylglycerols that were undesirably carried together with the desired substances to be removed during neutralization.

The first step performed was the alkaline hydrolysis, with 10 % of NaOH (mass of NaOH solution (50 wt. %) / mass of soapstock on a dry matter basis), of all ester bonds present in the lipids. As mentioned in Chapter 3, triacylglycerols were represented in this work, in the simulator, by a component that already came within the simulator called soybean oil. By the molecular formula and molecular weight provided, it was probably based on triolein properties. Therefore, the hydrolysis equation for triacylglycerols assumed here is presented in Equation 5.1.

$$Triolein + 3\ Sodium\ hydroxide \rightarrow Glycerol + 3\ Sodium\ oleate \tag{5.1a}$$

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3\ NaOH \rightarrow C_3H_8O_3 + 3\ C_{18}H_{33}NaO_2 \tag{5.1b}$$

Phospholipids were represented in the simulation by the ethanolamine (2-azaniumylethoxy)[(2S)-2,3-bis(octadecanoyloxy)propoxy]phosphinic acid. The hydrolysis of the phospholipids was assumed to be as presented in Equation 5.2. Free fatty acids (in the soap form) were represented by sodium linoleate.

$$\begin{gathered}Phosphatidylethanolamine + 3\ sodium\ hydroxide \rightarrow \\ Glycerol + 2\ Sodium\ stearate + sodium\ ;2 - phosphonooxyethylazanide\end{gathered} \tag{5.2a}$$

$$C_{41}H_{82}NO_8P + 3\ NaOH \rightarrow C_3H_8O_3 + 2\ C_{18}H_{35}NaO_2 + C_2H_7NNaO_4P \tag{5.2b}$$

The hydrolysis was performed at ambient pressure, 100 ºC, during four hours. Next, the saponified soapstock was dried until 10 % of moisture was achieved. According to Haas (2005), effective esterification could be achieved even if residual water up to a level of 10 wt.% was present in the saponified soapstock.

Next, the product was cooled and sent to the esterification reactor, where all saponified fatty acids reacted with methanol in the presence of an acid catalytic (H_2SO_4) at a molar ratio of 1:30:5 (fatty acid/ MeOH / H_2SO_4) (Equations 5.3a to 5.3d). The theoretical yield was considered to be achieved. SuperPro Designer database already provided a substance called BioDiesel and its molecular weight matched molecular weight of a methyl ester formed from an oleic acid and a methanol molecule. Therefore, this substance was chosen to represent FAME formed from sodium oleate. The same properties of this substance were chosen to represent FAME obtained from sodium stearate and sodium linoleate, but to achieve stoichiometric ratio, molecular formula and weight were adapted.

$$Sodium\ (FFA) + Methanol \xrightarrow{H_2SO_4} FAME + Sodium\ hydroxide \tag{5.3a}$$

$$C_{18}H_{35}NaO_2 + MeOH \xrightarrow{H_2SO_4} C_{18}H_{35}O_2CH_3 + NaOH \tag{5.3b}$$

$$C_{18}H_{33}NaO_2 + MeOH \xrightarrow{H_2SO_4} C_{18}H_{33}O_2CH_3 + NaOH \tag{5.3c}$$

$$C_{18}H_{31}NaO_2 + MeOH \xrightarrow{H_2SO_4} C_{18}H_{31}O_2CH_3 + NaOH \tag{5.3d}$$

Due to other substances and excess of acid and base used, during the esterification reaction, a solid layer was formed. This solid layer was then separated from both liquid layers by filtration. The solid contained 25 % of the total FAME produced and after water washing and centrifugation, 23 % of the total FAME produced could be recovered. The liquid fraction was centrifuged and the FAME rich layer was separated from the methanol rich layer. Haas et al. (2000) recovered 60% of the FAME produced in the methanol rich layer. As industrial operations here were based on data from Haas et al. (2006), and in that occasion, practically all FAME was recovered in FAME rich layer, here the same assumption was made. Both streams rich in FAME (from solid wash and liquid centrifugation) were gathered together and successively washed with dilute solutions of NaCl, $NaHCO_3$ and $Ca(OH)_2$ to achieve less than maximum levels of impurities and free fatty acids allowed for biodiesel specifications.

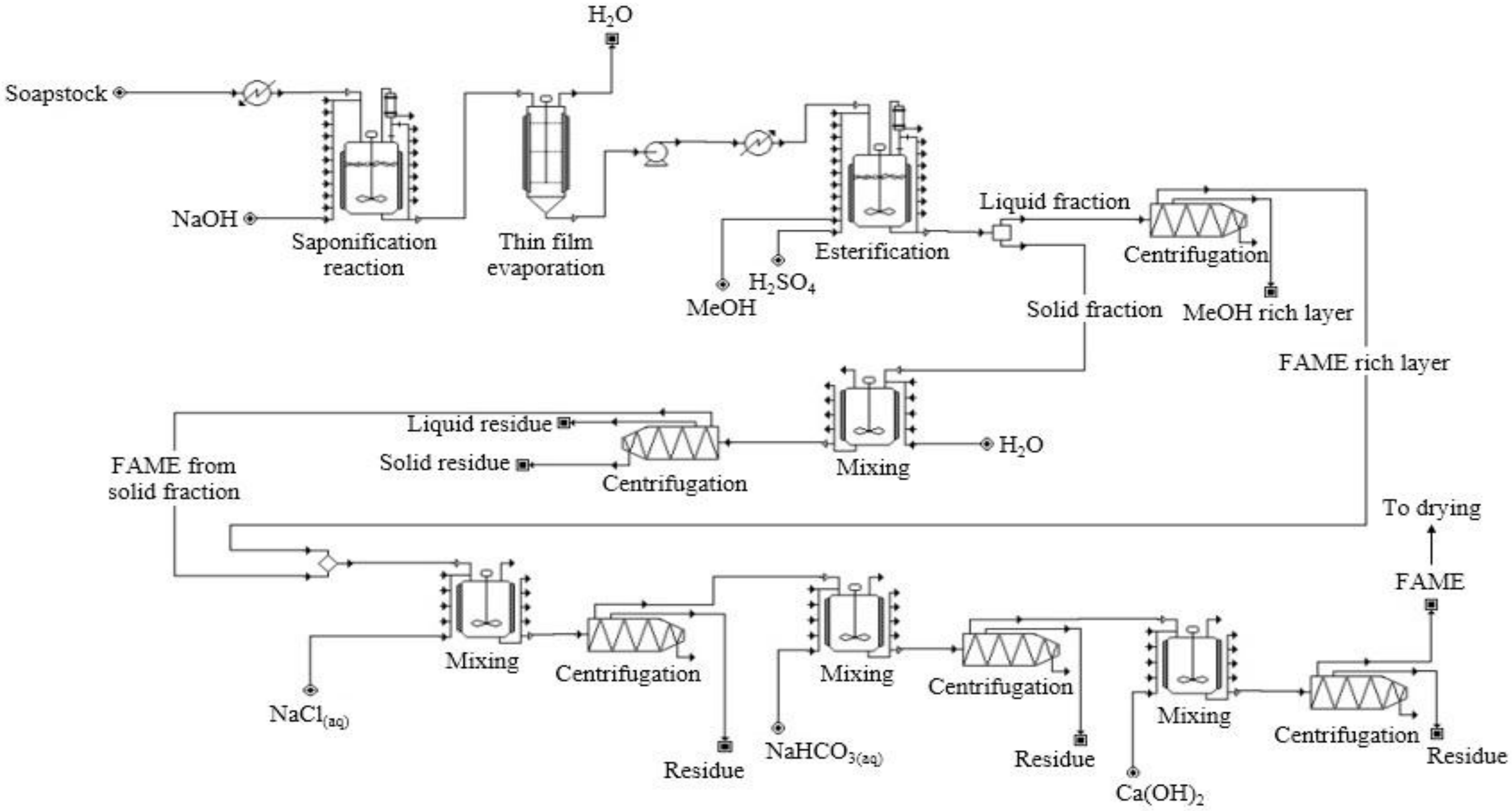
5.3.2 Results and discussion

Table 5.3 presents the soapstock composition (soapstock + soapy water) obtained in this work during neutralization step together with the one presented by Haas and Scott (1996) for comparison.

In the studies describing this process after final centrifugation, biodiesel had water level content within specifications. However, as in Haas et al. (2006), industrial processing of biodiesel in a very similar way was performed and after final centrifugation biodiesel stream still contained 2.4 % of water content and passed through a vacuum drier to achieve a final content of 0.045 %, and same conditions were assumed here. Figure 5.2 shows the scheme obtained for this process. The figure does not show the vacuum drier. As the same operation is performed in biodiesel production from degummed oil section (which was based on Haas et al. (2006), see section 3.2.4), it was considered that both biodiesel stream would share the same piece of equipment. The same can be said for glycerol recovery section.

Table 5.3 – Soapstock (soapstock + soapy water) composition

Component	Percentage composition (%)	
	Haas and Scott (1996)	This work
Triacylglycerols	10.10	10.10
Diacylglycerols	1.80	-
Phospholipids	8.50	10.96
Phosphatidylethanolamine	3.60	-
Phosphatidylcholine	2.70	-
Phosphatidylinositol	2.20	-
Free fatty acids	10.00	12.27
Phytosterols	-	2.42
Tocopherols	-	0.42
Squalene	-	0.02
Solvent soluble	10.50	-
Solvent insoluble	14.00	-
Others	-	26.70
Water	45.10	37.10
TOTAL	100.00	100.00



Main data:

Saponification reaction: $m_{NaOH}/m_{soapstock} = 0.1$, $P = P_{atm}$, $T = 100$ °C, $t = 4$ h.

Esterification reaction: $n_{FFA}/n_{MeOH}/n_{H_2SO_4} = 1/30/5$, $\eta = 100$ %, $P = P_{atm}$, $T = 35$ °C, $t = 2$ h.

Figure 5.2 – Simplified scheme for biodiesel production from soapstock

Every kilogram of soapstock processed resulted in 0.31 kg of biodiesel. This is a value quite inferior when compared to biodiesel produced from degummed soybean oil, which is one kilogram of biodiesel per kilogram of degummed oil (value from this work and from Haas et al. (2006)). This is mainly due to the composition of the feedstocks. While degummed soybean oil has ca. 97 wt. % of acylglycerols (data from this work) and free fatty acids and phospholipids content of 0.36 wt % and 0.36 wt. % (measured as phosphorous, 120 ppm; to convert to phospholipids a factor of 30 is used), respectively (Gunstone, 2011) (0.65 and 0.45 wt. % were the values obtained in this work), soapstock has only ca. 30.40 wt. % (Haas and Scott, 1996) of components that can be converted into biodiesel. In addition, due to other components present in soapstock, a greater effort for purification is needed. In this way, biodiesel from soapstock also generates a larger amount of residues.

Successive washes with 8.79 kg NaCl solution, 0.11 kg $NaHCO_3$ solution and 0.083 kg $Ca(OH)_2$ solution / kg of soapstock in liquid fraction plus 0.33 kg water / kg soapstock in solid fraction are necessary.

For every kilogram of biodiesel produced, the process requires 9.37 kg of saturated steam at 127.41 ºC and 2.84 kg of saturated steam at 275.58 ºC. The production of biodiesel from degummed oil requires 0.11 kg of saturated steam at 127.41 ºC and 0.30 kg of saturated steam at 275.58 ºC for 1 kg of biodiesel produced. This huge difference is mainly because the amount of methanol used during biodiesel production from soapstock (1 mole of saponified soapstock: 30 moles of methanol) is much greater than the amount used for traditional process (1 mole of degummed oil: 3 moles of methanol). This makes the effort on recovering methanol much greater. Furthermore, after soapstock is saponified, it also needs to be dried, increasing steam consumption too.

5.4 BIODIESEL PRODUCTION FROM SPENT BLEACHING EARTH

This process was mainly based on information provided by Huang and Chang (2010). Industrial pieces of equipment were based on Haas et al. (2006).

5.4.1 Process description

The first step of this process is to extract oil adsorbed in the clay earth. Huang and Chang (2010) recovered the oil by extraction with n-hexane (1:4 wt./wt. ratio) in a soxhlet extractor in a bench scale. This operation resembles the oil extraction from soybean seeds. Therefore, to perform an industrial scale simulation, it was assumed the same set of equipment and operations as the ones used for crude oil extraction from the seed and solvent recovery. It was also assumed that 73 wt. % of oil could be recovered (Alhamed and Al-Zahrani, 1999).

Next, two consecutive esterification reactions were performed. Firstly, free fatty acids present in residual oil were esterified (Equation 5.4) in mass proportion of 100:29:1 (oil / methanol / H_2SO_4) at 60 ºC, ambient pressure for 1 hour. Then, the oil layer was separated and washed with distilled water to remove excess of methanol and sulfuric acid and then dried. This process was repeated once to assure a level of free fatty acids inferior to 1.7 wt. %. Secondly, oil was transesterified (Equations 5.5 and 5.6) at 80 ºC for 1.5 hour with molar ratio of 1:6:1 (oil / methanol / NaOH). The FAME layer was separated by centrifugation and washed with dilute acetic acid solution and warm water, centrifuged and vacuum dried. The biodiesel yield was assumed 85%.

$$Linoleic\ acid + MeOH \xrightarrow{H_2SO_4} Water + FAME \tag{5.4a}$$

$$C_{18}H_{32}O_2 + CH_3OH \rightarrow H_2O + C_{18}H_{31}O_2CH_3 \tag{5.4b}$$

$$Triolein + 3\ MeOH \rightarrow Glycerol + 3\ FAME \tag{5.5a}$$

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3\ CH_3OH \rightarrow C_3H_8O_3 + 3\ C_{18}H_{33}O_2CH_3 \tag{5.5b}$$

$$\begin{gathered} Phosphatidylethanolamine + 3\ methanol \rightarrow \\ Glycerol + 2\ Sodium\ stearate + 3\text{-}Aminopropyl\ dihydrogen\ phosphate \end{gathered} \tag{5.6a}$$

$$C_{41}H_{82}NO_8P + 3\ CH_3OH \rightarrow C_3H_8O_3 + 2\ C_{18}H_{35}O_2CH_3 + C_2H_7NO_4PCH_3 \tag{5.6b}$$

For the simulation in SuperPro Designer, same FAMEs, acylglycerols and phospholipids compounds were used as those of soapstock. Free fatty acids were again represented by linoleic acid, but here not as a sodium soap (it was not saponified during neutralization).

5.4.2 Results and discussion

Table 5.4 present the spent bleaching earth obtained after bleaching step and Figure 5.3 the simplified scheme for biodiesel production from SBE. Hexane could be recovered from the clay earth stream and both could be reused as described in many studies presented in Section 2.4.5, although this set of operations were not simulated here.

Table 5.4 – Spent bleaching earth composition

Component	Percentage composition (%)
Triacylglycerols	9.83
Free fatty acids	11.44
Phospholipids	0.75
Phytosterols	0.17
Tocopherols	0.55
Squalene	0.02
Carotenoids	0.26
Chlorophyl/pheophytins	< 0.01
Others	14.47
Clay earth	62.50
Water	0.00
TOTAL	100.00

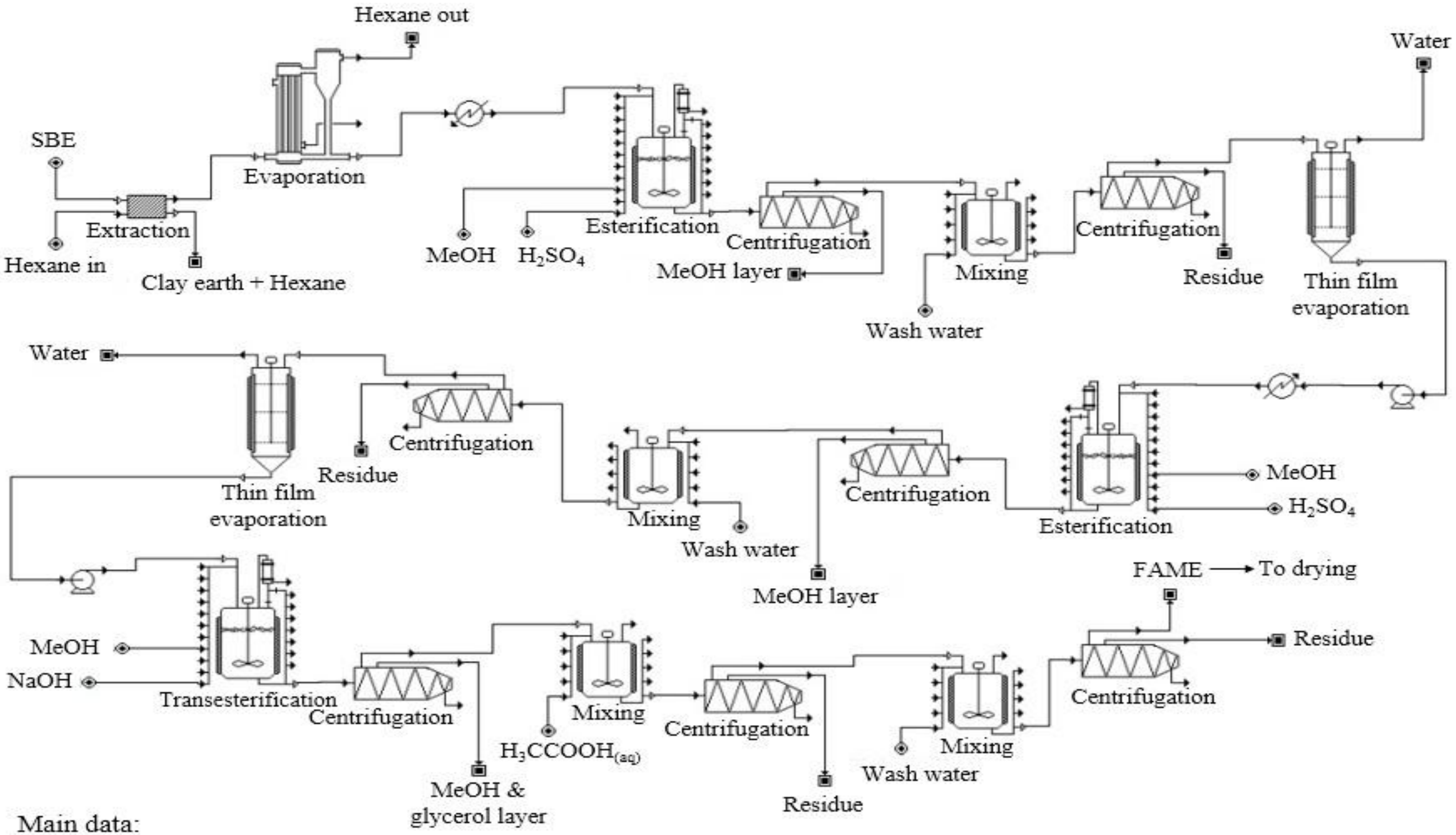
Huang and Chang (2010) heated the final product (biodiesel) to 105 ºC to remove water. Here, again, this step was assumed to be performed by the same piece of equipment used for biodiesel from degummed oil and soapstock and the same assumption was also made for glycerol purification and methanol recovery sections.

From total amount of SBE generated (clay earth included), the process yields 0.14 kg of biodiesel per kg of spent bleaching earth. This is less than obtained from soapstock (0.30) and from degummed soybean oil (1.00).

Huang and Chang (2010) performed a two-step esterification for the production of biodiesel from SBE, where first, free fatty acids were converted to FAME in the presence of an acid catalyst. Next, acylglycerols were reacted with methanol in the presence of an alkaline catalyst and, in the best conditions, 90 % yield was obtained for the transesterification step. To perform economic evaluation, the authors considered an overall yield of 85 %. Haas et al. (2000) on the other hand, to produce biodiesel from soapstock, first hydrolyzed, using an alkali, all lipid links present in the mixture, converting all fatty matter into soap. Next, all soaps from fatty acids were esterified with methanol in the presence of an acid catalyst and obtained the theoretical maximal yield. The latter authors, in their paper, commented that in initial investigations, two consecutives esterification reactions were performed, first alkaline transesterification followed by acid-catalyzed esterification, to convert, respectively, the ester-linked and free fatty acids to FAME (the opposite order performed by Huang and Chang (2010)). High degrees of overall conversion were obtained in this case too, but the authors later verified that soapstock saponifies readily and the saponified soapstock is also readily esterified by alcohol in the presence of mineral acid as catalyst. As the latter scheme involved fewer steps and less expensive reagents, this one was chosen over the first.

It was not informed how much water was necessary for the washes performed during the process; therefore, the amount of residue generated during this process cannot be precisely stipulated. Nevertheless, to enable the process to be simulated, it was assumed a requirement of one volume equivalent to wash the input stream and that the residue generated would not be sent to glycerol and methanol recovery section, so the thermal demand would not be so compromised.

The production of biodiesel from SBE extracted oil required 1.76 kg of saturated steam at 127.41 ºC and 0.40 kg of saturated steam at 275.58 ºC per kilogram of biodiesel produced. This is less than the amount required during soapstock exploitation for biodiesel production due to lower amount of methanol used, although more steps and more pieces of equipment were used, which is true even if the comparison is made to the equipment required to produce biodiesel from degummed oil, since here it is necessary to dry feedstock prior to the second esterification and transesterification stages.



Main data:
Extraction operation: $m_{hexane}/m_{oil} = 4$, Oil recovery = 73 %.
Esterification reactions: $n_{FFA}/n_{MeOH}/n_{H_2SO_4} = 1/2.5/0.03$, $P = P_{atm}$, $T = 60$ °C, $t = 1$ h.
Transesterification reaction: $n_{TAG}/n_{MeOH}/n_{NaOH} = 1/6/1$, $P = P_{atm}$, $T = 80$ °C, $t = 1.5$ h.
$\eta_{total} = 85$ %.

Figure 5.3 – Simplified scheme for the production of biodiesel from spent bleaching earth

5.5 CONCENTRATION OF TOCOPHEROLS FROM DEODORIZER DISTILLATE

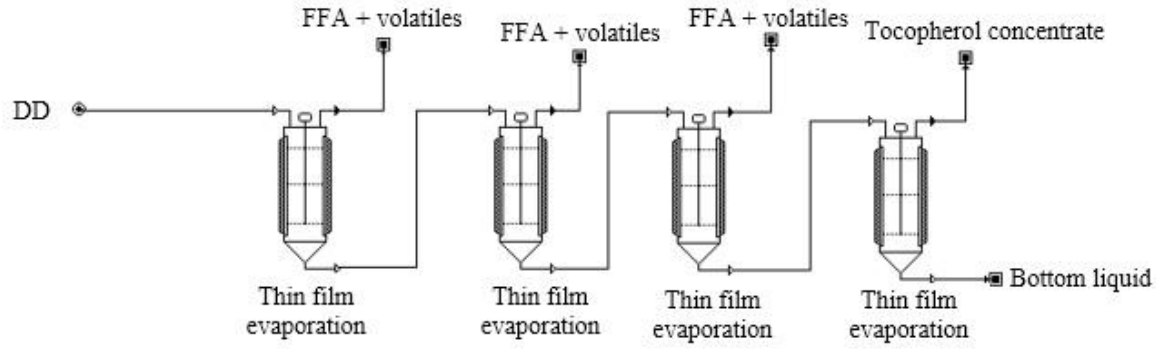
Deodorizer distillate (DD) is produced in the last step of soybean oil refining. The main goal is removing volatile substances resulting from breaking down of soybean oil components during refining. However, during stripping, while removing these pro-oxidant molecules, valuable components are also carried with stripping steam, such as tocopherols, phytosterols and squalene. Torres (2004) studied the concentration of tocopherols and phytosterols from soybean deodorizer distillate through molecular distillation. The separation occurs due to the different values of components vapor pressure present in DD.

5.5.1- Process description

The data used for designing this process was based on Torres (2004). To obtain a stream with 30 wt. % of tocopherols in distillate, four falling film molecular evaporators were placed in series. In the first one, 47 wt. % of the feed stream leaves as vapor, rich in free fatty acids. These fatty acids are those originally present oil and some others that were formed during refining process, especially in bleaching step. Although bleaching earth main target is to adsorb undesirable substances, it also exhibits some chemical and catalytic behavior, such as the conversion of soaps and triacylglycerols into free fatty acids (Shahidi, 2005). The liquid stream proceeds to the second evaporator. In the second evaporator, 32 wt. % of the feed leaves as vapor, which, as the one produced in first evaporator, is rich in fatty acids and volatile compounds. The liquid stream coming from the second evaporator, now more concentrated in tocopherols and phytosterols, is sent to the third evaporator, where the same process is repeated. Finally, the liquid from the third evaporator enters the last one, where the vapor phase, with a tocopherol concentration of 30 % leaves in the vapor phase. The first three evaporators operate at 125 ºC and 0,133 Pa, while the last one operates at 185 ºC and 0,133 Pa.

5.5.2- Results and discussion

The flowsheet developed with SuperPro Designer v. 9.0 is presented is Figure 5.4.



Main data:
First evaporation operation: $m_{FFA+volatiles}/m_{DD} = 0.47$, P = 0.133 Pa, T = 125 °C.
Second evaporation operation: $m_{FFA+volatiles}/m_{input\ stream} = 0.32$, P = 0.133 Pa, T = 125 °C.
Third evaporation operation: $m_{FFA+volatiles}/m_{input\ stream} = 0.15$, P = 0.133 Pa, T = 125 °C.
Fourth evaporation operation: $m_{tocopherols}/m_{tocopherol\ concentrate} = 0.30$, P = 0.133 Pa, T = 185 °C.

Figure 5.4 – Tocopherols concentration from soybean deodorizer distillate

The thermodynamic models available in SuperPro Designer along with properties information obtained for the components were not able to perform a proper simulation of this set of operations. In such cases, an option is available in this unit model, allowing the user to inform which component and its amount that goes to the vapor or to the liquid phase. To overcome the mentioned problem, this option was set and each phase composition was informed manually, based on data provided by Torres (2004).

For each kilogram of deodorizer distillate fed to this process, 0.26 kg of tocopherol concentrate at 30 % wt. could be produced, with a tocopherol recovery of 81.31 %.

As the evaporators operate at 125 ºC and 185 ºC, 0.30 kg of saturated steam at 180 ºC and 0.12 kg saturated steam at 275.58 ºC per kilogram of DD was required to fulfill the thermal energy requirements for all the evaporators used in this process.

5.6- ELECTRICITY PRODUCTION FROM SOYBEAN MOLASSES

There is a considerable number of studies for the utilization of soybean molasses. Many of them focus on the production of bioethanol from it (Qureshi et al., 2001; Siqueira et al., 2008; Romão et al., 2012; Silva et al., 2012) or on its use as a fermentation media for other products (Gao et al., 2012; Solaiman et al., 2007). The main issue in using soybean molasses as a fermentation media is that a significant amount of total sugars present in soybean molasses are not readily available for most common commercial yeasts. They are sugars with a α-1,6 glycosid bounds and cleaved by the enzyme α-galactosidase, which most common yeasts do not produce.

Siqueira et al. (2008) reported that 48 % of soybean molasses' sugar were not fermented by the *Saccharomyces cerevisiae* strain used for the production of bioethanol, although a significant result could be achieved in an industrial scale, producing 10 m^3 of bioethanol per day with a yield of 163.6 L of anhydrous ethanol per tonne of dry molasses. It was also reported by the authors that enzymatic and acid hydrolysis prior to fermentation increased ethanol yield, but the improvement did not compensate the additional costs. Another issue observed was the great amount of vinasse produced – at every 100 m^3 of ethanol yielded, 1300 m^3 of vinasse, a residue of the process, was also generated with a high pollution load (77.3 g O_2/L), leading to great discharge costs or to another search for some application to this new residue (Sanada et al., 2009; Karp et al., 2011).

Schopf et al. (2014) reported the development of firing systems capable to operate with low calorific liquids such as soybean molasses. They reported an existing industrial unit in operation in Araucária- PR, Brazil, and another one in Bečej, Serbia. Due to the low energy content of soybean molasses, the system needs another fuel with higher calorific value for starting and supporting the process, but it does not account for more than 20 % of the total fuel input. The high quantity of ash present in soybean molasses, where, in the first place, appears to be an issue, showed to be appropriate as fertilizer, with high concentration of potassium. The boiler was designed to handle appropriately these ashes generated.

Based on information above presented, the use of soybean molasses for the production of electricity was evaluated for the biorefinery in study.

5.6.1- Process description

To evaluate surplus electricity soybean molasses could generate, the situation in which all fuels available in soybean biorefinery were burned generating steam for the two backpressure steam turbine system, presented in Chapter 4, was chosen. The amount of degummed oil diverted to refined oil or biodiesel production does not influence the amount of molasses produced, and, therefore, does not influence surplus of electrical energy generated by soybean molasses.

The simulator needs as input the weight percent concentration of carbon, hydrogen, nitrogen, oxygen, sulfur, water and ash present in the fuel. The composition of soybean molasses in terms of carbohydrates, proteins, lipids, fibers and ash is presented in Table 5.5, on a dry matter basis (dmb). The amount of water may vary depending on the degree of miscella concentration during the SPC production. The miscella concentration step presented in Chapter 3 was such that the final concentration was 25 wt. % of moisture. At this point, it is worth remembering that in Chapter 4, the necessary energy to produce SPC or SPI were not taken into account. Based on amino acids distribution in soybean seed, amino acids composition of molasses proteins was estimated (Table 5.6). The lipids were considered to be triolein. Fibers were considered as cellulose.

Table 5.5 – Soybean molasses composition

Component	wt. % composition (dmb)	Molecular formula	Molar mass (kg/kmol)
Stachyose	18.6	$C_{24}H_{42}O_{21}$	666.580
Raffinose	9.68	$C_{18}H_{32}O_{16}$	504.439
Sucrose	28.4	$C_{12}H_{22}O_{11}$	342.298
Fructose	0.127	$C_6H_{12}O_6$	180.157
Glucose	0.243	$C_6H_{12}O_6$	180.157
Galactose	0.254	$C_6H_{12}O_6$	180.157
Proteins	9.44	(see Table 5.6)	(see Table 5.6)
Lipids	21.2	$C_{57}H_{104}O_6$	885.438
Fibers	5.7	$(C_6H_{10}O_5)_n$	162.141
Ash	6.36	-	-

Source: Siqueira (2007). Molar mass was calculated based on molecular formula.

The amount of soybean molasses produced was added to the fuel stream and the amount of surplus electricity generated by the addition of this new residue as fuel was computed.

Table 5.6 – Estimation of amino acid composition present in soybean molasses protein

Amino acid	Composition (g / 100g)	Molecular formula	Molar mass (kg/kmol)
Lysine	6.50	$C_6H_{14}N_2O_2$	146.188
Histidine	2.60	$C_6H_9N_3O_2$	155.155
Arginine	7.30	$C_6H_{14}N_4O_2$	174.202
Aspartic acid	11.80	$C_4H_7NO_4$	133.103
Threonine	3.90	$C_4H_9NO_3$	119.120
Serine	5.50	$C_3H_7NO_3$	105.093
Glutamic acid	18.60	$C_5H_9NO_4$	147.130
Proline	5.50	$C_5H_9NO_2$	115.131
Glycine	4.30	$C_2H_5NO_2$	75.067
Alanine	4.30	$C_3H_7NO_2$	89.094
Valine	4.60	$C_5H_{11}NO_2$	117.147
Cysteine	1.40	$C_3H_7NO_2S$	121.159
Methionine	1.10	$C_5H_{11}NO_2S$	149.212
Isoleucine	4.60	$C_6H_{13}NO_2$	131.174
Leucine	7.80	$C_6H_{13}NO_2$	131.174
Tyrosine	3.80	$C_9H_{11}NO_3$	181.189
Phenylalanine	5.00	$C_9H_{11}NO_2$	165.190
Tryptophan	1.40	$C_{11}H_{12}N_2O_2$	204.226

Source: Wolf (2000). Molar mass was calculated based on molecular formula.

5.6.2 Results and discussion

The mass flow of molasses obtained from the SPC production is presented in Table 5.7. Flowrate and composition in terms of elements, water and ash is presented in Table 5.8.

Table 5.7 – Soybean molasses mass flow and stream composition

Component	Mass flow (kg/h)	%
Proteins	1427.01	7.08
Lipids	3204.72	15.9
Carbohydrates	8661.81	42.975
Fiber	861.65	4.275
Ash	961.41	4.77
Water	5038.87	25
TOTAL	20155.5	100

Table 5.8 – Flowrate and composition in terms of elements, water and ash

Component	Flowrate (kg/h)	Composition (wt. %)
C	7193.97	35.7
H	1094.6	5.43
N	195.472	0.97
O	5662.48	28.09
S	8.6605	0.04
H_2O	5038.87	25
Ash	961.416	4.77
TOTAL	20155.5	100

Once molasses mass flow and composition in terms of elements was introduced into the simulator, the electricity surplus could be calculated and for 20155.5 kg/h of soybean molasses processing (obtained for processing 2500 MT raw seed / day), a surplus electricity of 20.56 MW was achieved.

In Chapter 4, when all straw, hulls and biodiesel available were burned using the BP cogeneration system and diverting all degummed oil to biodiesel production, it was possible to achieve an electricity surplus of 57.08 MW for the same input of raw seed (2500

MT/day). The electricity soybean molasses can generate represents about 22.4 % of the electrical energy surplus the BP cogeneration system provides when burning all available fuels with all degummed oil diverted to biodiesel production and no SPC and molasses produced. It is worth remembering once more that the energy required for SPC production process was not accounted in Chapter 4 analyses. Furthermore, this energy demand could not be accounted in this chapter, nor could the electrical energy demand exclusively for exploitation of the residues gums, soapstock, SBE and DD because it was not found in the literature the amount of electricity these processes consume, nor enough information was available from simulation of the process in SuperPro Designer v. 9.0 in order to extract these values.

5.7 BIOREFINERY INTEGRATION

As can be seen, the residues generated during soybean processing can find further applications. Several alternatives for applications were presented in Chapter 2. In this chapter and in Chapter 4, some alternatives for most of these residues were simulated using SuperPro Designer v. 9.0. All these residues applications integrated with the traditional soybean process can form a soybean based biorefinery, which is represented in Figure 5.5.

In the presented biorefinery, planned to process 2,500 MT of raw seeds per day (= 104,167 kg/h) (which is a common capacity found in industry (Informa economics, 2011; Illinois Soybean Association, 2012; Gabruch and Gietz, 2014; ABIOVE, 2014)), half of soybean straw generated (52,083 kg/h; LHV = 16.42 MJ/kg) could be brought from the field and used as fuel to generate thermal and electrical energy for the process, together with soybean hulls (7,720 kg/h; 15.21 MJ/kg) and soybean molasses (20,155 kg/h; 14.20 MJ/kg) resulted from seed preparation and protein meal concentration steps, respectively.

Based on market demand, a variable amount of degummed oil (17,698 kg/h) could be diverted to refining step or to biodiesel production. If not all degummed oil is diverted to biodiesel production, the refining process generates the residues named gums, soapstock, spent bleaching earth and deodorizer distillate, which could be further handled to generate more products. From drying the gums, a commercial emulsifier named lecithin (0.0185 $kg_{lecithin}/kg_{degummed\text{-}oil}$ or 0.51 $kg_{lecithin}/kg_{gums}$) could be obtained. For that, 0.64 kg of saturated steam at 127.41 ºC / kg of gums would be necessary.

From soapstock and spent bleaching earth (SBE), biodiesel (37.68 MJ/kg) could be produced, and if desired, also used in the cogeneration system. The yields for applications are 0.31 $kg_{biodiesel}/kg_{soapstock}$ and 0.14 $kg_{biodiesel}/kg_{SBE}$. It would be required 9.37 kg of saturated steam at 127.41 ºC and 2.84 kg of saturated steam at 275.58 ºC to produce 1 kg of biodiesel from soapstock and 1.76 kg of saturated steam at 127.41 ºC and 0.40 kg of saturated steam at 275.58 ºC per kilogram of biodiesel produced from SBE.

The last residue generated, deodorizer distillate, could have its tocopherols (TC) content concentrated, reaching a final concentration of 30 wt. % and a yield of 0.26 kg of tocopherols concentrate / kg of deodorizer distillate using 0.30 kg of saturated steam at 180 ºC and 0.12 kg saturated steam at 275.58 ºC per kilogram of deodorizer distillate processed.

Table 5.9 summarizes the products to feedstock ratios and steam to product ratios. It also presents the mass flow in the case that all degummed oil is diverted to the production of refined oil.

Table 5.9 – Feedstock and products mass flow if all degummed oil is used to produce refined oil in a soybean crushing facility with capacity of 2500 MT/day, products to feedstock ratios and steam demands

Feedstock		Product			Steam demand		
Residue name	Mass flow (kg/h)	Product name	Mass flow (kg/h)	Product / feedstock ratio (kg_{prod} / kg_{feed})	Steam 127.41 ºC and 2.5 bar (kg_{steam} / kg_{prod})	Steam 180 ºC and 10.03 bar (kg_{steam} / kg_{prod})	Steam 275.58 ºC and 60 bar (kg_{steam} / kg_{prod})
Gums	648.67	Lecithin	327.61	0.51	1.27	-	-
Soapstock	702.87	Biodiesel	217.92	0.31	9.37	-	2.84
SBE	276.35	Biodiesel	39.06	0.14	1.76	-	0.40
DD	48.07	TC	12.37	0.26	-	1.18	0.46

Not enough data were found in the literature to estimate the electricity demand of these new processes that exploit the residues gums, soaptstock, SBE and DD. As for thermal demand, using all straw (14.47 kg/s) as the only fuel and either two backpressure (BP) steam turbines or one extraction-condenser (EC) steam turbine cogeneration system, there would still be enough steam to fulfill the whole process of the integrated biorefinery (depicted in Figure 5.5) in both cases. The operating conditions of the two backpressure steam turbines and the extraction-condenser steam turbine cogeneration system for the soybean biorefinery process that converts all degummed oil into refined oil, in which all residues of oil refining are exploited and that uses only soybean straw as boiler fuel, are illustrated in Figures 5.6 and 5.7, respectively. As can be noticed in Figure 5.6, 35.86 kg/s of steam at 2.5 bar in the two BP steam turbines system are not effectively used. The electrical energy generated in this operating condition is 37.38 MW for the BP turbines system and 51.46 MW for the EC turbine system. When the applications for the residues of oil refining is not considered (see Chapter 4, case study Bio-0, evaluation scenario 1), electricity generated is 37.48 MW, 29.65 MW of which is surplus (bearing in mind that electricity demand for SPC production and for exploitation of residues of oil refining is not being accounted) for the 2 BP steam turbines system. As for the EC steam turbine cogeneration system, 60.91 MW is the amount of electricity generated and 53.08 MW the electricity surplus.

Figure 5.8 shows the two backpressure steam turbines cogeneration system for the same biorefinery process, but that uses also hulls and soybean molasses as boiler fuel. As expected, since more fuel is burned, more steam at 60 bar is generated. Since the biorefinery process is the same, the demand for steam of the different pressure levels is the same, which implies that more electricity is generated (53.78 MW). If the same conditions are used, changing only the cogeneration system to an extraction-condenser steam turbine system, as shown in Figure 5.9, it is possible to obtain a total electricity of 78.83 MW.

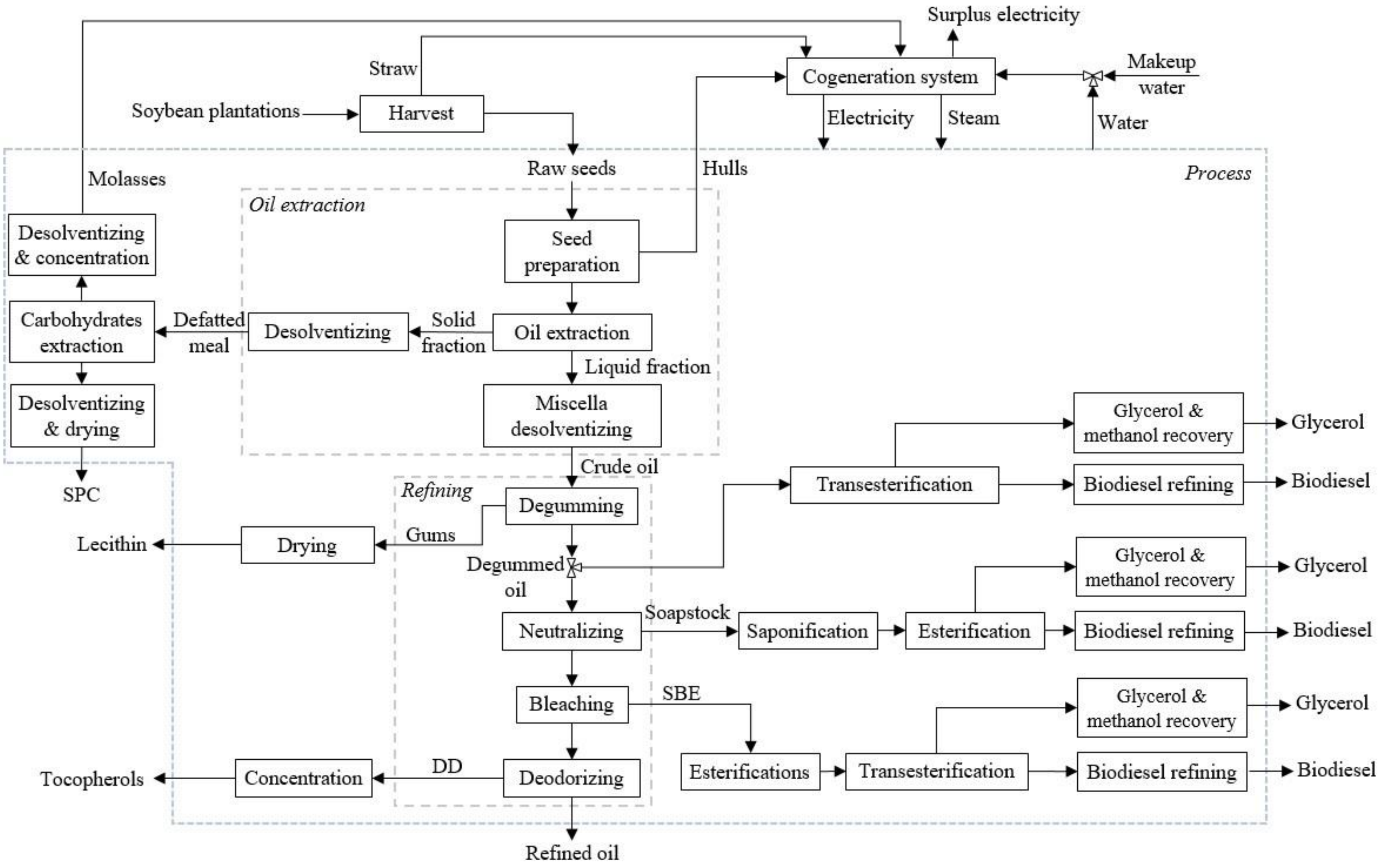


Figure 5.5 – Integrated biorefinery

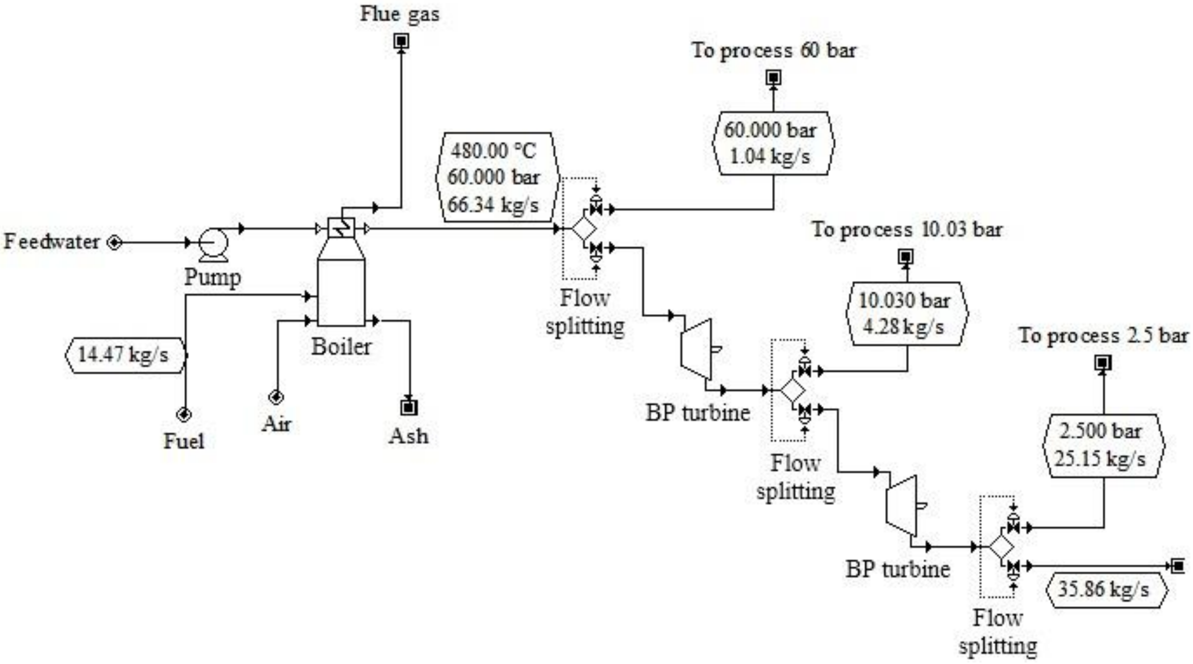


Figure 5.6 – Cogeneration system with two backpressure steam turbines and only soybean straw as fuel, in which the amount of steam required by the process is diverted before it enters the turbine or it is sent to the condenser. The soybean biorefinery operating condition corresponds to the situation in which all degummed oil is converted into refined oil and all residues generated during oil refining are exploited.

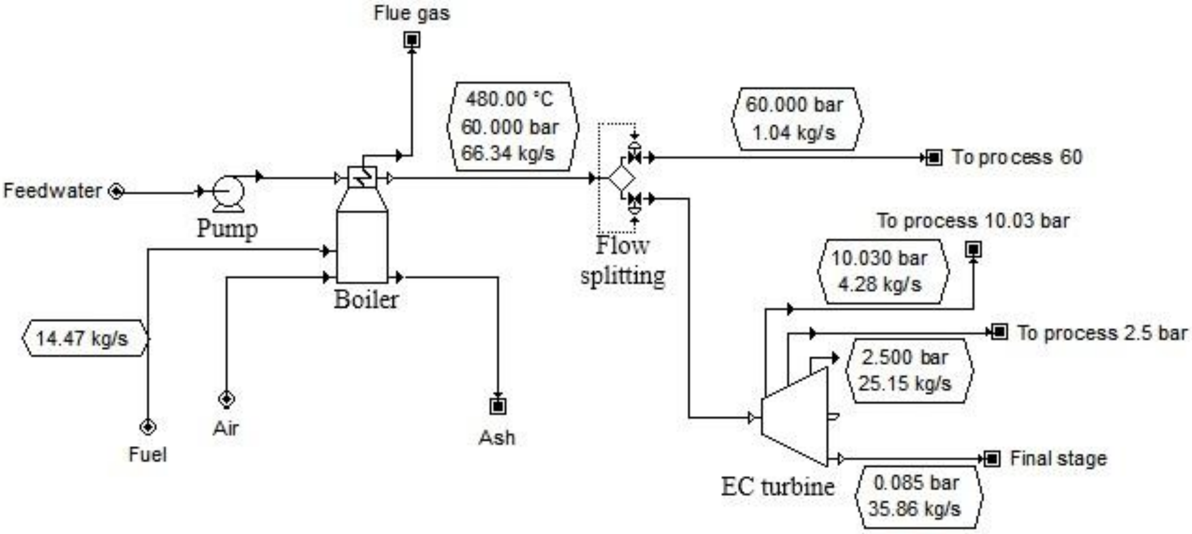


Figure 5.7 – Cogeneration system with one extraction-condenser steam turbine and only soybean straw as fuel, in which the amount of steam required by the process is diverted before it enters the turbine or it is sent to the condenser. The soybean biorefinery operating condition corresponds to the situation in which all degummed oil is converted into refined oil and all residues generated during oil refining are exploited.

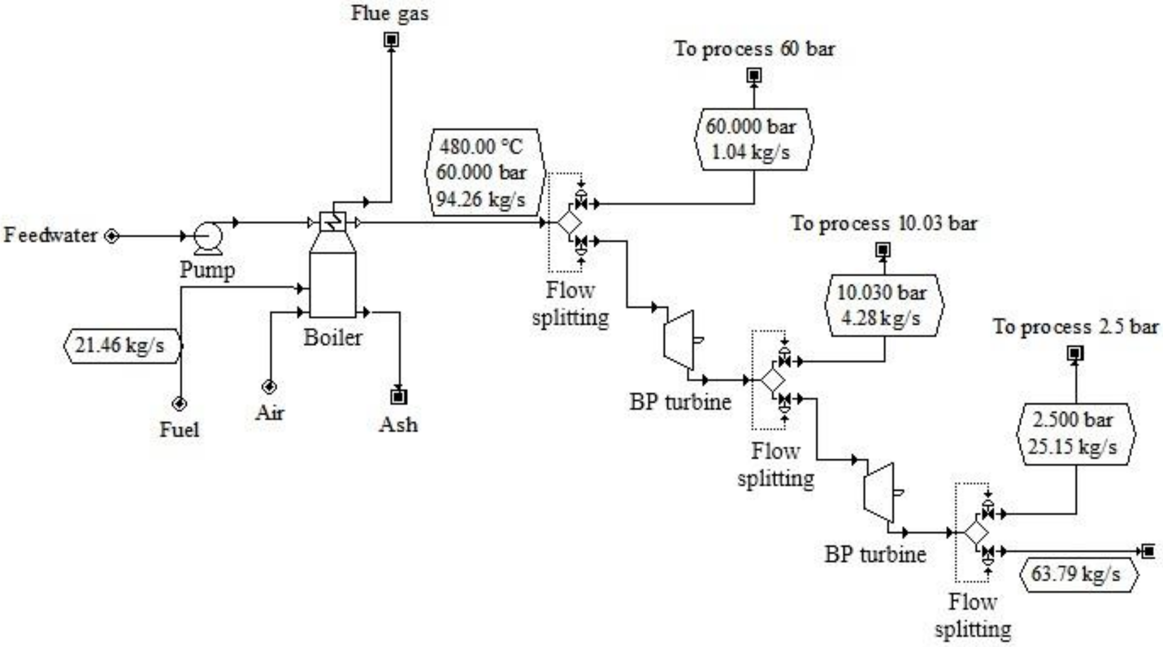


Figure 5.8 – Cogeneration system with two backpressure steam turbines and soybean straw, hulls and molasses as fuel, in which the amount of steam required by the process is diverted before it enters the turbine or it is sent to the condenser. The soybean biorefinery operating condition corresponds to the situation in which all degummed oil is converted into refined oil and all residues generated during oil refining are exploited.

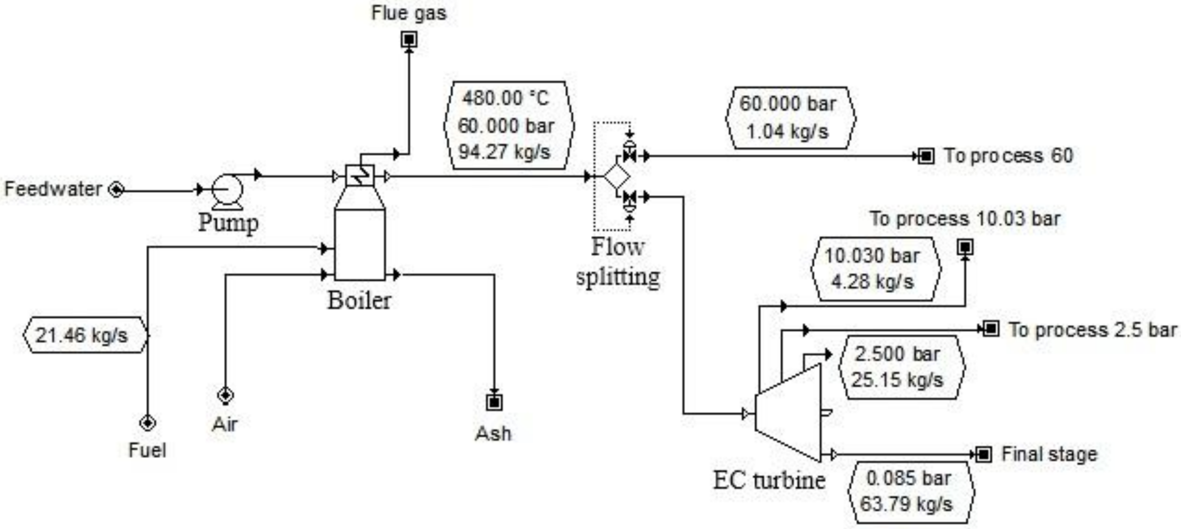


Figure 5.9 – Cogeneration system with one extraction-condenser steam turbine and soybean straw, hulls and molasses as fuel, in which the amount of steam required by the process is diverted before it enters the turbine or it is sent to the condenser. The soybean biorefinery operating condition corresponds to the situation in which all degummed oil is converted into refined oil and all residues generated during oil refining are exploited.

The integrated biorefinery mass balance in terms of mass of product or intermediate product to raw soybean seed mass ratio is presented Table 5.10.

Table 5.10 – Integrated biorefinery mass balance in terms of mass of product or intermediate product to raw soybean seed mass ratio

Product or intermediate product	kg of product or intermediate product / 1,000 kg of soybean seed[1]
Raw soybean seed	1000.00
Defatted soybean meal	662.07
Soybean protein concentrate	502.50
Molasses	193.49
Crude soybean oil	172.67
Degummed soybean oil	169.90
Biodiesel from degummed oil	170.70
Gums	6.23
Lecithin	3.15
Neutralized oil	165.81
Soapstock	6.75
Biodiesel from soapstock	2.09
Bleached oil	164.81
Spent bleaching earth (SBE)	2.65
Biodiesel from SBE	0.37
Refined oil	164.37
Deodorizer distillate	0.46
Tocopherols concentrate	0.12

1- After degumming the crude oil, the degummed oil can be diverted to biodiesel or refined oil production. Hence, data for biodiesel from degummed oil or data of the streams generated during refining process are presented assuming 1,000 kg of seeds (i.e., 169.90 kg of degummed oil) are diverted to the respective process section.

6 CONCLUSIONS AND FUTURE WORKS SUGGESTIONS

With a trend towards more sustainable processes and the opportunity of applying the biorefinery concept to a soybean crushing and refining facility, this work aimed to analyse the employment of this concept to such a facility, exploiting applications for the residues generated during the process.

For that, first, information and data from literature about the traditional manufacture process of soybean meal and refined soybean oil were collected and the residues produced during this process were identified. Data in academic literature about possible applications for these residues were also collected. The traditional process for producing soybean refined oil and defatted meal was simulated using a commercial simulator, SuperPro Designer v. 9.0, and the amounts of residues generated and energetic requirements were calculated. The amount of residues generated during soy protein concentrate (SPC) and soy protein isolate (SPI) production processes was also obtained by their simulations. Finally, an application for each residue (except SPI residues) was simulated in the same software and the results were analysed.

Based on the results obtained, the use of soybean straw and soybean hulls as fuel to supply the energetic demand of the processes of crushing, refining and biodiesel production has shown to be interesting, at least from the technical point of view. Production of lecithin from gums is already an established process in industry. The biodiesel production from soapstock and SBE generates more residues and requires more energy to recover methanol when compared to biodiesel production from degummed oil. Based only on the results obtained in this work, it cannot be stated that the production of biodiesel from these residues is a good alternative. Evaluation on residues impacts and costs would have to be performed to come to an answer. Again, from a technical point of view, the utilization of DD to concentrate tocopherols seems interesting since it does not require complicated processing and does not generate more residues than the original one.

As far it is known, publications concerning a soybean-based biorefinery exploited the utilization of only one residue generated from the process or further processing of streams that would already be a product with considerable commercial value (e.g. biodiesel from degummed oil or biomaterials from soybean meal). Therefore, the major contribution of this work was to perform a study of a soybean-based biorefinery in its broadest definition, where the production of transportation fuels, bioenergy and high-value products was evaluated. But this broad approach came with a price: due to time limitation and the difficulty to translate published results – which were obtained in its majority, in a bench scale and with not enough data to simulate the process (of course because it was not the goal of the published studies) – to an industrial scale and with operations matching the available ones in a commercial simulator, it was not possible to perform an economic evaluation, which is fundamental to the decision whether a process is worth being implemented or not. Therefore, for future works, the economic evaluation of such residues applications in an integrated facility is suggested. A study in the exploitation of SPI residues was also not performed. Therefore, it is also suggested for future works. Further analysis related to soybean molasses is also suggested, whether there would be more interesting options for this residue than burning it in the boiler (for example, producing bioethanol).

From the point of view of the software used, it can be concluded that it could fit the needs for the aim proposed in this work, but, if it was desired to perform energetic integration of the whole process, the task would be hardly performed, since academic version of SuperPro Designer v. 9.0 allows the use of only 25 unit operations per file. The same can be stated if recycle streams are important for the analysis and the output / input operations do not belong to the same file.

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