Écoconception de procédés: application à la production de biodiesel

Rapport de stage
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RÉSUMÉ

Le travail de stage consiste à appliquer une démarche de conception développé au Laboratoire de Génie Chimique (LGC) de l’ENSIACET mettant en œuvre une simulation globale du procédé sous Aspen Plus, une évaluation économique et environnementale à partir d’une Analyse du Cycle de Vie. La production de biodiesel à partir d’huiles végétales usagées, en tant qu’alternative à des combustibles fossiles sert de cas d’étude. Une première analyse «porte à porte» est effectuée en vue de comparer et de valider le modèle de simulation développé à partir de résultats de la littérature. Plusieurs schémas de procédés sont ainsi étudiés et comparés.

Ces schémas de procédés ont été rigoureusement mis en œuvre et simulés d’abord avec des procédés déjà connus, sur lesquels plusieurs études ont été développées dans la littérature et dans l’industrie. C’est pour cette raison que, dans cette étude, deux de ces cas ont été répliqués avec succès et qu’en plus, une étude économique est réalisée et plusieurs de ces indicateurs environnementaux sont calculés pour comprendre et vérifier les différents aspects de la production de biodiesel.

De plus, on a développé une étude comparative des variantes des procédés pour la production de biodiesel les plus communs dans l’industrie.
1. INTRODUCTION

1.1. Origin of the project

The scarcity of conventional fossil fuels, growing emissions of combustion generated pollutants, and their increasing costs are one of the problems that more affects our society. Furthermore, the use of these fossil fuels has more many disadvantages. The majority of energy demand is fulfilled by conventional energy sources like coal, petroleum, and natural gas. Petroleum-based fuels are limited reserves concentrated in certain regions of the world and there is a high scarcity of known petroleum reserves. These sources are on the verge of reaching their peak production and experts suggest that current oil and gas reserves would suffice to last only a few more decades due to world energy demand continues to rise, as it can be seen in Figure 1.

![Figure 1: Projection of energy demand for the near future [1].](image)

The most feasible way to meet this growing demand is by using alternative fuels. To meet the rising energy demand and replace reducing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of alternative technologies. Finding new alternative fuels makes biomass sources more and more attractive. Accordingly, the viable alternative for compression-ignition engines is biodiesel [2].

As aforementioned, biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources, such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial [3]. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission
profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, which minimizes the impact of biodiesel combustion on the greenhouse effect. Biodiesel has a high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel [4].

Biodiesel is briefly defined as the monoalkyl esters of vegetable oils or animal fats. Biodiesel burns like petroleum diesel as it involves regulated pollutants. On the other hand, biodiesel probably has better efficiency than gasoline. Biodiesel also exhibits great potential for compression-ignition engines. Diesel fuel can also be replaced by biodiesel made from vegetable oils. Biodiesel is now mainly being produced from soybean, rapeseed, and palm oils. [2].

This necessity for finding alternatives to petroleum-based fuels is what drives this report. Hence, it aims to provide a comprehensive explanation about biodiesel and its production by studying several possible cases for producing it and to show biodiesel’s advantages and disadvantages by making an environmental and economic study.

1.2. History of biodiesel

The process for making fuel from biomass feedstock used in the 1800s is basically the same one used today, what means that producing biodiesel from vegetable oils (transesterification of triglycerides in oils) is not a new process. The history of biodiesel is more political and economic than technological. The early 20th century saw the introduction of gasoline powered automobiles. Oil companies were obliged to refine so much crude oil to supply gasoline that they were left with a surplus of distillate, which is an excellent fuel for diesel engines and much less expensive than vegetable oils [2].

Life for the diesel engine began in 1893, when German inventor Dr. Rudolph Diesel published a paper entitled “The theory and construction of a rational heat engine” [5]. The paper described a revolutionary engine in which air would be compressed by a piston to a very high pressure, thereby causing a high temperature. This engine followed the ideal Diesel cycle, which is shown in the following figure (Figure 2).
This cycle consists of two adiabatic compression-expansion processes, an isobaric heat addition process and an isochoric heat rejection process.

In 1900, Dr. Diesel used peanut oil to fuel one of his engines at the Paris Exposition. Since the engine was capable to withstand very high temperatures, it could run with a variety of vegetable oils including hemp and peanut oil. Later, at World’s Fair in Paris, in 1911, Dr. Diesel ran his engine on peanut oil and declared that the diesel engine could be fed with vegetable oils and would help considerably in the development of the agriculture of the countries which used it. Vegetable oils were used in diesel engines until the 1920s, when diesel engine manufacturers altered their engines to utilise the lower viscosity of petro-diesel, rather than vegetable oil [2].

The use of vegetable oils as an alternative renewable fuel competing with petroleum was proposed again in the early 1980s. The advantages of vegetable oils as diesel fuel are its portability, ready availability, renewability, higher heat content, lower sulphur content, lower aromatic content and biodegradability. The energy supply concerns of the 1970s renewed interest in biodiesel, but commercial production did not begin until the late 1990s [2].

In fact, Dr. Diesel believed that engines running on vegetable oils had potential and that these oils could one day be as important as petroleum-based fuels. Since the 1980s, biodiesel plants have opened in many European, South American and Asian countries, and some cities have run buses on biodiesel, or blends of petro and biodiesels. More recently, Renault and Peugeot have approved the use of biodiesel in some of their truck engines. Biodiesel plants are now being built by several companies in Europe; each of these plants will produce up to 1.5 million gallons of fuel per year. The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005 [2].
1.3. Background for biodiesel production

At present, the commercialization of biodiesel is a major problem due to its high cost compared to petroleum-based diesel. It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil. Exploring ways to reduce the high cost of biodiesel is very interesting in recent researches, especially for those methods concentrating on minimising the raw material cost. As an example, Zhang et al. [7], [8] developed a process design, a technological assessment and an economical evaluation of the biodiesel production from waste cooking oil. This is apparently an effective way to reduce raw material cost since it is estimated that waste cooking oil costs as about half the price of virgin oil. Moreover, it is of major importance to notice that several alternatives for biodiesel production exist nowadays. Zhang et al. [7], [8] studied different alternatives to explore potential economical exploits.

On the other hand, using waste cooking oil would also help to solve the problem of waste oil disposal. The latter evidences the necessity of making environmental assessments of the processes involved in biodiesel production, not only related to waste cooking oil disposal but on the several environmental aspects involved, e.g. CO₂ released.

In order to effectively evaluate technological, environmental and economic feasibility of a biodiesel plant, the process as a whole has to be considered. Therefore, there is a need to design a complete continuous process and assess its performance for the view point of an entire plant. This is why the present research is focused on developing whole process simulations, several environmental indicators calculation and, finally, economical evaluations.

The processes to be considered in this research are based in Zhang et al. [7], [8] research, namely, an acid-catalysed process and an alternative based on hexane extraction.

1.4. Objectives

The objectives for this work are the following ones:

1) Analyse the different biodiesel production ways with their pros and cons.
2) Simulate the different flowsheets by taking as example literature cases.
3) Aim to obtain similar results as in literature.
4) Compare and analyse the results obtained between cases.
5) Develop an economic assessment to the cases.
6) Calculate different environmental indicators.
2. SYSTEMS FOR BIODIESEL PRODUCTION

The most common way to produce biodiesel is by transesterification, which refers to a catalysed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. The main component of vegetable oil, triacylglycerols, consists of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (methanol is the most commonly used alcohol because of its low cost), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product, as it is shown in Figure 3 [7].

![Figure 3: Schematic representation of the transesterification of triglycerides with methanol to produce biodiesel [7].](image)

This reaction is normally composed by three steps, which must be consecutive and are reversible. In the first step, diglyceride is obtained from triglycerides. Then, monoglyceride is obtained from diglyceride. In the last step, the monoglyceride is converted in glycerine. In all these reactions esters are produced. The steechiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product [9].

In the following lines, the aforementioned three steps are explained:

\[
\text{Triglycerides} + R'^{\text{OH}} \leftrightarrow \text{Diglycerides} + R'^{\text{COOR}}_1
\]

\[
\text{Diglycerides} + R'^{\text{OH}} \leftrightarrow \text{Monoglycerides} + R'^{\text{COOR}}_2
\]

\[
\text{Monoglycerides} + R'^{\text{OH}} \leftrightarrow \text{Glycerine} + R'^{\text{COOR}}_3
\]

The most relevant variables that this kind of reaction are the following:

- Reaction temperature
- Ratio of alcohol to vegetable oil
- Amount of catalyst
- Catalyst
Apart from the transesterification reaction, the actual process of biodiesel production includes many processes steps from raw material to product separation and purification.

The following scheme (Figure 4) resumes a general biodiesel production.

![Figure 4: Basic scheme for biodiesel production [9].](image)

In this scheme, both methanol and vegetable oils enter the transesterification reaction in company of a catalyst, which can be acid or alkaline. Crude glycerine and biodiesel leave the reactor to be refined to desired purity specifications and methanol is recovered in other to be recycled to the reactor.

As it was mentioned before, catalysts play a very important role in the reaction and in the process as a whole. In fact, there are several potential catalysts that can be used in such a process. Each one of them has its advantages and disadvantages. For example, if the catalyst is enzymatic, the biodiesel production costs are significantly affected [10]. A recently studied possibility is the production of biodiesel without catalysts, feeding raw materials in supercritical conditions; nevertheless, these conditions are extremely severe and can punish either the yield of the process and the final products [9].

This research will be focused on processes which use alkaline (or basic) and acid catalysts, and that are described in the subsequent sections.

2.1. Alkali-catalysed system

This system consists of a reaction temperature near the boiling point of the alcohol (e.g., 60°C for methanol) and a 6:1 molar ratio of alcohol to soybean oil. On the results, approximately, 90-98% oil conversion to methyl esters can be observed within 90 min [11], [12]. The common catalyst
employed during alkaline transesterification at industrial level application includes the homogeneous catalysts like sodium hydroxide or potassium hydroxide.

One of the limitations of the alkali-catalysed process is that it may drive to a saponification reaction if the content of free water and free fatty acids in vegetal oils feed is high. Moreover, the biodiesel and glycerine produced have to be purified to remove the basic catalyst and need its separation by washing with hot distilled water twice or thrice [13].

Nevertheless, the alkali-catalysed process for biodiesel production has been applied industrially with noted successful commercial applications in Europe [7].

2.2. Acid-catalysed system

Acid-catalysed transesterification has been largely ignored because of its relatively slower reaction rate. The transesterification of soybean oil with methanol using 1wt.% concentrated sulphuric acid (based on oil), a temperature of 65 °C and a molar ratio of 30:1 methanol to oil, it takes 69 hours to obtain more than 90% oil conversion to methyl esters [11].

Studies of the acid-catalysed system have been very limited in number. No commercial biodiesel plants to date have been reported to use the acid-catalysed process. Despite its relatively slow reaction rate, the acid-catalysed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a pre-treatment step. These advantages favour the use of the acid-catalysed process when using waste cooking oil as the raw material [7].
3. PROCESSES FOR BIODIESEL PRODUCTION

In his article, Zhang et al. [7], [8] propose four different continuous process flowsheets for biodiesel production from virgin vegetable oil or waste cooking oil under alkaline or acid conditions on a commercial scale. The first process is an alkali-catalysed process using virgin vegetable oil; the second one, an alkali-catalysed process using waste cooking oil; the third one, and acid-catalysed process using cooking oil and the forth and the last one, an acid-catalysed process using hexane extraction and waste cooking oil. These four processes will be explained in the following paragraphs. In chapter 4, only two of these processes, process III and process IV, have been simulated and studied, as it will be explained later.

Zhang et al. [7], [8] use the software Aspen HYSYS for their simulations, unlike the simulations done in this rapport which are done with the software Aspen Plus, as it is explained in chapter 4. So all figures in the next paragraphs are flowsheets developed with Aspen HYSYS.

3.1. Process I: Alkali-catalysed process using virgin vegetable oil

The schema for this process is the one that is shown in the Figure 5 [7].

This flowsheet represents a continuous alkali-catalysed process using virgin oil as a raw material. Fresh methanol (stream 101), recycled methanol (stream 1201) and sodium hydroxide (stream 103) are mixed and pumped by pump P-101 to the reactor R-101. The reaction of transesterification produced in this reactor is the following one:

\[
\text{Triolein} + 3 \ \text{Methanol} \leftrightarrow 3 \ \text{FAME} + \text{Glycerol}
\]
At the same time, virgin vegetable oil (stream 105) enters to the reactor R-101 after being heated in exchanger E-101. In the reactor, a big part of oil is assumed to be converted in FAME and glycerol is produced as a by-product. Then, stream 106 from the reactor is introduced to methanol distillation column T-201.

Distillation column T-201 is used to separate methanol from the other components. Upper stream 201 is a pure methanol distillate which is used as a recycled methanol in stream 1201, as aforementioned. Bottom stream 202 is pumped by pump P-202 and cooled in E-201 before being sent to washing column T-301. The purpose of using this column is to separate the FAME from the glycerol, methanol and catalyst by adding water. After this process, FAME goes through the vessel X-301 which makes a second separation to improve FAME’s purity. Then, FAME with traces of unconverted oil, methanol and water goes through stream 301A. In stream 303, there is all the glycerol with traces of water, methanol and sodium hydroxide.

In order to obtain the purest biodiesel as possible, stream 301A goes to distillation column T-401, where a condenser is used to provide an easy separation of the FAME from water and methanol. Water and methanol are removed as vent gases (stream 401A) and FAME product is obtained in stream 401 as liquid distillate. Unconverted oil remained at the bottom of T-401. Since only a small amount of unconverted oil is left, it is treated as a waste in stream 402.

At the same time, stream 303 is fed to reactor R-201 to remove sodium hydroxide by adding phosphoric acid. In this reactor, it is produced the following reaction:

\[
3 \text{ NaOH} + \text{H}_3\text{PO}_4 \leftrightarrow \text{Na}_3\text{PO}_4 + 3 \text{H}_2\text{O}
\]

The resulting Na₃PO₄ is removed in gravity separator X-302 (stream 306). After removing the sodium hydroxide, the glycerol of stream 305 must be purified. For that, distillation column T-501 is used. Water and methanol are removed in distillate stream 501. At the bottom, in stream 502, glycerine is obtained as a high quality by-product.

3.2. Process II: Alkali-catalysed process using waste cooking oil

This continuous alkali-catalysed process from waste cooking oil is developed in order to lower the cost of biodiesel. For this purpose, a pre-treatment unit, including esterification of the free fatty acids, glycerine washing and methanol recovery is added to process I. This pre-treatment is shown in Figure 6 [7], while remainder of the process is identical to that shown in Figure 5.
Fresh methanol (stream 101), recycled methanol (stream 1111) and H₂SO₄ (stream 103) are mixed and pumped by pump P-101 to the esterification reactor R-100. Waste cooking oil (stream 105) is firstly pumped by pump P-105 and then heated in exchanger E-100 before entering R-100. In R-100, all the free fatty acids are converted to methyl esters. In this reactor, it is carried the following reaction:

\[
\text{Oleic acid} + \text{Methanol} \leftrightarrow \text{FAME} + \text{Water}
\]

Then, stream 106 is cooled in exchanger E-100 and it is sent to glycerine washing column T-100 to remove sulphuric acid and water. Subsequently, the waste cooking oil is sent to transesterification unit R-101, in order to produce more biodiesel. On the other hand, methanol is recovered to column T-301 and is recycled to R-100. Once the refined oil without fatty acids is obtained, the downstream units are identical to those in process I.

Compared to process I, despite the decrease in raw material cost by using waste cooking oil, the addition of a pre-treatment unit to reduce the content of free fatty acids in the feedstock oil in process II would be expected to offset the savings.
3.3. Process III: Acid-catalysed process using waste cooking oil

This process seems to be a promising alternative to the alkali process due to an acid-catalysed system is insensitive to any free fatty acids in the oil, as it has been previously explained. Figure 7 shows the flowsheet of this process [7].

![Acid-catalysed process to produce biodiesel from waste oils.](image)

In this process, fresh methanol (stream 101) and sulphuric acid (stream 103) are mixed and pumped by the pump P-101 to another mixer, where they are mixed with recycled methanol (stream 1201). Then, they are fed to the transesterification reactor R-101. At the same time, waste cooking oil (stream 105) is heated by exchanger E-101 before entering the reactor R-101. There are two identical reactors operating in series, indicated as R-101A/B. The transesterification reaction carried in the reactor is the following one:

\[
\text{Triolein} + 3 \text{Methanol} \leftrightarrow 3 \text{FAME} + \text{Glycerol}
\]

In order to reduce the large excess of methanol in the downstream units, stream 106 is fed to methanol distillation column T-201. From this column, a high percentage of methanol is recovered (stream 201) and recycled to R-101. Bottom stream 202 is sent to acid removal unit R-201. In reactor R-201, by adding calcium oxide (CaO), sulphuric acid is completely removed in a neutralisation reaction to produce CaSO₄ and H₂O, as it is shown in the following reaction:

\[
\text{H}_2\text{SO}_4 + \text{CaO} \leftrightarrow \text{CaSO}_4 + \text{H}_2\text{O}
\]

Then, a gravity separator, X-201, is used to remove the CaSO₄. There are two resulting streams: stream 203B is considered as a solid waste and stream 203C is sent to water washing column T-301.
The remaining water washing column (T-301) and purification units (i.e. FAME purification column T-401 and glycerol purification column T-501) are similar to those used in process I.

3.4. Process IV: Acid-catalysed process using hexane extraction

In this process, the use of hexane is proposed as a solvent to separate FAME from other components in order to avoid the formation of emulsions due to water washing. The operating conditions for the units from reactor R-101 to methanol distillation column T-201 are the same as those in process III (Figure 7). The following figure (Figure 8) shows the flowsheet of the units downstream of methanol distillation column T-201 of process III [7].

![Figure 8: Alternative acid-catalysed process to produce biodiesel from waste oils using hexane extraction.](image)

Stream 110 has the same volumetric flow of hexane as there is of methanol in stream 203. Fresh hexane (stream 110), recycled hexane (stream 1401), water (stream 111) and methanol (stream 203) are mixed and sent to hexane extraction column T-301A. Upper stream 205A goes to a second washing unit (T-301B), where methanol, recycled methanol (stream 1501) and water are added too. After T-301B, neither glycerol nor sulphuric acid remained in the FAME and hexane stream 301A. It is then sent to the FAME distillation column T-401 to remove the hexane. In this column, vent gases (stream 401A) are discharged from the top of T-401 and recycled to T-301A in order to reduce the necessity of fresh hexane solvent (stream 110). Distillate stream 401 is the FAME product with a high purity and stream 402 from the bottom of the T-401 contains some unconverted oil.
At the same time, stream 205B from T-301A is mixed with stream 301B from T-301B. The mixed stream is sent to reactor R-201 for sulphuric acid removal by adding calcium oxide. As in process III, the reaction that is carried in this reactor is the following one:

\[ \text{H}_2\text{SO}_4 + \text{CaO} \leftrightarrow \text{CaSO}_4 + \text{H}_2\text{O} \]

Subsequently, stream 303 is sent to a gravity separator in order to remove the CaSO₄. The resulting stream 303B is considered as solid waste. The other resulting stream, stream 303A, is sent to distillation column T-501 to glycerine purification. Glycerine with the desired purity is obtained in the stream 502. A portion of top stream 501 is returned to T-301B as the solvent for the second washing unit. The other portion of stream 501 is considered as liquid waste.

3.5. Process comparisons

After studying all the processes of the article of Zhang et al. [7], [8], a comparison between them is developed next.

The total number of major processing units in each process is summarised in Table 1.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Process I</th>
<th>Process II</th>
<th>Process III</th>
<th>Process IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactors</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Columns</td>
<td>4</td>
<td>6</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Exchangers</td>
<td>8</td>
<td>11</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Pumps</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Gravity separators</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>21</strong></td>
<td><strong>29</strong></td>
<td><strong>21</strong></td>
<td><strong>25</strong></td>
</tr>
</tbody>
</table>

Table 1: Number of main units required for each process [7].

Knowing the number of each type of unit used in each process is useful to estimate the quantity of energy that each process is going to need or which process is going to be more expensive in terms of processing units (without taking into account the raw materials). For example, distillation columns are the most used unit operation in chemical processes. Nevertheless, they represent the most expensive equipment in terms of capital and operating costs [14]. Indeed, to produce the same quantity and quality of product, the less number of distillation columns, the more economical.

Another important consideration to take into account is that, as processes III and IV are acid-catalysed, they are insensitive to free fatty acids and can use waste cooking oil as a raw material without the requirement of a pre-treatment unit. By contrast, process II is alkali-catalysed and, consequently, does need this pre-treatment unit to avoid a saponification reaction between the free fatty acids and the alkaline catalyst. Process I does not need a pre-treatment unit because it uses virgin oil as a raw material and it has no free fatty acids.
4. SIMULATION OF BIODIESEL PRODUCTION PROCESSES

This rapport is focused in two of the four processes explained before. Specifically, the acid-catalysed processes, process III and process IV, are going to be simulated with the software Aspen Plus. Then, the obtained results are going to be compared with those obtained by Zhang et al. [7], [8] and be analysed to calculate the environmental indicators (chapter 5) and to develop an economic assessment (chapter 6).

4.1. Simulation of process III: Acid-catalysed process using waste cooking oil

The first step to do to model the process flowsheet for the later simulation is to define the substances that are part of the process and the thermodynamic model used. The substances used in this process are shown in the following table (Table 2).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>C₃H₈O₃</td>
</tr>
<tr>
<td>Triolein</td>
<td>C₁₃H₁ₐ₄O₆</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₄O</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Methyl-Oleate (FAME)</td>
<td>C₁₉H₃₆O₂</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>CaO</td>
</tr>
<tr>
<td>Calcium Sulphate</td>
<td>CaSO₄</td>
</tr>
</tbody>
</table>

Table 2: Substances used in process III.

As a thermodynamic model, it was used the UNIQUAC (Universal Quasi-Chemical) model due to important non-idealities between certain components of the process, which means that there is a high presence of polar components, like methanol and glycerol, that make that the liquid phase is non-ideal [15].

The following step is to define the feed conditions to reactors and distillation columns [7]. The transesterification reaction conditions in R-101A/B are set to a 50:1 molar ratio of methanol to oil, a 1,3:1 molar ratio of sulphuric acid to waste oil, a reaction temperature of 80 °C and a pressure of 400 kPa. In reactor R-201, sulphuric acid is completely removed in a neutralisation reaction. It works at 60 °C of temperature and at 400 kPa of pressure. Methanol distillation column T-201 is made of five theoretical stages and it operates with a molar reflux ratio of 2 and under vacuum. Water washing column T-301 has four theoretical stages. FAME distillation column T-401 is used to obtain a final biodiesel product with the desired purity and it has four theoretical stages and a molar reflux ratio of 2. Glycerine purification column is designed with four theoretical stages and a molar reflux ratio of 2.
In terms of Aspen Plus modules used to simulate the most important unit operations, namely, reactors and distillation columns, the former are modelled with ideal conversion reactors (RStoic) since reaction temperature and conversion are known. The latter are modelled with the RadFrac module, which uses a rigorous phase equilibrium model to model distillation columns. Other modules such as heat exchangers are modelled ideally since the approach adopted in this work do not need further results.

In the following tables (Table 3 and Table 4), the results obtained from the simulation in each stream are displayed.

<table>
<thead>
<tr>
<th>Mass Fraction</th>
<th>101</th>
<th>102</th>
<th>103</th>
<th>105B</th>
<th>106</th>
<th>201</th>
<th>202</th>
<th>203B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,064</td>
<td>0,00</td>
<td>0,074</td>
<td>0,00</td>
</tr>
<tr>
<td>Triolein (oil)</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>1,00</td>
<td>0,019</td>
<td>0,00</td>
<td>0,022</td>
<td>0,00</td>
</tr>
<tr>
<td>Water</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>Methanol</td>
<td>1,00</td>
<td>0,746</td>
<td>0,00</td>
<td>0,00</td>
<td>0,205</td>
<td>1,00</td>
<td>0,078</td>
<td>0,00</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0,00</td>
<td>0,254</td>
<td>1,00</td>
<td>0,00</td>
<td>0,093</td>
<td>0,00</td>
<td>0,108</td>
<td>0,00</td>
</tr>
<tr>
<td>FAME (biodiesel)</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,619</td>
<td>0,00</td>
<td>0,718</td>
<td>0,00</td>
</tr>
<tr>
<td>CaO</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>1,00</td>
</tr>
<tr>
<td><strong>Total Flow [kmol/h]</strong></td>
<td>6,750</td>
<td>15,280</td>
<td>1,530</td>
<td>1,160</td>
<td>16,440</td>
<td>7,000</td>
<td>9,440</td>
<td>1,515</td>
</tr>
<tr>
<td><strong>Total Flow [kg/h]</strong></td>
<td>216,285</td>
<td>590,643</td>
<td>150,062</td>
<td>1,160</td>
<td>1,027,121</td>
<td>1,027,121</td>
<td>1,027,121</td>
<td>1,027,121</td>
</tr>
<tr>
<td><strong>Total Flow [l/min]</strong></td>
<td>4,546</td>
<td>11,233</td>
<td>1,364</td>
<td>1,364</td>
<td>19,136</td>
<td>31,354</td>
<td>224,297</td>
<td>1,161</td>
</tr>
<tr>
<td><strong>Temperature [°C]</strong></td>
<td>25,0</td>
<td>25,0</td>
<td>65,9</td>
<td>80,0</td>
<td>81,4</td>
<td>103,3</td>
<td>60,0</td>
<td></td>
</tr>
<tr>
<td><strong>Pressure [bar]</strong></td>
<td>1,0</td>
<td>4,0</td>
<td>1,0</td>
<td>4,0</td>
<td>4,0</td>
<td>1,9</td>
<td>2,0</td>
<td>1,3</td>
</tr>
</tbody>
</table>

Table 3: Summary of results obtained by stream in process III.

<table>
<thead>
<tr>
<th>Mass Fraction</th>
<th>301</th>
<th>302</th>
<th>303</th>
<th>401</th>
<th>401A</th>
<th>402</th>
<th>501</th>
<th>502</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>0,00</td>
<td>0,461</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,463</td>
</tr>
<tr>
<td>Triolein (oil)</td>
<td>0,029</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,829</td>
<td>0,00</td>
</tr>
<tr>
<td>Water</td>
<td>0,00</td>
<td>0,00</td>
<td>0,150</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,015</td>
<td>0,151</td>
</tr>
<tr>
<td>Methanol</td>
<td>0,020</td>
<td>0,384</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,985</td>
<td>0,382</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>FAME (biodiesel)</td>
<td>0,944</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,157</td>
<td>0,00</td>
</tr>
<tr>
<td>CaO</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,014</td>
<td>0,00</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td><strong>Total Flow [kmol/h]</strong></td>
<td>4,362</td>
<td>5,704</td>
<td>2,580</td>
<td>1,720</td>
<td>0,062</td>
<td>0,025</td>
<td>5,679</td>
<td></td>
</tr>
<tr>
<td><strong>Total Flow [kg/h]</strong></td>
<td>1,059,268</td>
<td>224,788</td>
<td>763,430</td>
<td>259,887</td>
<td>35,952</td>
<td>0,803</td>
<td>223,986</td>
<td></td>
</tr>
<tr>
<td><strong>Total Flow [l/min]</strong></td>
<td>21,183</td>
<td>3,829</td>
<td>18,741</td>
<td>3,279,065</td>
<td>1,081</td>
<td>0,017</td>
<td>3,802</td>
<td></td>
</tr>
<tr>
<td><strong>Temperature [°C]</strong></td>
<td>50,0</td>
<td>60,0</td>
<td>277,2</td>
<td>277,2</td>
<td>369,6</td>
<td>43,0</td>
<td>57,5</td>
<td></td>
</tr>
<tr>
<td><strong>Pressure [bar]</strong></td>
<td>1,1</td>
<td>1,2</td>
<td>0,4</td>
<td>0,4</td>
<td>0,5</td>
<td>0,4</td>
<td>0,5</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Continuation of Table 3.

The whole process simulation is illustrated in the following figure (Figure 9).
Figure 9: Aspen Plus flowsheet of the process III.
4.2. Simulation of process IV: Acid-catalysed process using hexane extraction

The substances in this process are shown in the Table 5. As this process is very similar to process III but using hexane extraction, the substance are the same as process III and adding hexane.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>C_3H_8O_3</td>
</tr>
<tr>
<td>Triolein</td>
<td>C_{57}H_{104}O_6</td>
</tr>
<tr>
<td>Water</td>
<td>H_2O</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH_4O</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>H_2SO_4</td>
</tr>
<tr>
<td>Methyl-Oleate (FAME)</td>
<td>C_{19}H_{36}O_2</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>CaO</td>
</tr>
<tr>
<td>Calcium Sulphate</td>
<td>CaSO_4</td>
</tr>
<tr>
<td>N-hexane</td>
<td>C_6H_{14}-1</td>
</tr>
</tbody>
</table>

Table 5: Substances used in process IV.

As a thermodynamic model, it was used the NRTL (Non-Random Two Liquids) model due to important non-idealities between certain components of the process, which means that there is a high presence of polar components, like methanol and glycerol, that make that the liquid phase is non-ideal [15].

The operating conditions for the units from reactor R-101 to methanol distillation column T-201 are the same as those in process III. The following discussion pertains to the units downstream of methanol distillation column T-201 [7]. Instead of a liquid-liquid extraction unit, component splitters T-301A and T-301B are used in simulating the hexane extraction of FAME and the methanol/water washing. Based on the methanol volume in stream 203, an equal volume of hexane is added to T-301A and the volumetric ratio of water to methanol is 1:10. T-301A works at a temperature of 40 °C and at a pressure of 190 kPa. In T-301B, 80:20 v/v of methanol-water is added. Splitter T-301B works at 30 °C of temperature and 160 kPa of pressure. In terms of distillations columns, apart from methanol distillation column T-201 which is the same as in process III, there are T-401, which is principally used for distilling hexane from FAME and T-501, which is used to purify glycerine. FAME distillation column T-401 is made of five theoretical stages and it operates with a molar reflux ratio of 3. On the other hand, glycerine purification column T-501 is made of five theoretical stages and it operates with a molar reflux ratio of 2.

In this process, a design specification was included to Zhang’s simulation in order to obtain the same results as Zhang. This design specification consists in adding a TEE and varying the purge ratio to obtain the desired recycled hexane ratio and, consequently, the FAME purity desired.

In terms of Aspen Plus modules, they are the same that have been used in process III (chapter 4.1).
After running the simulation, the following results were obtained (Table 6 and Table 7).

<table>
<thead>
<tr>
<th>Mass Frac</th>
<th>101</th>
<th>102</th>
<th>103</th>
<th>105</th>
<th>106</th>
<th>201</th>
<th>203</th>
<th>205A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,064</td>
<td>0,000</td>
<td>0,074</td>
<td>0,000</td>
</tr>
<tr>
<td>Triolein (oil)</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>1,000</td>
<td>0,019</td>
<td>0,000</td>
<td>0,022</td>
<td>0,024</td>
</tr>
<tr>
<td>Water</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
</tr>
<tr>
<td>Methanol</td>
<td>1,000</td>
<td>0,746</td>
<td>0,000</td>
<td>0,000</td>
<td>0,205</td>
<td>1,000</td>
<td>0,077</td>
<td>0,000</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0,000</td>
<td>0,254</td>
<td>1,000</td>
<td>0,000</td>
<td>0,093</td>
<td>0,000</td>
<td>0,108</td>
<td>0,000</td>
</tr>
<tr>
<td>FAME (biodiesel)</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,619</td>
<td>0,000</td>
<td>0,718</td>
<td>0,800</td>
</tr>
<tr>
<td>CaO</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,169</td>
</tr>
<tr>
<td>Total Flow [kmol/h]</td>
<td>6,743</td>
<td>15,273</td>
<td>1,530</td>
<td>1,160</td>
<td>16,433</td>
<td>7,000</td>
<td>9,433</td>
<td>6,159</td>
</tr>
<tr>
<td>Total Flow [kg/h]</td>
<td>216,074</td>
<td>590,408</td>
<td>150,039</td>
<td>1,027,120</td>
<td>1,617,528</td>
<td>224,295</td>
<td>1,393,233</td>
<td>1,272,375</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>25,0</td>
<td>53,2</td>
<td>25,0</td>
<td>25,0</td>
<td>80,0</td>
<td>81,4</td>
<td>46,8</td>
<td>36,8</td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>1,0</td>
<td>4,0</td>
<td>1,0</td>
<td>1,0</td>
<td>4,0</td>
<td>1,9</td>
<td>2,0</td>
<td>2,0</td>
</tr>
</tbody>
</table>

Table 6: Summary of results obtained by stream in process III.

<table>
<thead>
<tr>
<th>Mass Frac</th>
<th>301C</th>
<th>303A</th>
<th>303B</th>
<th>401</th>
<th>401A</th>
<th>402</th>
<th>501</th>
<th>501C</th>
<th>502</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>0,000</td>
<td>0,276</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,798</td>
</tr>
<tr>
<td>Triolein (oil)</td>
<td>0,024</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,533</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
</tr>
<tr>
<td>Water</td>
<td>0,000</td>
<td>0,170</td>
<td>0,000</td>
<td>0,000</td>
<td>0,011</td>
<td>0,000</td>
<td>0,194</td>
<td>0,194</td>
<td>0,124</td>
</tr>
<tr>
<td>Methanol</td>
<td>0,000</td>
<td>0,528</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,806</td>
<td>0,806</td>
<td>0,000</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,023</td>
</tr>
<tr>
<td>FAME (biodiesel)</td>
<td>0,804</td>
<td>0,014</td>
<td>0,000</td>
<td>0,996</td>
<td>0,164</td>
<td>0,467</td>
<td>0,000</td>
<td>0,000</td>
<td>0,039</td>
</tr>
<tr>
<td>CaO</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,013</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0,000</td>
<td>0,000</td>
<td>1,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0,169</td>
<td>0,000</td>
<td>0,000</td>
<td>0,824</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
<td>0,000</td>
</tr>
<tr>
<td>Total Flow [kmol/h]</td>
<td>6,117</td>
<td>10,949</td>
<td>1,499</td>
<td>3,229</td>
<td>2,771</td>
<td>0,117</td>
<td>8,840</td>
<td>8,752</td>
<td>2,109</td>
</tr>
<tr>
<td>Total Flow [kg/h]</td>
<td>1,266,439</td>
<td>375,959</td>
<td>204,096</td>
<td>954,582</td>
<td>258,147</td>
<td>53,710</td>
<td>246,060</td>
<td>243,600</td>
<td>129,898</td>
</tr>
<tr>
<td>Total Flow [l/min]</td>
<td>28,086</td>
<td>7,032</td>
<td>1,149</td>
<td>21,070</td>
<td>17,511,2</td>
<td>1,433</td>
<td>5,162</td>
<td>5,111</td>
<td>2,202</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>65,4</td>
<td>40,0</td>
<td>40,0</td>
<td>182,9</td>
<td>182,9</td>
<td>289,7</td>
<td>47,3</td>
<td>47,4</td>
<td>99,8</td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>1,5</td>
<td>1,6</td>
<td>1,6</td>
<td>0,1</td>
<td>0,1</td>
<td>0,2</td>
<td>0,4</td>
<td>1,0</td>
<td>0,5</td>
</tr>
</tbody>
</table>

Table 7: Continuation of Table 6.

The whole process is illustrated in the following figure (Figure 10).
Figure 10: Aspen Plus flowsheet for the process IV.
5. ENVIRONMENTAL STUDY USING ENVIRONMENTAL INDICATORS

Different environmental indicators can be calculated for the case of biodiesel production. Based in Ruiz-Mercado et al. [16], where a list of different Environmental Indicators for Sustainability Assessment of Chemical Processes can be found, this rapport tries to calculate as many as possible just for the biodiesel production case and the materials aforementioned.

Indicators 1, 2 and 3 (number of hazardous materials input, mass of hazardous materials input and specific hazardous raw materials input, respectively) are calculated with the following formulas:

\[ N_{\text{haz,mat}} = \text{Number of hazardous substances fed to the process} \]
\[ m_{\text{haz,mat}} = \text{Total mass of hazardous materials fed to the process} \]
\[ m_{\text{haz,mat,spec}} = \frac{m_{\text{haz,mat}}}{\text{Mass of product}} \]

For process III, the input of hazardous materials are triolein and acid sulphuric. For process IV, there are the same hazardous materials input plus the hexane [17]. Streams 401 and 502 are considered as mass of product in both processes, since these streams refer to FAME and glycerol, respectively.

Indicator 4 (total mass of persistent, bioaccumulative and toxic chemicals used) was also discarded as there are no PBT materials in the biodiesel production process [18].

Indicator 5 (chemical exposure index) reflects the relative acute health hazard potential from possible chemical release incidents. As there is no information about the possible chemical release incidents, this indicator is also discarded.

Indicator 6 (health hazard, irritation factor) is calculated with the volume of irritating substances in the workplace. Chemical agents are the main cause of occupational skin diseases and disorders. These agents are divided in two types: primary irritants and sensitizers. Primary or direct irritants act directly on the skin through chemical reactions. Sensitizers may not cause immediate skin reactions, but repeated exposure can result in allergic reactions. A worker’s skin may be exposed to hazardous chemicals through: direct contact with contaminated surfaces, deposition of aerosols, immersion or splashes [19]. As there are no compounds with these characteristics in the biodiesel production process, this indicator is also discarded.

Indicator 7 (health hazard, chronic toxicity factor) takes into account the volume of air polluted to a workplace threshold value. In this process, it is considered that all the emissions go outside the workplace, so this indicator is discarded.
Indicator 8 (safety hazard, mobility) includes two safety aspects: the volatility of substances (depending on process pressure and temperature and the vapour pressure of the substance) and the probability that a new phase is generated (boiling or melting point close to process temperature). Pressurised gases receive the highest ranking of 1, dust and normal gases have an index value of 0.8, and dissolved or suspended solids are considered harmless \[20\]. To calculate this indicator, it is necessary to know the mass released into the air in case of failure and this information is not available.

Indicator 9 indicates the safety hazard, fire/explosion. A substance is identified to be a fire/explosion hazard, if it can serve as fuel, ignition source or oxygen source for combustion. Fuels are analysed using flashpoint or legal classification schemes. Substances that cause combustion of other material by providing oxygen (oxidising substances, risk phrase R7, R8, R9) are considered to be oxygen sources. For estimating the physical value, the probability of fire/explosion (the difference between flashpoint and process temperature) is multiplied with the combustion enthalpy \[20\]. The substances that exhibit potential combustion reactions are biodiesel, methanol, glycerol triolein and hexane (this last only for process IV). For the sake of simplicity, this indicator is going to be calculated just for the products (biodiesel and glycerol) and methanol since it is an alcohol and, consequently, very inflammable. The formula to calculate it is:

\[
SH_{\text{fire/explosion}} = \frac{\text{Probable energy potential for reaction with } O_2}{\text{Mass of product}}
\]

Indicators 10 and 11 (safety hazard, reaction/decomposition I and safety hazard, reaction/decomposition II) cannot be calculated due to, for that, there is the necessity to know the probability of undesired reaction or decomposition and this information is not available.

Indicator 12 expresses the safety hazard, acute toxicity. To calculate this indicator, it is needed to know the European legislation about National emission ceilings for certain atmospheric pollutants. There is a directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on national emission ceilings for certain atmospheric pollutants \[21\]. This Directive covers emissions in the territory of the Member States and their exclusive economic zones from four pollutants which arise as a result of human activities: emissions of sulphur dioxide (SO\(_2\)), emissions of nitrogen oxides (NO\(_x\)), emissions of volatile organic compounds (VOC) and emissions of ammonia (NH\(_3\)). These pollutants are responsible for the phenomena of acidification, eutrophication and tropospheric ozone formation (also called “bad ozone”, present at low altitude, as opposed to stratospheric ozone), irrespective of the sources of pollution. Now it is necessary to check if glycerol is a VOC, as there are no emissions of sulphur dioxide, of nitrogen oxides or of ammonia. In the
European Union’s definition, a VOC is any organic compound having an initial boiling point less than or equal to 250 °C measures at a standard atmospheric pressure of 101.3 kPa and can do damage to visual or audible senses [22]. As glycerol’s boiling point is 290 °C, it is not considered as a VOC and this indicator is discarded.

Indicator 13 (fault tree assessment) is calculated as the probability of system failure if the reliability of individual components is known. Due to the difficulty to calculate the reliability of the individual components of the biodiesel production process, this indicator is also discarded.

Indicators 14 and 15 (specific toxic release and toxic release intensity, respectively) are rejected due to the inexistent mass of toxics (TRI) released [23]. In general, chemicals covered by TRI program are those that cause cancer or other chronic human health effects, significant adverse acute human health effects or significant adverse environmental effects [24].

Indicator 16, which corresponds to environmental quotient, can be calculated with the following formula:

\[
EQ = \frac{\text{Total mass of waste}}{\text{Mass of product}}
\]

In process III, stream 203B, 401A, 402 and 501 are considered as waste since they are not recycled. In process IV, the streams that are considered waste are 303B, 402 and SS.

Indicator 17 (human health burden, cancer effects) can be calculated with the formula below:

\[
EB_{\text{cancer eff.}} = \frac{\text{Total mass of benzene equivalents (EB)}}{\text{Sales revenue or value added}}
\]

To calculate the total mass of benzene equivalents, the following formula is used:

\[
P_{F_{\text{substance}}} = \frac{OEL_{\text{benzene}}}{OEL_{\text{substance}}} = \frac{0.0625}{0.05} = 1.25
\]

where \(OEL_{\text{benzene}}=0.0625\) and \(OEL_{\text{H}_2\text{SO}_4}=0.05\). As the \(\text{H}_2\text{SO}_4\) is the only compound that can affect negatively to the human health [17], it is the only substance to be taken into account. Once the \(P_{F_{\text{substance}}}\) is calculated, the next formula used to calculate the total mass of benzene equivalents (EB) is:

\[
EB = W(\text{kgH}_2\text{SO}_4) \cdot P_{F_{\text{substance}}}
\]

where \(W\) is the weight of the substance (in this case \(\text{H}_2\text{SO}_4\)) [25]. To this calculate indicator, the results of the economic assessment (chapter 6) are needed (Table 12).
Indicator 18 (environmental hazard, persistency of organic substances) can be calculated with the following formula:

\[ EH_{\text{degradation}} = \frac{\text{Mass released of organic substances}}{\text{Mass of product}} \]

As the processes have methanol and oil as waste streams (and process IV has also hexane), and they are organic chemical compound, this indicator is easily calculated with the formula above.

Indicator 19 (environmental hazard, air hazard) is calculated with the following formula:

\[ EH_{\text{air}} = \frac{\text{Volume of limit concentration air emission equivalents}}{\text{Mass of product}} \]

In any of the processes there are no air emissions due to there is no vapour or gas released, so this indicator cannot be calculated.

Indicator 20 (environmental hazard, water hazard) can be calculated with:

\[ EH_{\text{water}} = \frac{\text{Volume of limit concentration water release equivalents}}{\text{Mass of product}} \]

In process III, there are two streams which release limit concentration water (streams 401A and 501). On the contrary, in process IV there is any stream which release limit concentration water.

Indicator 21 (environmental hazard, solid waste (inorganic pollutants)), can be calculated with the following formula:

\[ EH_{\text{solid}} = \frac{\text{Total mass of inorganic solid waste}}{\text{Mass of product}} \]

In process III as well as in process IV, there is one stream which is an inorganic solid waste: stream 203B and stream 303B, respectively, which the solid waste is the CaSO₄.

Indicator 22 (environment hazard, bioaccumulation (the food chain or in the soil)) is discarded due to there is no information about how the biodiesel production process affects the food chain.

Indicators 23 and 24 refer to global warming potential and global warming intensity, respectively. In any of the two processes there are gases that affect to global warming [17], so these indicators are not calculated.

Indicators 25 and 26 define the stratospheric ozone-depletion potential and the stratospheric ozone-depletion intensity, respectively. The potency factor for this category is based on the potential to deplete ozone in the upper atmosphere relative to chlorofluorocarbon-11 (ODP – the
ozone depletion potential) [25]. In any of the processes there are chlorofluorocarbons, so these indicators cannot be calculated.

Indicators 27 and 28 show the photochemical oxidation (smog) potential and the photochemical oxidation (smog) intensity, respectively. Potency factors for this category are obtained from the potential of substances to create ozone photochemically. The unit to calculate this indicator is ethylene equivalent. As in the process of biodiesel production there is any compound that can be expressed in ethylene equivalent, these indicators are discarded [25].

Indicators 29 and 30 show the atmospheric acidification potential and the atmospheric acidification intensity, respectively. The potential of certain released gases to form acid rain and acids to water is the potency factor for atmospheric acidification. The unit to calculate this indicator is sulphur dioxide (SO$_2$) equivalent. As in the process of biodiesel production there is any compound that can be expressed in SO$_2$ equivalent, these indicators are discarded [25].

Indicators 31 and 32 refer to aquatic acidification potential and aquatic acidification intensity, respectively. To calculate them, the total mass of released H$^+$ is needed. Nevertheless, none of the compounds released are acids, so none of the compounds released have H$^+$

Indicators 33 and 34 (aquatic basification potential and aquatic basification intensity, respectively) can be calculated with the following formulas:

$$WP_{\text{basification}} = \frac{\text{Total mass of released OH}^- \text{ ions}}{\text{Mass of product}}$$

$$WPI_{\text{basification}} = \frac{\text{Total mass of released OH}^- \text{ ions}}{\text{Sales revenue or value added}}$$

The only compound released with potential to release OH$^-$ ions is methanol, so the total mass of methanol is needed to calculate these indicators.

Indicators 35 and 36 (aquatic salinization potential and aquatic salinization intensity, respectively) can be calculated with the following formulas:

$$WP_{\text{salinization}} = \frac{\text{Total mass of released Na}^+, \text{ Cl}^-, \text{ SO}_4^{2-}, \text{ Mg}^{2+}, \text{ Ca}^{2+}, \text{ K}^+}{\text{Mass of product}}$$

$$WPI_{\text{salinization}} = \frac{\text{Total mass of released Na}^+, \text{ Cl}^-, \text{ SO}_4^{2-}, \text{ Mg}^{2+}, \text{ Ca}^{2+}, \text{ K}^+}{\text{Sales revenue or value added}}$$

In the case of biodiesel production, only SO$_4^{2-}$ must be taken into account due to there is the only ion which is presented in this process [25]. To calculate them, the mass of CaSO$_4$ released is needed.
Indicators 37 and 38 (aquatic oxygen demand potential and aquatic oxygen demand intensity) can be calculated with:

\[
WP_{O_2 \text{ dem}} = \frac{\text{Total mass of dissolved O}_2 \text{ removed (EB value)}}{\text{Mass of product}}
\]

\[
WPI_{O_2 \text{ dem}} = \frac{\text{Total mass of dissolved O}_2 \text{ removed (EB value)}}{\text{Sales revenue or value added}}
\]

The Stoichiometric Oxygen Demand (StOD) has been chosen as the potency factor. It represents the maximum potential of emissions to water to remove dissolved oxygen that would otherwise support fish and other aquatic life. StOD is expressed as tones of oxygen required per tonne of substance.

There is a method to calculate the StOD, which is based in the knowledge of the chemical structure and the calculation of the following empirical formula: \(C_cH_hN_nClClNaNaOsPsSs\). Then calculate the StOD in tones \(O_2\) per tonne of substance from the equation:

\[
\text{StOD} = \frac{16 \cdot (2 \cdot c + 0.5 \cdot (h - Cl) + 2.5 \cdot n + 3 \cdot s + 2.5 \cdot p + 0.5 \cdot Na - o)}{\text{Molecular Weight}}
\]

Sulfuric acid (\(H_2SO_4\)) with a molecular weight of 98,079 g/mol:

\[
\text{StOD} = \frac{16 \cdot (0.5 \cdot 2 + 3 \cdot 1 - 4)}{98,079} = 0 \text{ tonnes of } O_2 \text{ per tonne of } H_2SO_4
\]

Triolein (canola oil, \(C_57H_{104}O_6\)) with a molecular weight of 885,432 g/mol:

\[
\text{StOD} = \frac{16 \cdot (2 \cdot 57 + 0.5 \cdot 104 - 6)}{885,432} = 2,891 \text{ tonnes of } O_2 \text{ per tonne of } C_{57}H_{104}O_6
\]

Methanol (\(CH_4O\)) with a molecular weight of 32 g/mol:

\[
\text{StOD} = \frac{16 \cdot (2 + 0.4 \cdot 4) - 1}{32} = 1,769 \text{ tonnes of } O_2 \text{ per tonne of } CH_4O
\]

As aforementioned, these numbers are the potency factor (PF). To calculate the total mass of dissolved \(O_2\) removed (EB value), the following formula is needed:

\[
\text{EB value} = W \cdot PF
\]

where \(W\) is the weight of the substance in tonnes [25].

Indicators 39 and 40 refer ecotoxicity to aquatic life potential and ecotoxicity to aquatic life intensity, respectively. To calculate them, the total mass of formaldehyde equivalents is needed but, in any of the two processes, there is any compound which has formaldehyde.
Indicators 41 and 42 refer to ecotoxicity to aquatic life potential by metals and ecotoxicity to aquatic life intensity by metals, respectively. To calculate them, the total mass of copper equivalents is needed but, in any of the two processes, there is any compound which has copper.

Indicators 43 and 44 refer to eutrophication potential and eutrophication potential intensity, respectively. To calculate them, the total mass of phosphate equivalents is needed but, in any of the two processes, there is any compound which has phosphate.

Indicators 45 and 46 (specific emergy intensity and emergy intensity, respectively) are calculated with the following formulas:

\[
\text{SMI}_M = \frac{\text{Total emergy consumed in the process}}{\text{Mass of product}}
\]

\[
\text{MI}_M = \frac{\text{Total emergy consumed in the process}}{\text{Sales revenue or value added}}
\]

Emergy is defined as the sum of all inputs of energy directly or indirectly required by a process to provide a given product when the inputs are expressed in the same form (or type) of energy. Most often, inputs to a process are the result of another process (or a chain of processes), in which energy has been concentrated and upgraded. Thus, the total emergy input is derived by summing all inputs used in the chain of processes that yielded the output in question [26]. The total emergy consumed in the process is calculated by doing a global enthalpy balance.

Indicator 47, which corresponds to environmental loading ratio, is calculated with the following formula:

\[
\text{ELR} = \frac{\text{Total emergy supplied from nonrenewable resources}}{\text{Total emergy supplied from renewable resources}}
\]

The environmental loading ratio (ELR) is the ratio of purchased (F) and non-renewable indigenous emergy (N) to free environmental emergy (R). It is an indicator of the pressure of the process on the local ecosystem and can be considered a measure of the ecosystem stress due to production activity. This means that the environmental loading (stress applied to the environment) can also be expressed by the fraction of renewable emergy driving a process. The lower the fraction of renewable emergy used, the higher the pressure on the environment [26]. As the kind of resources it not taken into account in this work, this indicator cannot be calculated.

Indicator 48 corresponds to emergy yield ratio or resource-ECEC efficiency and it can be calculated using the following formula:
The emergy yield ratio (EYR) is the ratio of the emergy of the output (Y), divided by the emergy of those inputs (F) to the process that are fed back from outside the system under study. It is an indicator of the yield compared with inputs other than local inputs and gives a measure of the ability of the process to exploit local resources accounting for the difference between local and imported. The higher the EYR, the higher this ability, which is not a negligible factor in economic systems [26].

Indicator 49 expresses the emergy sustainability index and it is calculated with:

$$\text{ESI} = \frac{\text{Emergy yield ratio}}{\text{Environmental loading ratio}} = \frac{\text{EYR}}{\text{ELR}}$$

This indicator cannot be calculated since ELR (indicator 47) was no possible to calculate.

Indicator 50 expresses the breeding factor. The energy or exergy breeding factor assesses how much renewable resources are bred from non-renewable resources. To do so, renewable inputs have to be subtracted from the total input [27]. It is calculated with the following formula:

$$\text{BF}_M = \frac{\text{Total emergy content of the product}}{\text{Total emergy supplied from nonrenewable resources}}$$

Indicator 51 (renewability index) is calculated with the following formula:

$$\text{RI} = \frac{\text{Total emergy supplied from renewable resources}}{\text{Total emergy supplied to the process}}$$

As the kind of resources it not taken into account in this work, indicators 50 and 51 cannot be calculated.

Indicator 52 (total solid waste mass) can be calculated with the following formula:

$$m_{s,\text{tot}} = \text{Total mass of solid waste}$$

In process III as well as in process IV, there is one stream which is an inorganic solid waste: stream 203B and stream 303B, respectively.

Indicator 53 (specific solid waste mass) is calculated with the following formula:

$$m_{s,\text{spec}} = \frac{\text{Mass of specific type of solid waste}}{\text{Mass of product}}$$

Indicator 54 corresponds to the solid waste mass for recovery and it can be calculated with the following formula:
\[ m_{s,\text{recov}} = \text{Mass of recovered solid waste} \]

As there is no mass of recovered solid waste in any of the two processes, the value of this indicator in 0 in both cases.

Indicator 55 corresponds to the solid waste mass for disposal and it can be calculated with the following formula:

\[ m_{s,\text{disp}} = \text{Mass of nonrecovered solid waste} \]

All the mass of solid waste is non-recovered, so this indicator has the same value as indicator 52.

Indicator 56 expresses the recycling mass fraction and it is calculated with the following formula:

\[ w_{s,\text{recycl}} = \frac{\text{Mass of recycled solid waste}}{\text{Total mass of solid waste}} = \frac{\text{Indicator 54}}{\text{Indicator 52}} \]

Indicator 57 corresponds to the disposal mass fraction and it can be calculated with the following formula:

\[ w_{s,\text{nonrecycl}} = \frac{\text{Mass of nonrecovered solid waste}}{\text{Total mass of solid waste}} = \frac{\text{Indicator 55}}{\text{Indicator 52}} \]

Indicators 58, 59 and 60 (hazardous solid waste mass fraction, total hazardous solid waste disposal and specific hazardous solid waste, respectively) were discarded due there is no hazardous solid waste in this process (CaSO₄ is no hazardous) [17].

Indicators 61 and 62 (total non-hazardous solid waste disposal and non-hazardous solid waste intensity, respectively) can be calculated with the following formulas:

\[ m_{s,\text{nhaz}} = \text{Mass of nonhazardous solid waste released into the environment} \]

\[ m_{s,\text{nhaz,spec}} = \frac{\text{Mass of nonhazardous solid waste released}}{\text{Sales revenue or value added}} \]

As it has been mentioned before, all the solid waste is non-hazardous. To calculate indicator 62, the results of the economic assessment (chapter 6) are needed (Table 12).

Indicators 63 and 64 (total volume of liquid waste and specific liquid waste volume, respectively) can be calculated with the following formulas:

\[ V_{l,\text{tot}} = \text{Total volume of liquid rated as a waste} \]

\[ V_{l,\text{spec}} = \frac{\text{Total volume of liquid waste}}{\text{Mass of product}} \]
In process III, streams 401A, 402 and 501 are considered as liquid waste and, in process IV, the streams that are considered liquid waste are 402 and SS.

Indicator 65 corresponds to non-polluted liquid waste volume and it can be calculated with:

\[ V_{l,\text{nonpoll}} = \text{Total volume of liquid waste rated as nonpolluted} \]

This indicator has a value of 0 due to all the liquid waste is polluted.

Indicator 66 corresponds to polluted liquid waste volume and it can be calculated with:

\[ V_{l,\text{poll}} = \text{Total volume of liquid waste rated as polluted} \]

After explaining all of the environmental indicators and calculating as many as possible, the obtained results were summarised in the following table (Table 8).
In this rapport, only the environmental indicators have been calculated but, according to GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multiObjective Process Evaluator), the effects of process changes toward sustainable development must be reflected as performance improvements in the environment, energy, efficiency and economic areas. That is why Ruiz-Mercado et al. [16] define indicators for these four areas. It is important to understand that the indicators are related to each other through implicit relationships. For this reason, it can occur that improvements have been achieved in one area and simultaneously other areas are affected negatively.

After calculating the indicators, the results have to be analysed and compared with reference states or measurement scales to know what sustainability level has been achieved. Ruiz-Mercado et al. [16] propose reference states for each indicator based on the identification of a value corresponding to a highest (best) sustainability score and another worst-case value representing the worst sustainability score. The best cases are scenarios in which the exceedances of material and energy resources are minimized or eliminated, there are no releases, the potential EHS risks are negligible, a highest industrial profitability is achieved, and the capital, manufacturing, product, production, utility, and treatment costs are minimised or eliminated. In contrast, the worst cases are represented by extreme scenarios where all raw materials are hazardous and non-renewable; all wastes are released without any treatment, there are high potential EHS risks and there is no profitability.

| Table 8: Environmental indicators for process III and process IV. |
|-----------------|--------|--------|--------|
| Ws,recycl       | kg/kg  | 0      | 0      |
| Ws,nonrecycl    | kg/kg  | 1      | 1      |
| Ws,haz          | kg/kg  | 0      | 0      |
| mhs,haz         | kg/h   | 0      | 0      |
| mhs,haz,spec    | kg/kg  | 0      | 0      |
| mhs,nhaz        | kg/h   | 206,2010 | 204,0962 |
| mhs,nhaz,spec   | kg/$   | 1,5607 | 1,3542 |
| Vl,tot          | m³/h   | 196,8098 | 0,2584 |
| Vl,spec         | m³/kg  | 0,1993 | 0,00024 |
| Vl,nonpoll      | m³/h   | 0      | 0      |
| Vl,poll         | m³/h   | 196,8098 | 0,2584 |
6. ECONOMIC ASSESSMENT

To calculate the economic assessment related to the operating costs of the two simulated processes, the prices of the table below (Table 9) are taken into account [8]. This table shows the prices of all the chemicals used for the production of biodiesel, as well as the prices of all the utilities (cooling water, electricity, low pressure steam and high pressure stem) and the waste treatment (which changes if the waste is a liquid or a solid). The positive prices indicate the costs of the process and the negative prices indicate the benefits of the process.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>SPECIFICATIONS</th>
<th>PRICE [$/tonne]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemicals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biodiesel (FAME)</td>
<td></td>
<td>-600</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Glycerine</td>
<td>92 wt.%</td>
<td>-1.200</td>
</tr>
<tr>
<td></td>
<td>85 wt.%</td>
<td>-750</td>
</tr>
<tr>
<td>Hexane</td>
<td>USD</td>
<td>410</td>
</tr>
<tr>
<td>Methanol</td>
<td>99,85</td>
<td>180</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>Tech.</td>
<td>340</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NF/FC</td>
<td>4.000</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>98%</td>
<td>60</td>
</tr>
<tr>
<td>Virgin canola oil</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Waste cooking oil</td>
<td></td>
<td>200</td>
</tr>
<tr>
<td><strong>Utilities</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling water</td>
<td>400 kPa, 6ºC</td>
<td>$ 0,007/m³</td>
</tr>
<tr>
<td>Electricity</td>
<td></td>
<td>$ 0,062/kWh</td>
</tr>
<tr>
<td>Low pressure steam (superheated)</td>
<td>450 kPa, 210 ºC</td>
<td>6.8</td>
</tr>
<tr>
<td>High pressure steam (superheated)</td>
<td>2.799 kPa, 500 ºC</td>
<td>10</td>
</tr>
<tr>
<td><strong>Waste treatment</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>Hazardous</td>
<td>150</td>
</tr>
<tr>
<td>Solid</td>
<td></td>
<td>37</td>
</tr>
</tbody>
</table>

Table 9: Basic conditions for the economic assessment of each process [8].

Looking to the chemicals, it is easily observed that the benefits for the processes are FAME (biodiesel) and glycerine, which is a by-product. Glycerine is a benefit due to its use in the cosmetic industry and it is used too in other chemical processes like, for example, the separation of ethanol from water [28].

In terms of cooling water, there are three types of utilities to take into account: heat exchangers where the input temperature is higher than the output temperature, the condenser of distillation columns (T-101, T-102 ...) and the reactors where the heat duty is less than zero.
Utilities that use electricity are pumps, compressors and flash vessels. None of the studied processes have compressors or flash vessels, so the only electricity costs come from the pumps.

In terms of low pressure steam (LP steam), the utilities that must be taken into account are: heat exchangers where the input temperature is lower than the output temperature, the reboiler of distillation columns (T-101, T-102 ...) and the reactors where the heat duty is more than zero.

HP steam and LP steam refer to heating utilities. The main differences between HP steam and LP steam (besides pressure) are input and output temperatures, and therefore, heat transfer potential. Indeed, HP steam has a higher transfer potential than LP steam.

Finally, in terms of waste treatment, it is essential to difference between liquid wastes and solid wastes. Liquid wastes are those that come from distillation columns and solid wastes are those that come from filters.

The following table (Table 10) shows all the costs of the process III.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Stream</th>
<th>kg/h</th>
<th>tonne/h</th>
<th>$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel (FAME)</td>
<td>401</td>
<td>595,260</td>
<td>0,595</td>
<td>-357,156</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>CaO</td>
<td>85,790</td>
<td>0,086</td>
<td>3,432</td>
</tr>
<tr>
<td>Glycerine</td>
<td>502 (42,25%)</td>
<td>0</td>
<td>0</td>
<td>223,993</td>
</tr>
<tr>
<td>Hexane</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Methanol</td>
<td>101</td>
<td>216,285</td>
<td>0,216</td>
<td>38,931</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>103</td>
<td>150,062</td>
<td>0,150</td>
<td>9,004</td>
</tr>
<tr>
<td>Virgin canola oil</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Waste cooking oil</td>
<td>105</td>
<td>1,027,120</td>
<td>1,027</td>
<td>205,424</td>
</tr>
<tr>
<td><strong>TOTAL chemicals</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>-268,360</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Utilities</th>
<th>Unit</th>
<th>kg/h</th>
<th>$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling water</td>
<td>E-201</td>
<td>8,541,006</td>
<td>0,0600</td>
</tr>
<tr>
<td></td>
<td>R-101AB</td>
<td>9,306,327</td>
<td>0,0651</td>
</tr>
<tr>
<td></td>
<td>T-201</td>
<td>34,340,714</td>
<td>0,2404</td>
</tr>
<tr>
<td></td>
<td>T-401</td>
<td>43,675,739</td>
<td>0,3057</td>
</tr>
<tr>
<td></td>
<td>T-501</td>
<td>133,496</td>
<td>0,0009</td>
</tr>
<tr>
<td>Electricity</td>
<td>Unit</td>
<td>kW</td>
<td>$/h</td>
</tr>
<tr>
<td></td>
<td>P-101</td>
<td>0,103</td>
<td>0,0064</td>
</tr>
<tr>
<td></td>
<td>P-103</td>
<td>0,319</td>
<td>0,0198</td>
</tr>
<tr>
<td></td>
<td>P-201</td>
<td>0,061</td>
<td>0,0038</td>
</tr>
<tr>
<td>Low pressure steam (superheated)</td>
<td>Unit</td>
<td>kg/h</td>
<td>$/h</td>
</tr>
<tr>
<td></td>
<td>R-201</td>
<td>1,538,662</td>
<td>10,463</td>
</tr>
<tr>
<td></td>
<td>T-501</td>
<td>0,456</td>
<td>0,0031</td>
</tr>
</tbody>
</table>

34
The resultant cost for the process III is the sum of the costs of the chemicals, the utilities and the waste treatment. This sum has a value of -132,121 $/h, which means that this process produces a benefit of 132,121 $/h. Assuming that operating hours for a biodiesel plant are 8,000 h/year [8], the total benefits for this process are 1,056,967 $/year.

For process IV, the costs are shown in the following table (Table 11).
As in process III, to calculate the total costs of the process IV, the costs of the chemicals, the utilities and the waste treatment must be summed. The sum has a value of -150,712 $/h, which means that this process produces a benefit of 150,712 $/h and 1,205,693 $/year.

In the following table (Table 12), there is a summary of the benefits of each process.

Table 12: Summary of the benefits of each process.

Table 11: Economic assessment of process IV.

<table>
<thead>
<tr>
<th>Unit</th>
<th>kg/h</th>
<th>$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-201</td>
<td>1,503,166</td>
<td>10,222</td>
</tr>
<tr>
<td>T-201</td>
<td>389,335</td>
<td>2,647</td>
</tr>
<tr>
<td>T-501</td>
<td>478,852</td>
<td>3,256</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unit</th>
<th>kg/hr</th>
<th>$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-401</td>
<td>3,204,170</td>
<td>32,042</td>
</tr>
</tbody>
</table>

**TOTAL utilities**  49,956

<table>
<thead>
<tr>
<th>Waste treatment</th>
<th>Stream</th>
<th>kg/h</th>
<th>tonne/hr</th>
<th>$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>501C</td>
<td>243,600</td>
<td>0,244</td>
<td>36,540</td>
</tr>
<tr>
<td></td>
<td>402</td>
<td>184,617</td>
<td>0,185</td>
<td>27,693</td>
</tr>
<tr>
<td></td>
<td>SS</td>
<td>103,305</td>
<td>0,103</td>
<td>15,496</td>
</tr>
<tr>
<td>Solid</td>
<td>303B</td>
<td>204,096</td>
<td>0,204</td>
<td>7,552</td>
</tr>
</tbody>
</table>

**TOTAL waste treatment**  87,280

Table 12 shows that process IV produces more benefits than process III.
7. CONCLUSIONS

Simulations for biodiesel production were accomplished satisfactorily since the same results as in the literature have been obtained, which means that objective 3 from chapter 1.4 has been successfully achieved.

On the other hand, calculation of different environmental indicators is very useful to a better understanding of the environmental implications of the processes and production ways. These indicators have high importance in terms of Life Cycle Analysis and have to be taken into account when designing the process, since the preoccupation for the environment has been improving during the last years.

In terms of the economic analysis, both processes exhibit important benefits which may indicate that biodiesel is a viable alternative to fossil fuels. Also, it important to highlight that by using process simulators, these kind of analysis can be developed in order to demonstrate the general usefulness (or not) of a proposed way of production of certain final product.

To finalise, the objectives proposed at the beginning of this research were all successfully accomplished.
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Figure 2: Pressure-volume diagram of an ideal Diesel cycle [6].

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Table 11: Economic assessment of process IV.

Table 12: Summary of the benefits of each process.
REFERENCES


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