Preliminary design of the green diesel production process by hydrotreatment of vegetable oils

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ABSTRACT
In this work, a conceptual design is presented of a HVO/green diesel production unit with a processing capacity of 74 ton/h (500 000 ton/year) of vegetable oils and a production rate of 59 ton/h of diesel. Firstly, an extensive literature review has been conducted regarding the state-of-the-art techniques as well as process equipment, mechanisms of reaction and thermodynamical properties. A market analysis is also presented which estimates feedstock availability and target production rate. With this information, a preliminary Process Flow Diagram is proposed, along with explanations on the type of equipment used and its operating conditions. Process design and simulation has been performed using Aspen Plus®, while Aspen Custom Modeler® has been used to develop more accurate models where necessary. The present study concludes with an analysis of process flexibility, considerations for heat integration and an economic assessment.

KEYWORDS Green diesel; Hydrotreatment of Vegetable Oils; Computer-aided Process Engineering

Introduction
In the last decade, alternative fuels have gained increasing attention from the scientific community, given the growing energy demand and the global warming effect derived from CO₂ emissions. Even though fossil fuels are still the main source of energy across the globe, the European Union has made great effort to change the current situation through the Renewable Energy Directive (RED), which enforces a 20% target for renewable energy sources and a 10% in the transportation sector by the year 2020.

With no more than a year to reach the due date, the EU has been working on a second version of the RED directive, the RED II, which raises the target of renewable energy to 32% by the year 2030 [1]. Given the current paradigm shift, it is clear that changes must be made in the appropriate direction.

The two main biofuels used in transportation are bioethanol used in gasoline and biodiesel or FAME (Fatty Acid Methyl Ester) in diesel. As promising as the word biofuel sounds, there are two main concerns affecting these products which shall be carefully considered. On one hand, engine compatibility makes it undesirable to use blends of more than 7% of FAME in conventional diesel engines, mainly due to its stability and cold flow properties [2]. On the other hand, the sustainability of these processes has been questioned, since the food-based crops that are commonly used as feedstock tamper with food prices and availability in the regions of growth, a problem that has been addressed carefully by Articles 17 and 18 of the RED [3].

In light of the facts, it only seems logical to propose an alternative renewable fuel that is fully compatible with current fossil fuels, as not avoid any changes in the current transportation infrastructure and conventional engines. Green diesel obtained from hydrotreatment of vegetable oils is one, well-established example. Even though it uses the same feedstock as biodiesel, green diesel yields a product with better qualities, which is also indistinguishable from fossil fuel-derived diesel. Table 1 compares the properties of conventional diesel, biodiesel and green diesel.

Hydrotreated vegetable oils (HVOs) seem like a suitable alternative to biodiesel due to their improved cold flow properties, low content in sulfur, aromatics and oxygen, and engine compatibility.

The objective of the present work is to develop a conceptual design for the processing of vegetable oils into green diesel. Technical, economical and environmental aspects will be taken into account as indicators of the quality of the project.

First, a literature review is presented in order to gather the
necessary information for the design of the process and selection between alternatives, followed by a market review to support the financial viability of the venture. The selected process and its variables are then put to test through simulation in Aspen Plus®, allowing for the optimization of process variables and consumption of utilities through heat integration.

Upon completion of the simulation and technical design stage, an economic assessment will help decide on the economical feasibility of the project and identify main cost contributors. Another, no less important key aspects such as carbon consumption and sustainability of the process are also studied.

**Literature review**

Literature research for this project attains the technology used for stand-alone processing of vegetable oils into green diesel. Many refiners prefer instead to follow the coprocessing scheme, where vegetable oils are injected into the fuel mixture going to the hydrotreaters in a refinery. Minor investment and revamping is needed with the latter, but the possibility of a 100% renewable fuel is left out. Therefore, this work will focus only in stand-alone processing of HVOs.

Hydrotreatment of vegetable oils could, as a first approach, be compared to the conventional hydrotreatment units used to remove sulfur from refinery products. Annex 1 contains a schematic representation of this process which, when compared with the novel green diesel technologies developed in the last decade, provides substantial proof of the similarity between both hydrotreatment processes.

The two main technologies for hydrotreatment of vegetable oils are NExBTL® by Neste Oil and Ecofining™ by UOP and ENI. The basic scheme for both is quite alike, as can be seen in Figures 1 and 2. Other companies, such as Axens IFP or Haldor Topsoe, have also developed similar technologies by the name of Vegan™ and Hydroflex™.

![Figure 1](image1.png)

**Figure 1** Schematic representation of UOP’s Ecofining technology [5].

Both processes consist of a primary phase called deoxygenation, where hydrogen is used to break down the triglycerides and eliminate oxygen molecules at high temperatures and pressures. The result is a linear hydrocarbon mixture in the diesel boiling range which is mainly paraffinic, as well as CO, CO₂, water and light hydrocarbons. After separation in a three phase flash tank, the mixture of paraffins is partially isomerized in order to improve its cold flow properties. Isomerization is essential in order to obtain a high quality product, but it comes at the expense of partial loss of the diesel product due to cracking. As a result, a final stabilizer column is needed in order to separate lighter hydrocarbons from the heavier ones, resulting in four possible products: LPG and naphtha as head products, jet fuel and green diesel as bottom product.

Deoxygenation and isomerization take place in presence of catalysts, mainly CoMo and NiMo catalysts for the hydrotreatment section and Pt-based catalysts for the isomerization unit [7]. The conditions in which these reactions take place are what determine the level of cracking, and thus the amount of by-products that are obtained.

Nevertheless, given the need for a flexible and a robust process, the design will include a stabilizing unit which allows to vary the amounts of green naphtha and jet fuel that are obtained, depending on market demand and suitability. Regarding the separation of gaseous products, an amine unit can be used to separate hydrogen, light hydrocarbons, and contaminants such as CO and CO₂.
Feedstock and feedstock pretreatment

Before entering the hydrotreating reactor, feedstock must go through a purification unit as to remove any impurities and metals contained in it. Pretreatment becomes indispensable, as it ensures metals (Ca, Mg) and phosphorus will not interfere with the catalysts in the reactor [8].

The pretreatment unit is based on a bleaching unit, and its operating conditions vary depending on the type of feedstock. Bleaching takes place by degumming with addition of an acid such as H$_3$PO$_4$, neutralization with NaOH, and washing with demineralized water. In order to further reduce the level of impurities, the feedstock can be fed through silica and/or bleaching earth [9].

There are three feedstock alternatives for this project: palm, rapeseed, and sunflower oil. None of these would allow the final product to enter the second generation biofuels category, but on the other hand they may imply reduced expenses in the pretreatment unit, since they are cleaner than waste oils.

Vegetable oils are made up mostly of triglycerides, which are hydrocarbon structures containing three fatty acid chains and a glycerol backbone in an ester. Processing of these triglycerides will include (I) Saturation of double bonds in the hydrocarbon chains, (II) Separation from the glycerol backbone in the form of propane, and (III) Elimination of oxygen molecules through reduction with hydrogen.

![Example of triglyceride structure typically found in palm oil](image)

One important difference between feedstock types is their iodine value, which refers to the number of double bonds present in the hydrocarbon chains belonging to the fatty acids. A higher iodine number implies a higher number of double bonds and thus an increased consumption of hydrogen when being processed [10]. Table 2 proves that, among the three options, palm oil is the one with a smaller iodine value.

![Iodine value of different vegetable oils](image)

<table>
<thead>
<tr>
<th>Vegetable oil</th>
<th>Iodine value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola</td>
<td>110–126</td>
</tr>
<tr>
<td>Corn</td>
<td>103–128</td>
</tr>
<tr>
<td>Coconut</td>
<td>6–11</td>
</tr>
<tr>
<td>Hazelnut</td>
<td>88–90</td>
</tr>
<tr>
<td>Olive</td>
<td>77–83</td>
</tr>
<tr>
<td>Palm</td>
<td>50–55</td>
</tr>
<tr>
<td>Peanut</td>
<td>80–106</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>94–120</td>
</tr>
<tr>
<td>Sesame</td>
<td>105–107</td>
</tr>
<tr>
<td>Soybean</td>
<td>125–130</td>
</tr>
<tr>
<td>Sunflower</td>
<td>127–129</td>
</tr>
<tr>
<td>Walnut</td>
<td>118–149</td>
</tr>
</tbody>
</table>

Another important aspect of feedstock is its availability. World production of vegetable oils has increased dramatically in the past decade. As of 2017, world production of vegetable oils and fats is 226 million tons [11]. Top world producers of rapeseed oil include China, Germany, and Canada. Germany produces up to 3.5 million tons of rapeseed oil per year, mainly to feed livestock. Sunflower oil is produced in less quantities, Russia being its biggest producer with an annual average production between 1993 and 2014 of 1.9 million tons.

Palm oil takes the lead in terms of production: 65 million tons per year. This means that palm oil accounts for more than half of the world market share together with soybean oil. In terms of location, palm oil is mainly grown in tropical countries, Malaysia and Indonesia being its main producers. All production data was retrieved from the Food and Agriculture Organization of the United Nations [12].

The final - and probably most important - aspect regarding feedstock selection is price. The surge of interest in biofuels has translated into uncertainty and price volatility in the recent years. Sunflower, rapeseed, and palm oil are all within the category of middle-priced vegetable oils, although palm oil is considerably cheaper than the rest [13]. A better insight of this matter is presented in the Market Analysis section.

Annex 2 contains information on the composition of all three types of feedstock, according to the literature [14-16], as well as practical information about the estimation of their physical properties, according to the fragment approach model proposed by Zong et al. [17].

Deoxygenation of vegetable oils

Most of the literature regarding the processing of vegetable oils focuses mainly on its deoxygenation. This is due to the recent interest hydrotreatment processes have sparked in the recent years, but also because companies carefully keep confidential information safe and away from the eyes of the competition.

As a result, there are many questions regarding the mechanism of this process: reaction kinetics, catalyst use and deactivation, and reactor design and conditions. Through this work, the authors have the objective of laying down the basic information regarding this complex process and its simulation.

Basics of deoxygenation of vegetable oils

Many authors have contributed greatly to the understanding of the deoxygenation of VOs [2,18-25]. Out of all of them, the work of Kubicka et al. and Tirado et al. [26-27] deserve a special mention, due to their outstanding and practical approach on both reaction mechanisms and modeling approaches. While Kubicka has been a prominent researcher in the field, the work of Tirado elaborates a synthesis of previous works regarding reaction kinetics and reactor modeling.

The mechanism of hydrotreatment of triglycerides takes place in two phases. First, double bonds in the hydrocarbon chains are saturated by hydrogen. Then, reduction takes place by the elimination of oxygen atoms through three possible parallel mechanisms: hydrodeoxygenation, decarboxylation and decarbonilation. A schematic representation of this mechanism is shown in Figure 4.

As seen in Figure 4, decarbonylation and decarboxylation...
reactions (DCO) yield paraffins with an odd number of carbons, as fatty acids are usually conform of an even number of them, whereas hydrodeoxygenation reactions (HDO) yield paraffins with an even number of carbon atoms.

It is unknown whether decarbonylation is part of the process, as the reaction byproduct CO could also be involved in the complex reaction system between CO₂, CO, CH₄ and water that is depicted in Figure 5. As a result, there is no unequivocal evidence to support whether decarbonylation takes place, according to gas chromatograms obtained from different experiments [2, 18-19, 30].

Regarding hydrogen consumption, one could infer from the reaction mechanism depicted in Figure 4 that HDO routes should be avoided, as it consumes three times the amount of hydrogen. However, this would only be true if CO₂ and CO obtained in these reactions didn’t take part in the hydrogen-consuming reactions depicted in Figure 5. In fact, if the opposite was to happen, studies confirm as much as 19% more hydrogen would be consumed in the DCO route [2, 26].

Furthermore, the HDO route yields a cleaner green diesel product, as only 3 atoms of carbon per triglyceride are not recovered in the liquid fuel, as opposed to the 6 carbon atoms lost in the DCO route, three more carbon atoms lost in the form of CO and CO₂ which will have to be separated downstream.

Catalyst systems in deoxygenation reactions

Sulphided NiMo and CoMo catalysts supported on alumina are the most common catalysts used in the industrial scale production of green diesel [7]. These are also the same type of catalysts used in conventional hydrotreatment units, which, together with their high activity, explains their widespread use.

The high activity of NiMo /Al₂O₃ catalyst systems allow to reach the 100% conversion rates widely reported in the literature [2, 26, 29]. However, these catalysts need a continuous addition of sulfur-containing agents in order to prevent deactivation, worsening the emission performance of the final product [31]. Nevertheless, given the sulfur-free quality of vegetable oils, green diesel contains less sulfur than conventional diesel [4]. As for the addition of these agents, sulfur concentration in any typical hydrogen feed coming from a conventional hydrotreatment unit in a refinery will suffice.

As alternatives, several studies have focused mainly on the use of sulfur free, noble metals such as Pt and Pd. Whereas NiMo and CoMo sulphided catalysts yield products through both HDO and DCO mechanisms, noble metals show high selectivity for DCO routes, resulting in higher CO₂ and CO production [20, 23].

Other disadvantages of noble metals such as Pt or Pd include their high price, lower yields, and rapid deactivation in the presence of sulfur and water. Xin Le et al.[29] made a thorough review of these types of catalysts and concluded that, in spite of their cleaner performance, there is still progress to be made in these aspects.

Furthermore, Sotelo-Boyás et al.[7] studied the effect of zeolite-supported Pt catalysts and compared them to NiMo/Al₂O₃. He concluded that the stronger acidic sites of the first induced a higher yield of isomerized products at the expense of a higher degree of cracking, with the subsequent loss of valuable diesel product.

As a result, it seems more proper to invest in two separate reactor systems: one for deoxygenation and another one for isomerization. This way, NiMo/Al₂O₃ catalysts can be used to achieve total conversions in the first reactor and, after proper separation of products, cold flow properties can be improved over Pt-zeolites by control isomerization to avoid cracking.

Reactor conditions

When controlling deoxygenation, main reactor variables and conditions are: temperature, pressure, H₂/oil ratio and liquid space hourly velocity (LSHV). As shown in Table 3, typical operating conditions do not vary considerably from one study to another.

In one particular study, Bezergianni et al.[32] concluded that increasing reactor temperature above 360 °C translated into an undesirable degree of cracking.

In another study, Srifa et al.[21] experimented with a wide range of hydrotreating conditions for palm oil over a sulphided NiMo/Al₂O₃ catalyst. Results supported the hypothesis that, under 300 °C, partial conversion of triglycerides took place, whereas cracking and isomerization broke down diesel molecules above 360°C.

Regarding H₂/oil ratios, 3 to 5 times the theoretical consumption is recommended in order to ensure gas-to-liquid mass transfer resistance of hydrogen does not play a role of interference in the process [2, 21].

LSHV values, on the other hand, may vary between 1 and 5 h⁻¹ [33], although higher values could affect the level of conversion.

Estimation of properties

For the estimation of thermophysical properties in the hydrocarbon mixtures, it is recommended in the literature that the Redlich-Kwong or Peng-Robinson equations of state be used [19,
Table 3 Typical reactor operating conditions for hydrotreatment of vegetable oils over sulphided catalysts, as found in the literature.

<table>
<thead>
<tr>
<th>Study number</th>
<th>Operating conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>390 C, 50 bar, 1.5 h⁻¹</td>
<td>[34]</td>
</tr>
<tr>
<td>2</td>
<td>300 C, 30-50 bar, 1.2 h⁻¹, 500-1500 Nm³/m³</td>
<td>[21]</td>
</tr>
<tr>
<td>3</td>
<td>300 C, 50 barg, 10-100 h⁻¹ (WSHV), 1250 Nm³/m³</td>
<td>[2]</td>
</tr>
<tr>
<td>4</td>
<td>350 C, 40 bar, 7.6 h⁻¹, 800 Nm³/m³</td>
<td>[35]</td>
</tr>
<tr>
<td>5</td>
<td>340 C, 40 bar, 1 h⁻¹, 500-1000 Nm³/m³</td>
<td>[36]</td>
</tr>
<tr>
<td>6</td>
<td>335-360 C, 30-60 bar, 20 mol H₂/mol oil</td>
<td>[18]</td>
</tr>
</tbody>
</table>

27, 37]. If the presence of water is important, then the NRTL property package needs to be included [37]. All of these property packages are included in Aspen Plus®.

Regarding the properties of triglycerides, two methods were found in the literature for their estimation with a reasonable level of precision within less than 10% of error: Zhong’s’s fragment approach method, which allows to calculate both thermodynamic and transport properties and is illustrated in Annex 2, and Smejkal’s group contribution method, which is based in Joback’s group contribution method and shows excellent accuracy [17, 38].

Kinetics
Finding proper kinetic data proved to be harder than expected, given the presence of complex triglyceride molecules in the reactions. Furthermore, since the reactions take place in the surface of catalysts, kinetic parameters depend not only in reactor conditions (temperature, mainly) but also in the catalyst system being used.

The team decided that, in order to select appropriate kinetic data among the few options found in the literature, some restrictions had to be put in place:

1. Kinetic data must be calculated in a sulphided NiMo, CoMo catalyst, in order to match catalysts typically used in the industry, as discussed earlier.
2. Reaction pathways for the proposed mechanism must account for the formation of gases typically formed in the HDO and DCO mechanisms that take place in the industrial systems mentioned above (CO, CO₂, propane and H₂O).
3. Kinetic data must include Arrhenius’s constant, so that temperature dependence can be included in the model.
4. If possible, kinetic data should also include the effect of hydrogen pressure in their equations, in order to understand the effect of hydrogen presence in the reactor.

In light of these requirements, the studies of Vélez [18], Landberg [19], Kubicka [26] and Zhang et al. [39] all fit most of them. One of the common and advantageous aspects of all these mechanisms is that they are based on simple power kinetic models, given the incompatibility between more complicated models such as Langmuir-Hinshelwood’s and uncertainties linked to operation parameters in trickle-bed reactor systems [40].

As a starting point, Vélez’s kinetic studies provide a model which is simple enough to develop a simulation model that converges easily and is exempt of intermediate products. Furthermore, the model is in good agreement with what is known about the mechanism of the hydrotreatment of VOs, as discussed earlier.

Nevertheless, Vélez did not take into account the effect of hydrogen pressure and mass transfer resistance, and the predictions are not accurate enough (R² = 0.8). Table 4 represents the proposed reaction mechanism.

Once a model that is robust enough is developed, it could be adapted towards another and more sophisticated one, such as that of Kubicka et al. As for Landberg’s study, it was discarded as it does not explain the formation of CO₂ since it does not take into account the decarboxylation reaction in its proposed reaction pathway.

Table 4 Proposed mechanism and kinetic data for hydrotreatment of palm oil [18].
hydrogen) come into contact over a catalyst bed at high temperatures and pressures [41].

When compared to other heterogeneous reactors, trickle-beds offer poor heat transfer rates, thus leading to radial temperature gradients and the formation of hotspots. In order to prevent this situation, the reactor may count with interstage quenching systems, cooling jackets or, in more extreme cases, be designed as a multi-tubular reactor. Jeczmionek et al. [42] presents a useful study regarding the heat of reactions involved in hydrotreatment of vegetable oils.

Another important aspect of trickle-bed reactor systems are its hydrodynamics. Ranade and Chaudhari [43] present in their book a complete overview of the main parameters affecting the hydrodynamic effects in trickle-bed reactors.

For the estimation of the liquid hold-up in high pressure systems, Larachi et al. [44] provides simple correlations based in dimensionless numbers, while the wetting efficiency of the catalyst particles can be estimated with the Reynolds number, according to Giannetto and Specchia [45].

Trickle-bed models were thoroughly reviewed in order to develop a reactor model robust and complex enough to predict with fair accuracy the operation in a hydrotreatment plant for vegetable oils [46-48]. A detailed explanation of the equations used in the model can be found in Annex 4.

Isomerization
Isomerization takes place once gaseous products and water formed during deoxygenation are separated. As discussed earlier, noble metals such as Pt over SAPO zeolite supports are typically used in this operation [29].

Temperatures and pressures are similar to those in deoxygenation, and even if hydrogen is consumed in low quantities, the reaction can only take place in a high pressure hydrogen atmosphere [49].

For simulation, typical conversions found in the literature [50] can be used together with Calemma’s proposed pathway and kinetic information for isomerization of long hydrocarbon chains [51].

Market analysis

Crude oil prices are the most determining factor for fuel cost. As seen in Figure 6, the price of the barrel has been volatile in the last few months, mainly due to the uncertainty in global economy created by the trade war between China and the U.S. and political problems in Europe [52].

On the other hand, taking a look at the long term outlook of the oil market, supply is ensured due to new deposits being continuously discovered. Regarding the demand for oil and its future prices, experts do not expect the market share to increase, as environmental restrictions in developed countries grow tougher [53].

One such example of these restrictions is the cap for sulfur content in marine fuel, which is being lowered from 3.5 to 0.5% by the International Maritime Organization (IMO) [54]. The measure, which will be effective on the 1st of January of 2020, has brought many discussions to the table as to how to achieve it in the most cost-efficient manner.

As a possible solution, marine vessels could move towards cleaner versions of marine fuel such as low-sulfur diesel blends. In this aspect, green diesel seems like an excellent choice, as its content in sulfur is exceptionally low [4].

The measure, which affects the demand of 3.5 million barrels per day of high-sulfur fuel oil, will likely cause an increase in diesel prices in the future. As of 2018, the mean price of diesel in Spain is 1.1 €/kg [55].

Process capacity and feedstock availability
After studying feedstock prices for vegetable oils (Figure 7), one may notice there is a short gap between retail price for biodiesel and feedstock price. This is also typical for fossil fuel refining products, since the fuels market is close to perfectly competitive.

The Finnish company Neste oil, which provides valuable information on the fuel market distribution, proposes a method to fix the price of biodiesel based on margins and production costs which will be used and explained more thoroughly in the Economic Analysis section.

As a result, in order to ensure profitability of the venture, process capacity has to be carefully measured, following the economy of scale principle.

Main players in the HVO game for stand-alone units are, as mentioned earlier, Neste Oil and UOP/ENI. Neste owns 4 production facilities, two in Finland with a capacity of nearly 200,000 tons per year and another two with a capacity of 1000,000 tons per year in Rotterdam and Singapore. As for ENI, they are currently constructing a plant with a capacity of 500,000 tons in Italy [56].

In view of this data, production capacity for the plant is set to be 500,000 tons of green diesel per year, which implies a consumption of around 600,000 tons of vegetable oil per year (roughly 20% is converted into gas and cracking products, according to mass balances).
As discussed in the Literature Review, only the annual production of palm oil is high enough to ensure feedstock availability.

Furthermore, as seen in Figure 9, palm oil prices are considerably lower than rapeseed and sunflower oil prices, the latter of which is not depicted but data proves its price lands between the two [58].

The main drivers for choosing palm oil as feedstock in this project are price and availability.

However, the Renewable Energy Directive from the EU demands that GHG emissions be reduced by 60% or more in order to be considered as a biofuel [3].

Oil companies such as Neste and Repsol count with special certifications known as the International Sustainability and Carbon Certifications (ISCC) that ensure biofuel lifecycle from cradle to cradle is sustainable. One representative example depicting control over GHG emissions in the transport of palm oil to the refinery is shown in Annex 3.

**Process Design**

The information found and portrayed in the Literature Review section allowed the team to perform a conceptual design of the process, the result of which is described in the following paragraphs and depicted in Figure 8. A summary table for the input and output stream conditions is shown in Table 5. A more comprehensive table for all process streams can be found in Annex 6.

The process can be divided into three main sections: hydrotreatment, isomerization, and final product separation. First, palm oil is purified in a pretreatment plant, where it undergoes degumming and bleaching in order to remove metals, phosphorous and any solid particles that might affect the catalyst negatively.

After purification, palm oil enters reactor R-101, which is a trickle bed reactor with catalyst beds disposed in series for intermediate quenching with hydrogen. The catalyst is made of NiMo supported on alumina and conversion is nearly total.

Liquid products obtained in the hydrotreatment reactor are mainly n-alkanes in the diesel boiling range (270-320°C), resulting in a product with high cetane number but poor cold-flow properties. In order to improve the quality of the product, it is essential for the mixture to enter a second reactor.

Reactor R-102 operates similarly to the hydrotreatment reactor, this is, at high temperatures and pressures and with considerable supply of hydrogen gas. In this case, catalyst bed is made of Pt supported in a SAPO zeolite and alumina. Any triglycerides that have not reacted in R-101 will thus finish reacting here.

Improving the cold-flow properties of the product comes at the expense of inevitable cracking of the diesel, which yields

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**Figure 8** Process flow diagram (PFD) of the proposal for the hydrotreatment of vegetable oils. See corresponding annex for more details on stream characteristics.

**Figure 9** Vegetable oil prices ($/ton) for rapeseed (above) and palm oil (below) in the last 4 years [57].
variable quantities of lower boiling point mixtures such as jet fuel and naphtha, depending on reactor conditions.

The resulting mixtures are separated in a distillation column where naphtha and gaseous products are obtained as top products, diesel as bottom product, and jet fuel is obtained through a side column. This way, the process is flexible enough to yield variable quantities of products different from green diesel, depending on the market demand.

Furthermore, since hydrogen is present in great quantities in both reactors but is not totally consumed, an amine unit was considered as the best option to recover and recycle most of it, as well as the light hydrocarbons and contaminants (CO and CO$_2$, mainly) present in the gaseous flows which are obtained in the flash tanks situated after each reactor.

The team did not go deeper into the design of the amine unit, as it was assumed the process would be integrated into an existing refinery. However, one interesting option which deserves further investigation would be to study the feasibility of transforming the light hydrocarbons into hydrogen in order to reduce external dependence.

### Process simulation and analysis

The proposed solution for the process was simulated using Aspen Plus® V10. Considering that reactor simulation options offered in this software are fairly limited, it was decided that the hydrotreatment reactor would be simulated using its programming modeling environment, known as Aspen Custom Modeler® (see support files).

Explanations for the developed model of the hydrotreatment reactor, which include mass transfer resistance calculations, are explained in detail in Annex 4. From the simulations, it was found that reactor dimensions are 25 meters in length and 5 meters in diameter. Conversion attains 99.9%, at nominal operation pressure (40 bar), slightly varying upon changing the operation conditions.

Regarding the isomerization reactor, only reaction kinetics was modeled using the RPlug block and the proposed reaction pathway and kinetic constants by Calemma et al.[51]. A brief explanation of this model is shown in Annex 5.

Basic calculations were made using typical LSHV values found in the literature for this process [50] and process data. Results provide an estimated reactor size of 18 meters in length.

**Table 5** Input (in green) and output (in blue) stream conditions for the proposed Process Flow Diagram.
Tripalmitin conversion

<table>
<thead>
<tr>
<th>Unit</th>
<th>Process conditions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-101</td>
<td>60°C, 1 atm</td>
<td>Below 60°C palm oil is semi-solid</td>
</tr>
<tr>
<td>C-101</td>
<td>360°C, 40 bar</td>
<td>Interstage cooling</td>
</tr>
<tr>
<td>R-101</td>
<td>300-360°C, 40-60 bar, 10-100 h⁻¹ (WSHV), H₂/oil ratio 500 Nm³/m³</td>
<td>NiMo/Al₂O₃ catalyst</td>
</tr>
<tr>
<td>R-102</td>
<td>360-380°C, 40 bar, 1 h⁻¹, H₂/oil ratio 500 Nm³/m³</td>
<td>Pt/SAPO-11/Al₂O₃ catalyst</td>
</tr>
<tr>
<td>V-101</td>
<td>30°C, 40 bar</td>
<td>Flash tank</td>
</tr>
<tr>
<td>V-102</td>
<td>30°C, 15 bar</td>
<td>Flash tank</td>
</tr>
<tr>
<td>T-101</td>
<td>26-300°C, 1 bar</td>
<td>Main column, 28 plates</td>
</tr>
<tr>
<td>T-102</td>
<td>215-240°C, 1 bar</td>
<td>Side column, 10 plates</td>
</tr>
</tbody>
</table>

Table 6 Operating conditions for main process equipment.

and 4 meters in diameter, with which a high quality diesel product with excellent cold-flow properties is obtained.

Simulation was useful when testing the fitness of the conditions and data found in the literature, as well as to systematically find and exploit possibilities for process optimization and flexibility (i.e. most important contributors to cost and heat integration options). Such possibilities are analyzed further in this chapter.

Final selected conditions for the main process equipment are shown in Table 6, while the mass and energy balance for all process flows is shown in Annex 6.

Process flexibility

One of the main advantages of simulation is the ability to test the flexibility of the process. This allows to perform a sensitivity analysis and study the effect key design parameters have on the quality and quantity of the product obtained.

Furthermore, evaluating process performance at different operating conditions proves the validity of the models used for simulation. In this case, flexibility of the process was studied for its main operations: hydrotreatment and isomerization.

The use of a custom model for the hydrotreating reactor has allowed for interesting analysis of the influence of operation and feed conditions on overall reactant conversion. Triolein and Tripalmitin being the main reactants in terms of feed composition, the first one is consumed in the first half of the reactor length, while Tripalmitin and Tristearin (generated from hydrogenated Triolein) reactions suffer from competitive inhibition and occur only in the second half of the reactor.

Two variables were found to be critical for reactant conversion: concentration of H₂ in the bulk liquid and temperature profile along the reactor.

- Concentration of H₂ in the bulk liquid is rather sensitive to pressure variations. A plot of Tripalmitin degree of conversion - the others being higher - against operating pressure can be seen in Figure 10. Note that other operating conditions, such as inlet temperature or cooling power, remain constant for this plot, but can be varied to operate at 40 bar with 99.9% degrees of conversion. A pressure threshold has been observed which varies between 38 and 48 bar, depending on other operating conditions (it is placed at 44 bar in Figure 10). If pressure becomes lower than this threshold, Tripalmitin conversion will steeply descend, although Triolein conversion is not as significantly affected.

- The temperature profile is also important for reactants’ conversion. The fast Triolein consumption in the first half of the reactor causes a great increase in temperature, which must be kept under 360°C with refrigeration. Interestingly, Tripalmitin and Tristearin consumption rates are enhanced by temperatures close to 300°C instead of higher ones. This is due to the higher volatility of hydrogen at higher temperatures, which decreases the amount of H₂ in the liquid, and to a worsening of the liquid-solid mass transfer coefficients also at higher temperatures. Temperature profiles should be kept as flat as possible, with higher values for Triolein reactions and lower values for Tripalmitin reaction. Consequently, hydrogen quenching arises as an interesting possibility for refrigeration, something that has nevertheless not been explored in this work.

The reactor performance is not significantly affected by changes in feed composition or feed temperature. In general, it can be said that operation of the hydrogenation reactor is flexible.
and that total conversion (> 99.9%) can be achieved in a wide range of situations.

Another interesting study was made regarding isomerization reactor R-102. Operating conditions that affect the degree of isomerization and cracking are: temperature, pressure, LSHV values and H₂/oil ratios.

While the effect of these parameters is studied elsewhere in the literature [50-51, 59-60], the team found most interesting to study the effect of temperature of the reactor. Reactor temperature was varied between 360 and 450°C and the yield of products was evaluated. Of course, this analysis also allowed to understand more deeply which variables had to be manipulated in the distillation columns to adapt to this variation.

As shown in Figure 11, increasing the temperature in R-102 increases the ratio of light to heavy products to the point where at 450°C no diesel is obtained as a product. Another interesting finding was that the proportion of jet fuel is in fact reduced from 420 to 450°C, due to the kinetics of the model.

From this sensitivity analysis it can be concluded that, with current market prices, the process becomes less profitable with increasing temperature of the reactor R-102.

Heat integration

Considerations for heat integration were made according to the pinch analysis results. Aspen Plus® offers an Energy Analysis package that is suitable for this operation.

In order to perform the pinch analysis, only the main process streams were included in the study, all of which flow through a heat exchanger in Figure 8. Thermal fluids for reactor cooling were not considered as options for heat integration.

As for the utilities, cooling water, medium and high pressure steam and fired heat were considered. The composite curve depicting heat flows from the hot and cold currents is depicted in Figure 12.

![Composite Curves](image)

**Figure 12** Composite curves for hot and cold flows considered in the pinch analysis. As it can be seen, demand for cold utilities is high given the misbalance between the currents.

The pinch temperature is the highest in the process: 360°C, an interesting result which can be explained by the high power to temperature (kW/ºC) ratio of the hot currents coming from the reactors compared to the cold currents. This is a result of the large amounts of hydrogen these hot currents carry.

As a result, the calculated heat exchanger design networks (HEN) do not offer many possibilities, given the misbalance between hot and cold currents and the excess heat being wasted in the process. Table 7 shows the potential savings from the HEN proposal depicted in Figure 13.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Base case</th>
<th>Integrated process (unbalanced)</th>
<th>Integrated process (balanced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating (MW)</td>
<td>35,9</td>
<td>1,8</td>
<td>3,7</td>
</tr>
<tr>
<td>Cooling (MW)</td>
<td>55,7</td>
<td>145,3</td>
<td>64,1</td>
</tr>
<tr>
<td>Operating cost (M€/yr)</td>
<td>3,35</td>
<td>1,12</td>
<td>0,92</td>
</tr>
<tr>
<td>Capital cost (M€)</td>
<td>1,84</td>
<td>2,89</td>
<td>3,39</td>
</tr>
<tr>
<td>Total cost (M€/yr)</td>
<td>3,6</td>
<td>1,49</td>
<td>1,82</td>
</tr>
<tr>
<td>Savings (M€/yr)</td>
<td>-</td>
<td>2,11</td>
<td>1,78</td>
</tr>
</tbody>
</table>

**Table 7** Potential saving from proposed integrated heat exchanger networks over a plant life of 15 years.

To keep a balance, one possibility would be to remove hydrogen in a high temperature flash vessel after each reactor, reducing the power to temperature ratio and thus allowing the pinch temperature to decrease before heat exchange.

The gaseous currents containing mainly hydrogen could then be cooled using air coolers since amine units operate at 30-40°C. Another option would be to design a different unit for hydrogen purification that can operate at higher temperatures, such as a pressure swing absorption unit (PSA).
The economic evaluation of the project starts by calculating the dependence of project profitability on the main contributors to cost. Product price is then calculated, and sensitivity analysis is performed in order to check the dependence of project profitability on the main contributors to cost.

Payback period and net present value are also calculated, and sensitivity analysis is performed in order to check the dependence of project profitability on the main contributors to cost.

Economic analysis

The economic evaluation of the project starts by calculating the capital cost of the plant and the variable production costs using Towler and Sinnott’s method [61]. Product price is then calculated according to the margin method proposed by Neste Oil, where margins are applied to the selling price of the product. Payback period and net present value are also calculated, and sensitivity analysis is performed in order to check the dependence of project profitability on the main contributors to cost.

Propane reforming

From stream 22 in the Process Flow Diagram (8) it can be seen that propane could be utilized for hydrogen generation through steam reforming:

\[ C_3H_8 + 6H_2O \rightarrow 3CO_2 + 10H_2 \quad (1) \]

Since 105 kmol per hour of propane are obtained and the required input for hydrogen is 1296 kmol per hour, propane could cover 80% of the hydrogen consumption, while the rest could be obtained from methane reforming, thus reducing its negative greenhouse impact.

Economic analysis

The economic evaluation of the project starts by calculating the capital cost of the plant and the variable production costs using Towler and Sinnott’s method [61]. Product price is then calculated according to the margin method proposed by Neste Oil, where margins are applied to the selling price of the product. Payback period and net present value are also calculated, and sensitivity analysis is performed in order to check the dependence of project profitability on the main contributors to cost.

Payback period and net present value are also calculated, and sensitivity analysis is performed in order to check the dependence of project profitability on the main contributors to cost.

Table 8: Main process equipment costs (installed).

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost (M€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor R-101</td>
<td>91,3</td>
</tr>
<tr>
<td>Vessel V-101</td>
<td>0,2</td>
</tr>
<tr>
<td>Reactor R-102</td>
<td>39,8</td>
</tr>
<tr>
<td>Vessel V-102</td>
<td>0,3</td>
</tr>
<tr>
<td>Tower T-101</td>
<td>0,2</td>
</tr>
<tr>
<td>Tower T-102</td>
<td>0,04</td>
</tr>
<tr>
<td>Compressor C-101</td>
<td>9,4</td>
</tr>
<tr>
<td>Heat exchangers</td>
<td>10,8</td>
</tr>
<tr>
<td>Pretreatment unit</td>
<td>10</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>162,0</strong></td>
</tr>
</tbody>
</table>

As expected, biggest contributors to capital investment are reactor costs. As much as 29% of the total investment is coming from the hydrotreatment reactor, a value which gives perspective on the importance of its design.

Investment of the plant seems to be in line with the €550 million which Neste Oil is estimated to have invested in its plant.
Since 105 kmol per hour of propane are obtained and the required input for hydrogen is 1296 kmol per hour, propane could contribute to the hydrogen production process.

### Production costs

Variable costs come from raw materials, utilities consumption, fungibles (catalysts) as well as waste stream treatment. Reference costs for utilities and waste water treatment were taken from Aspen Plus® and Turton except for the price of electricity, which was fixed at 83 €/MWh, according to the values for industrial consumption in Spain [65].

Cooling duty for the reactors was calculated using Aspen Plus®, according to the heat of reactions. It is assumed that part of this heat is absorbed by the hydrogen gas (quenching), although half of it is estimated to be removed by a thermal fluid, which also needs to be considered.

The price of hydrogen purification in an amine unit was estimated as 0,1€ per treated m³, three times its typical value in order to account for handling expenses [66].

Catalyst prices were estimated based on their Ni, Mo and Pt content as found in the literature and their price [21, 50]. Lifecycle of the catalyst was assumed as 1.5 years, based on typical hydrodesulfuration catalyst lifecycles [67].

Regarding feedstock, palm oil price is selected as 0,7 €/kg a base case scenario, based on the recent values shown in the Market Analysis. Hydrogen price, on the other hand, is fixed at 1 €/kg, assuming it can be generated within the plant.

Fixed costs are calculated assuming the plant is two operators are present at all times and a base salary of €50,000 per year. The rest of the costs can be calculated as percentages of labor and investment (ISBL and OSBL) costs, including: supervision, maintenance, property taxes, plant overhead, royalty fees and depreciation. For the latter, 5% of fixed capital cost was considered, assuming a plant life of 20 years.

Calculations for all costs as well as estimation details can be found in Annex 7. The proportion of production costs is depicted in Figure 14. The results confirm what was found in another similar study [68], where the cost of the raw material accounted for 75% of the production costs.

Given the volatility of the price for palm oil and its weight on the production costs, it is highly recommended in view of these results that future studies in the field focus on the possibility of adapting the process to less clean (but cheaper) waste oils such as cooking oil or oil from the fish and animal industry.

### Product price and profitability

Product price and revenue can be calculated by adding margins to production costs and comparing the result with current market values for biodiesel to ensure competitiveness of the product.

Plant production is roughly 468,000 metric tons per year of green diesel. Byproducts include: green jet fuel (15,900 t/yr), green naphtha (9,100 t/yr) and green LPG (39,500 t/yr).

Table 11 shows the calculated margin for green diesel produced in the process, considering a market value of 1,1 €/kg. The rest of the product prices are: 1€/kg for kerosene, 1,15 €/kg for naphtha, and 0,54 €/kg for LPG, according to the Spanish market [55]. The values obtained in Table 9 are similar to those shown by Neste Oil for their Renewable product margin estimation, although final margin values for Neste Oil are twice as high [69], probably due to tax exemptions and the high quality of the diesel which allows it to be sold at higher prices.

To calculate profitability of the plant, annual cash flow is determined considering the EBIT value obtained after subtracting production costs to revenues and a taxation of 15% over profits.
Due to the environmental value of the project.

Depreciation was considered as a linear function over the plant’s lifespan of 20 years (5%), as shown in the fixed costs of production. A realistic approach was used where the plant undergoes technical shutdowns once every two years, reducing its productivity to 90%. Furthermore, productivity on the first year was assumed to be 75% due to technical difficulties in start-up operations.

Annual cash flow is shown in Figure 15, where it can be noticed that the slope of the curve varies every two years due to the above-mentioned scheduled technical shutdowns. Also, construction of the plant is 2 years.

As seen in Figure 15 (for which the values are shown in Annex 7), payback period is 7 years. In order to determine the economic interest of the project, net present value has been used. The net present value or NPV can be calculated from the cash flow in each year and the discount rate, which is around 10%. However, since the interest rate depends on several factors and is hard to predict at this stage, the net present value has been calculated at different interest rates varying from 6 to 14%.

As seen in Figure 16, negative NPV values are not positive except for low values, a consequence of the high investment cost the project requires.

Considering palm oil and diesel prices are of decisive importance for the profitability of the venture, a sensitivity analysis was performed to study the effect of their fluctuation on the feasibility of this project. Palm oil prices are varied between 900 and 500 €/ton, while diesel prices are varied between 0,9 and 1,3 €/kg.

Table 12 represents the payback period and NPV for both analyses. As seen from the results, these variations have great effect over the results, both in a positive and in a negative way.

**Table 11** Product margin for a market value of green diesel of 1,1 €/kg.

<table>
<thead>
<tr>
<th></th>
<th>Green Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production (t/yr)</td>
<td>468175</td>
</tr>
<tr>
<td>Cost of palm oil (€/t)</td>
<td>700</td>
</tr>
<tr>
<td>Variable cost of production (€/t)</td>
<td>121,8</td>
</tr>
<tr>
<td>Fixed cost of prod (€/t)</td>
<td>70,1</td>
</tr>
<tr>
<td>Margin (€/t)</td>
<td>208,1</td>
</tr>
<tr>
<td>Final product cost (€/t)</td>
<td>1100</td>
</tr>
</tbody>
</table>

**Figure 15** Cash flow over the lifespan of the plant and its construction, in M€.

**Figure 16** Net Present Values at interest rates from 6% to 14%.

**Table 12** Sensitivity analysis results on profitability for diesel and palm oil prices.

<table>
<thead>
<tr>
<th>Diesel price (€/kg)</th>
<th>Payback period (yr)</th>
<th>NPV (M€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,9</td>
<td>Negative cash flow</td>
<td>-</td>
</tr>
<tr>
<td>1,3</td>
<td>3</td>
<td>4149</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Palm oil price (€/t)</th>
<th>Payback period (yr)</th>
<th>NPV (M€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3</td>
<td>5330</td>
</tr>
<tr>
<td>900</td>
<td>Negative cash flow</td>
<td>-</td>
</tr>
</tbody>
</table>

**Conclusions**

The EU’s Renewable Energy Directive RED is imposing ambitious improvements in the energy market in order to shift Europe’s energy mix towards a more sustainable selection of fuels.

In this regard, biofuels from vegetable oils are a valid option to allow the transition in the energy market, although regulations and process design should consider the sustainability of
the feedstock very closely for both plantation and transport. Furthermore, the high effect feedstock price has over process profitability should invite designers to consider alternative sources of oils such as waste products from the fish and animal industries or used cooking oil.

When hydrotreated and isomerized, vegetable oils not only yield a cleaner, higher quality product, but also present improved cold flow properties, making it an attractive product in northern European countries. In this design, a plant with a capacity of roughly 500,000 tons per year of green fuel (diesel, kerosene, naphtha and LPG) has been proposed, simulated, and its feasibility evaluated. The team found that, main aspects considered, the design of the hydrotreating reactor is essential to ensure total conversions and profitability. This importance is corresponded with proper design through simulation in Aspen Custom Modeler®.

Moreover, the isomerization reactor allows shifting the production in the desired direction, allowing to adapt the process to market demand. Regarding heat integration, the team found an imbalance between cold and hot streams in the process, making heat integration difficult and resulting in an excess of heat for which future investigations are needed. Another possible process improvement includes propane steam reforming to obtain hydrogen, as calculations show that it could cover 80% of its consumption rate.

Finally, the economic analysis shows a profitable process after the 7th year, although diesel and palm oil fluctuations make it a risky investment. In order to improve this situation, funding and governmental incentives would be needed.

Acknowledgements
The team would like to thank Professor Santos Galán for his support and guidance through the project as well as our path through university. Also, we thank Belén García from Repsol for the valuable information received regarding regulations for biofuels in the European Union.

References


