



Technical feasibility of biodiesel production from virgin oil and waste cooking oil: Comparison between traditional and innovative process based on hydrodynamic cavitation



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ABSTRACT

Biodiesel production calls for innovative solutions to turn into a competitive process with a reduced environmental impact. One of the process bottlenecks stands in the immiscibility of oil and alcohol as raw materials, so mixing process largely impacts the overall process cost. This process step, if carried out by using hydrodynamic cavitation, has the possibility to become a benchmark for large scale applications. In this paper a process analysis of biodiesel production scheme is developed starting from two different feedstocks, virgin oil and waste cooking oil. At the first the traditional process scheme has been simulated, in a second simulation, the reactor for the biodiesel production is interchanged with a hydrodynamic cavitation reactor. In the paper, the comparison between the traditional and innovative process by using life cycle costing approach has been presented, thus providing indications for industrial technological implementation coming from a professional tool for process analysis. It is worth noting that the introduction of hydrodynamic cavitation reduces of about 40% the energy consumption with respect to the traditional process. As regards the total treatment costs, when using virgin oil as feedstock, they were in the range 820–830 €/t (innovative and traditional process, respectively); while starting from waste cooking oil the costs decreased of about 60%, down to 290–300 €/t (innovative and traditional process, respectively).

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1. Introduction

The actual dependence on fossil fuels (more than 80% of the actual world energy demand is covered by fossil fuels) must be cut before 2030 (Goldemberg, 2007). The increase in the production and consumption of biofuels in the transportation sector is considered a suitable solution to decrease fossil fuels consumption and thus environmental pollution; nonetheless, there are several concerns regarding intensive bioenergy crops, endangering local biodiversity (Diaz-Chavez, 2011), food vs. fuel issue (Ajanovic, 2011; Cassman and Liska, 2007). The sustainability of biofuels must exclude bioenergetic crops over arable lands (Dismukes et al., 2008) and edible feedstocks but endorses the use of biological wastes and crops from non-arable lands (Gomez et al., 2008; Jefferson, 2008) (second and third generation biofuels), remaining economically competitive (Hill et al., 2006). In particular, the sustainability of many first-generation biofuels, which are produced primarily from food crops such as grains, sugar cane and vegetable

oils, has been increasingly questioned over concerns such as reported displacement of food-crops, effects on the environment and climate change. In general, there is growing consensus that if significant emission reductions in the transport sector are to be achieved, biofuel technologies must become more efficient in terms of net lifecycle greenhouse gas (GHG) emission reductions while at the same time be socially and environmentally sustainable. It is increasingly understood that most first-generation biofuels, with the exception of sugar cane ethanol, will likely have a limited role in the future transport fuel mix. The increasing criticism of the sustainability of many first-generation biofuels has raised attention to the potential second-generation biofuels produced by the waste. Depending on the feedstock choice and the cultivation technique, second-generation biofuel production has the potential to provide benefits such as consuming waste residues and making use of abandoned land. In this way, the new fuels could offer considerable potential to promote rural development and improve economic conditions in emerging and developing regions. However, while second-generation biofuel crops and production technologies are more efficient, their production could become unsustainable if they compete with food crops for

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available land. Thus, their sustainability will depend on whether producers comply with criteria like minimum lifecycle GHG reductions, including land use change, and social standards (IEA, 2010).

The identification and implementation of sustainable biofuel production alternatives should be based on rigorous assessments that integrate socioeconomic and environmental objectives at local, regional, and global scales (Correa et al., 2019).

At the moment, biodiesel is the commonest and most promising biofuel already introduced into the automotive fuels market (in mixture with petrodiesel) at the cost of small technological adaptation of automotive engines (Ahmed et al., 2014; Marulanda, 2012). Biodiesel consists of mixture of methyl or ethyl esters. It is produced through an organic reaction called transesterification, where low molecular weight alcohol -e.g. methanol or ethanol- reacts with lipid or fat (triglyceride) to produce biodiesel -fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) - and glycerol as a valuable byproduct. Transesterification can occur catalytically or without catalyst. Catalysts currently used in transesterification process are homogeneous base or acid catalysts, heterogeneous catalysts, acid or base and enzymes.

The biodiesel use strongly reduces the GHG (up to 78%), unburned hydrocarbons and particulate matter (Van Gerpen, 2005) but increases nitrogen oxides (NOx) emissions (Hoekman and Robbins, 2012).

The effects on injection timing, ignition delay, adiabatic flame temperature, radiative heat loss, and other combustion phenomena all play some role on NOx emissions. These emissions can be mitigated by modifying engine control settings, particularly by retarding injection timing and increasing exhaust gas recirculation. The absolute magnitude of the biodiesel NOx effect appears to be reduced with modern engines, although there are cases where the percentage change is still substantial. Chen et al. (2018) performed an overall experimental investigation on NOx emission based on combustion characteristics of biodiesel. The results showed that on the whole, NOx emission of biodiesel is higher than that of diesel in most cases, except in the condition of low loads under low and medium speeds (Chen et al., 2018).

Feedstocks, class of lands for bioenergy crops (whether or not arable) and the production process affect the biodiesel production sustainability (Dovi et al., 2009).

Therefore, exploring new bio-sources for biodiesel production such as the use of microalgae as feedstocks complies with the sustainability requirements (Mata et al., 2010; Piemonte et al., 2016) as well as the use of waste oils (Al-Sakkari et al., 2018). But to increase energy efficiency and minimize energy losses and waste materials, the traditional biodiesel production process (BPP) also known as mechanical stirring (MS) method requires some reconsiderations and modifications as well. Biodiesel is produced by means of transesterification reactions between a lipid and an alcohol to form esters and a byproduct, glycerol. Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. This process proceeds well in the presence of some homogeneous catalysts, as alkali ones. The most common alcohols widely used are methyl alcohol and ethyl alcohol. Among these two, methanol found frequent application in the commercial uses because of its low cost (Verma et al., 2016).

The energy consumption due to time reaction during MS and raw material cost are the major contributors to the total cost of biodiesel production. The innovative technologies as hydrodynamic cavitation (HC) allow to reduce the mass transfer rate between oil and alcohol and consequently the energy consumption. Increasing the mass transfer rate between oil and alcohol with minimal cost for biodiesel production in terms of raw material

price, energy consumption, time and scale up cost are some of the challenges for research in this industrial sector (Chuah et al., 2016). Hydrodynamic cavitation (HC) is a new technology, currently applied in a wide range of chemical engineering sectors as wastewater treatment (Capocelli et al., 2013; Bagal and Gogate, 2014; Innocenzi et al., 2018; Gagol et al., 2018; Dular et al., 2018; Innocenzi et al., 2019) and green process intensification protocols (Gude, 2018; Wu et al., 2019).

As for biodiesel production in the presence of catalyst, HC has the advantage of achieving complete conversion in a short reaction time. HC has proved to be an appropriate option to replace some of the steps of the conventional BPP, with several enhancements such as less waste streams, less energy losses and increased energy efficiency (Ladino et al., 2016; Günay et al., 2019; Asif et al., 2017). One of the major challenges in the BPP is the immiscibility of oil and alcohol as raw materials, which causes the formation of two separate phases thus decreasing mass transfer rate and increasing reaction time (typically a long reaction time -up to 12 h - depending on feedstock and catalyst, requiring in any case large reactor volumes); moreover, the contact surface is to be increased to improve mass transfer rate, and stirred-tank reactors are usually used in many industrial units at this scope, but with an insufficient mixture of the reactants. HC generates tiny cavities in the reaction mixture, thus yielding to an intensification of the process with increasing mass transfer between insoluble phases (Chuah et al., 2017) and decreasing reaction times (Chipurici et al., 2019). Additionally, energy consumption is reduced and the reaction temperature and pressure are lower (Chitsaz et al., 2018).

Besides HC, other technologies have been studied to intensify BPP and namely microwaves (MW) and ultrasonic cavitation (UC). A good review of the obtained results by using different techniques for transesterification reaction is reported in the review by Chuah and coworkers (2017). In the last review paper, the above mentioned techniques have been compared as for their efficiency in mixing with mechanical stirring (MS), and the yield efficiency (defined as yield of product per unit supplied energy to the system) in relation to the used technique is the following: $HC > MW > UC > MS$. HC is definitely the most feasible method to assist and intensify the transesterification reaction (Chuah et al., 2017). Nevertheless, HC is still a quite novel technique in the biodiesel field.

Currently, the biodiesel production techniques that are based on hydrodynamic cavitation, essentially focus on technology that involves the use of a high speed homogenizer (based on the rotor/stator model, also referred to as rotating generator, Crudo et al., 2016) or involves (especially in the past five/six years) the use of circular or slit Venturi or orifice plates (Maddikeri et al., 2014).

As for high speed homogenizer, this technology has been studied for the intensification of the synthesis of biodiesel from different vegetable oils (virgin soybean oil, spent soybean cooking oil and many others, virgin or waste oils). This rotating generator has proved to be an efficient, fast and cost-effective procedure for biodiesel preparation (Crudo et al., 2016). Process parameters such as inlet pressure, temperature, catalyst concentration, molar ratio, type of cavitating device have been studied.

The results obtained from this literature analysis focused on hydrodynamic cavitation applied to biodiesel production have been used for process simulation. In the present work, process simulations on alkali catalyzed transesterification by traditional and innovative method based on HC are presented: a professional software tool, *SuperPro Designer*[®], is used to simulate the whole process with energy and mass balances. Process performance is expressed in terms of biodiesel yield with respect to a traditional process scheme, to verify the method efficiency by using two different feedstocks, virgin oil and waste cooking oil. The results of

the process analysis have been used to carry out a preliminary economic analysis to identify the cost items that have the greatest impact on the cost-effectiveness of the biodiesel production process.

This is an attempt to explore potential alternatives to current biodiesel production methods, thus contributing to commercialization and more sustainable production of second-generation biofuels.

2. Materials and methods

In the following a description of the methods used to carry out the process analysis and simulation is provided. In details, [Section 2.1](#) reports the process simulation by using a commercial software and [Section 2.2](#) the input data, derived from literature analysis, used for the simulation.

2.1. Process simulation

The biodiesel production process was simulated by using the software SuperPro Designer[®]. The simulation refers to different stages starting from virgin oil and waste cooking oil as reported in [Fig. 1](#).

The procedures of process simulation include defining chemical components, selecting the operation mode, determining plant capacity and selecting the operative conditions for the various steps of the process. Information on most components, such as methanol, hydrochloric acid, water is available in the SuperPro Designer[®] component database. Regarding for other substances, as catalysts (Sodium methoxide, NaOCH₃), raw materials (virgin or waste oil) and biodiesel, the data are not available in the library of the software, hence were defined as new components.

In this study, NaOCH₃ has been selected as catalyst in alternative to hydroxides (i.e. sodium hydroxide or KOH, [Zhang et al., 2003](#)) because although it is less economical than hydroxides, has a greater efficiency for the transesterification process ([Freedman et al., 1984](#); [Hass et al., 2006](#)). The process analysis has been performed to define the mass and the energy balance considering that the proposed plant works in continuous mode for 7920 h per year, with a capacity of the plant of 1000 L/h. The final products were biodiesel and glycerol. Biodiesel to be commercialised shall meet ASTM D 6571 and EN 14214 standard specification ([ASTM D6751](#); [EN 14214](#)).

The annual production of biodiesel for the present case study was 8.23E+06 L, smaller than medium size plants ([Hass et al., 2006](#)).

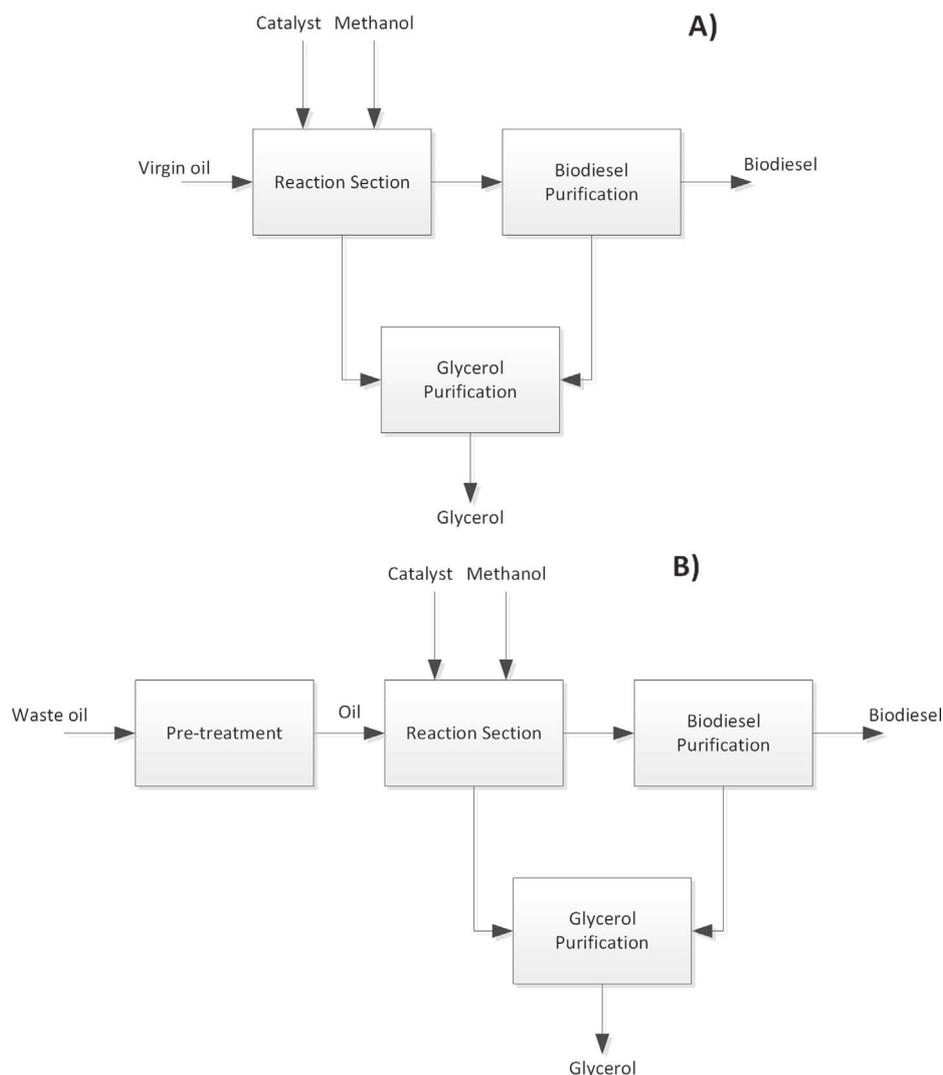


Fig. 1. Block scheme of traditional biodiesel production process; A) case-study A1: feedstock = virgin oil; B) case-study B1: feedstock = waste cooking oil.

2.2. Input data description

Based on the literature analysis, several scenarios have been considered: Case study A1, feedstock = virgin oil, traditional process; Case study B1, feedstock = waste cooking oil, traditional process; Case study A2, feedstock = virgin oil, innovative process; and Case study B2, feedstock = waste cooking oil, innovative process.

Process flowsheets are presented in Figs. S1–S7 (Supplementary materials).

In the first studied scenario, virgin oil is sent to a series of two reactors (P-13/R101 and P-14/R102) in which it reacts with methanol in the presence of the catalysts (catalyzed transesterification of the oil); then the products are centrifugated (P-15/DC101 and P16-DC102) to mainly separate biodiesel from glycerol. Biodiesel is sent to purification section that includes a washing of residual catalysts (P-18/V101, mixing vessel) in which hydrochloric acid reacts with sodium methoxide to product methanol and sodium chloride. Another centrifugation separates biodiesel and virgin oil from the other substances (i.e. methanol, sodium chloride, hydrochloric acid). Biodiesel is sent to a series of heat exchanges and after in a flash (P-23, V104), where water is separated from the product that can be stored and it is ready to be sold. Glycerol, instead, is refined in another section that includes equipment sized to remove methanol, the fatty acids and most of the product. Both glycerol stream and fatty acid contaminants exiting the reactors are pooled and treated with acid (HCl) (P-28/V101) to convert soaps into free fatty acids which are subsequently removed by centrifugation (P-30/DC-103). The fatty acid stream is destined to disposal. The glycerol stream is then neutralized with sodium hydroxide (P-33/V-103). The methanol contained in the glycerol stream is recovered by distillation (P-36/C-101) and recycled back to the first reactor (R-101). Finally, the glycerol stream is concentrated through another distillation step (P-38/C-102) that removes the water, which is recycled back to the mixing vessel (P-18/V-101).

In the second scenario (Case study B1), waste cooking oil before reaching the sections described above, is sent to a pre-treatment step, in which a physical treatment, as stationary screen or as alternative a filtration through sieving, removes the solid impurities coming from cooking operations. Waste oil contains a high concentration of free fatty acids that if are sent to a reaction section produce soaps, therefore a preliminary esterification reaction is necessary (P-7a, R-100). This reaction converts the fatty acids in fatty acid esters. The products are sent to another operation with glycerol (P-10a, WSH-101) to remove traces of reagents from oil before to be fed to the reaction section. The process unit for Reaction section is the same for the Case Study A1. Finally, the flow is sent to a distillation column (P-12a/C101) to recover methanol that is recycled to the esterification reactor.

As known, the mixing/heating (Case Study A1 and B1) is the most commonly adopted process worldwide industrial application for biodiesel production but requires a lot of energy, high catalyst, high molar ratio (alcohol to oil) and longer time to produce biodiesel. Considering these limitations, there is strong quest to develop an efficient, time saving, economically functional and environmentally friendly biodiesel production intensification process at industrial scale. Keeping this aspect into consideration HC is one of the intensification process that offers a substantial promise for biodiesel production in terms of methyl ester conversion, reaction rate, time, chemical consumption, energy consumption, scale up, clean and safe (Qiu, 2010). For that in the last two scenarios A2 and B2, the innovative process by using hydrodynamic cavitation is presented. Only a few studies have been done in biodiesel production using HC approach (Chuah et al., 2017) and most of them were just at laboratory scale.

The hydrodynamic cavitation has been simulated by generic box (P-13/GBX101) and replaces the reactors of the transesterifica-

tion for the Case Study A1 and B1 (Chuah et al., 2016). The other units of the processes remain unchanged. The experimental data by Chuah et al. (2016) has been chosen for the simulation because the HC research activity was conducted on a pilot scale closer to the industrial scale. However, there are not many published papers on plate geometry design, which is a crucial factor for large-scale reactor design that also improves methyl ester conversion performance.

3. Results and discussion

3.1. Process analysis for traditional processes

3.1.1. Case study A1, feedstock = virgin oil, traditional process

3.1.1.1. Transesterification. A continuous alkali-catalyzed process scheme by using virgin oil was developed (Fig. 1). The first section of the process is the transesterification (Fig. S1). The reaction was carried out with a 5:1 vol ration of methanol to oil, 0.3% wt sodium methoxide (catalysts based on oil), 60 °C and 4 bar. Fresh methanol (S3, 90 kg/h) and recycled methanol (S48, 75 kg/h) coming from glycerol purification section, are mixed with catalysts (a mixture of sodium methoxide, 25% and methanol, 75%, S10) prior to being pumped into reactor P-13/R-101.

Virgin oil was heated in P-12/HX-101 to increase the temperature from 25 °C until 60 °C (operative temperature in R-101). The residence time in the reactor R-101 is set to 1 h with an efficiency of 90% as reported in scientific literature (Hass et al., 2006).

The output (S17) from reactor is a mixture of biodiesel, methanol, catalyst, soybean oil, traces of water and glycerol that is a coproduct of transesterification. A centrifugation is employed to separate glycerol phase (P-15/DC-101) which is sent to glycerol purification and recovery section.

Biodiesel stream coming from centrifugation unit is sent to another reactor (P-14/R-102) to complete the transesterification reaction at a rate of 934 kg/h, adding methanol and sodium metoxide (around 1.6%wt of catalyst in methanol) at a rate of 17.6 kg/h. Also in this case, the residence time is set to 1 h with an efficiency of 90%, for an overall transesterification yield of 99%.

3.1.1.2. Biodiesel purification. Purification scheme process is reported in Fig. S2.

Biodiesel stream (S19) coming from reaction section is sent to a centrifugation to separate glycerol phase (see Fig. 3, P-16/DC-102) from biodiesel. The removal efficiency for the centrifugation is set to 99.9% for biodiesel and for the residual oil. From P-16/DC-102, the diesel-rich stream (S24, 931.2 kg/h) has around 96% of biodiesel, 1.6% glycerol, 1.4% of methanol, 1% of soybean oil and traces of catalysts; glycerol-rich (20.36 kg/h) having around 53% and 44.8% of glycerol and methanol, respectively, is sent to the purification glycerol section (see Fig. S3).

Current S24 is sent to purification unit that includes: a washing reaction (P-18/V-101) with a solution of hydrochloric acid and water (216.6 kg/h, 0.7%wt of HCl) with around 85% of water recycled from glycerol purification unit. The scope of the washing is to neutralize the catalysts and covert any soaps to free fatty acids, reducing their emulsifying capacities. The output is sent a centrifugation (P-19/DC-104) to separate mainly biodiesel from the other substances with an efficiency of 99.9%.

The output (S28, 924.5 kg/h) rich in biodiesel (around 96.6%) contains 2% of water, the concentration of water must be lower to 0.05% (v/v) to meet the biodiesel standard specifications (ASTM specifications, ASTM D6751). The content of water is reduced in a vacuum dryer simulated by a flash operation.

3.1.1.3. *Glycerol purification.* Glycerol Purification scheme process is reported in Fig. S3.

The streams coming from reaction section (S20) and from washing operation of biodiesel (S23 and S27) contain glycerol that can be recovered and valorised. It has been considered a percentage of 80% wt of glycerol in the final product, this product can be sold to industrial refiners (Hass et al., 2006). The solutions and hydrochloric acid are fed together into chemical reactor (P-28/V-101) in order to neutralize the residual catalyst and convert soaps to free acids. The products (373.4 kg/h) are sent to a centrifugation (P-30/DC-103) to separate the substance of interest from the residual free acids (14.4 kg/h) that after should be sold or be disposed of. In the present study in rather conservative way, this current has been considered as waste.

The glycerol is neutralized with sodium hydroxide in a reactor (P-33/V103) to convert hydrochloric acid in sodium chloride. After that there are two distillation columns to remove methanol and water, respectively. Methanol recovered from the first column (P-36/C-101) is recirculated into the reactor R-101, first reactor of the transesterification section (see Fig. S1). The bottom product (284.25 kg/h, 29% wt of glycerol and 70%wt of water and traces of other substances) is sent to the second distillation (P-38/C-102) to remove water. The distillate (around 181 kg/h, 99.99% wt of water) is recirculated to reactor (P-18/V-101) for the purification of biodiesel. Bottom product is glycerol-rich stream (80% in glycerol) that be storage and it is ready to be sold. C-101 has a theoretical stages equal to 4.8, operative cooling and heating temperature is set to 64 °C and 100.5 °C, the reflux ratio is 1.166. The second distillation column has a theoretical stages equal to 9.6, operative cooling and heating temperature is set to 100 °C and 127 °C, the reflux ratio is 0.122. The operative pressure for both distillation column is 1.013 bar.

3.1.2. *Case study B1, feedstock = waste cooking oil, traditional process*

3.1.2.1. *Pre-treatment.* In this second simulated process, it has been considered to use as raw material the waste cooking oil to reduce the operative costs. In comparison to *Case Study A1*, a pre-treatment unit has been added to prepare the feedstock before to feed the transesterification unit. Pre-treatment includes esterification of the free fatty acids, a washing with glycerol and methanol recovery. This section is described below, and Fig. S4 shows the flowsheet; whereas the remainder of the process is identical to *Case Study A1*, described in Figs. S1–S3, hence it has not been reported.

Waste cooking oil has a certain concentration of suspended solid, in this study has been considered around 1% wt of solid in the feed. A grid is necessary for the separation this solid from oil, after that the solution is sent to esterification reaction (P-7a/R100) at 70 °C and 4 bar. Methanol (around 146 kg/h) and pure sulfuric acid (10 kg/h) are fed into reactor to convert the free fatty acids in methyl esters. After 1 h of reaction, the stream is sent to a washing operation to remove the acid and water before proceeding to the alkali-catalyzed transesterification. By adding glycerine at 25 °C, water can be removed (Zhang et al., 2003).

Treated oil (1 m³/h) is sent to transesterification unit (as described for *Case Study A*), instead the stream S15a (around 215 kg/h) is reach in methanol (49%) and (37%) of glycerol with 8.5% of water and sulfuric acid. This current is sent to column distillation (P-12a) to recover methanol with seven stages of distillation, methanol is recovered as distillate with the following composition: 99.94%wt of methanol and 0.06% of water. This stream (95 kg/h) is recirculated for the esterification reaction. The bottom product is a mixture of glycerol (around 73.5%), 0.6% of methanol, 16% of water and around sulfuric acid. This current (S21a, about 109 kg/h) can be treated to recover mainly glycerol

but in the present study, it has been considered as a residual liquid waste.

For the other process unit (*Transesterification, Biodiesel purification and glycerol purification*) can be see the previous section.

3.2. *Process analysis for innovative process: biodiesel production by hydrodynamic cavitation*

3.2.1. *Case study A2, feedstock = virgin oil, hydrodynamic cavitation*

In this third simulated process (see Fig. S5), it has been considered to use as raw material the virgin oil. In comparison to *Case Study A1*, the chemical reaction section has been replaced by hydrodynamic cavitation reactor. The reaction was carried out with a 5:1 vol ration of methanol to oil, 1% of catalyst, 60 °C and 2 bar. Fresh methanol (around 90 kg/h) and recycled methanol (60 kg/h) coming from glycerol purification section, are mixed with catalyst (a mixture of sodium methoxide, 25% and methanol, 75%, 8 kg/h) prior to being pumped into reactor P-13/GBX-101 (hydrodynamic cavitation reaction).

Virgin oil was heated in P11/HX-101 to increase the temperature from 25 °C until 60 °C (operative temperature for the reaction in P-13). The residence time in the cavitation reactor is set to 15 min with an efficiency of 97% as reported in scientific literature (Chuah et al., 2017). The output (S12) from reactor is a mixture of biodiesel, methanol, catalyst, soybean oil, traces of water and glycerol that is a coproduct of aclyglycerol transesterification. A centrifugation is employed to separate glycerol phase (P-14/DC-101) which is sent to glycerol purification and recovery section.

Differently from the transesterification reaction (*Case Study A1* and *B1*), in this simulated process one stage of reaction has been considered given the high efficiency of the hydrodynamic cavitation. Another relevant aspect is the reaction, in this last case 15 min are enough to reach 97% of reaction yields. This efficiency was guaranteed by the operative conditions described below and chosen on the basis of the studies carried out by Chuah et al. (2016 and 2017). The results of these studies showed that the molar ratio of oil to methanol is one of the most important factors that affect the biodiesel production process. The reaction yields increased from 45 to 98% in 15 min for HC: it could be attributed to the higher methanol amount that generated more cavities and resulted in strong mass transfer between oil and methanol. A molar ratio less than 6 resulted in an incomplete transesterification reaction even after 1 h. The effect of catalyst concentration on biodiesel production by HC has been also studied by Chuah et al. (2017): it has been found that as the catalyst concentration increased, reaction yield also increased. An incomplete reaction occurred for catalyst amount less than 1%, this value was selected as an optimum catalysis concentration that allowed to reach around 97% of reaction yield in 15 min. The experimental results related to the effect of reaction temperature showed that as temperature increased, HC efficiency also increased due to the fast dispersion of methanol and viscosity reduction in waste cooking oil. This was favourable to enhance the solubility of the oil in methanol and improve the contact between the oil and methanol. 60 °C was selected as optimal temperature to improve the reaction efficiency (Chuah et al., 2016; 2017).

As regards the configuration of the HC system, the optimised geometry of orifice plate with 21 holes of 1 mm diameter was chosen in the present work. Multiple holes plate with smaller diameter was found to be effective in generating higher cavitation events. This is due to the fact that the smaller hole diameter in the orifice plate generates a larger number of small bubbles, resulting in a higher number of the cavitation events and better emulsification which in turn leads to a higher mass transfer and an increased turbulence, making the collapse of cavities more violent

and thus generating large magnitude pressure pulses (Chuah et al., 2016; Ghayal et al., 2013).

Another parameter which expresses the efficiency of the HC process is the cavitation number C_v (Eq. (1)) that

$$C_v = \frac{P_f - P_v}{\frac{1}{2} \rho V^2} \quad (1)$$

where P_f (in Pa) is the fully recovered downstream pressure, P_v (in Pa) is the vapour pressure of the mixture liquid, ρ (kg/m³) is the density of the mixture liquid and V (m/s) is the flow velocity through the orifice plate, which can be calculated by knowing the upstream flow rate and diameter of the orifice. Decreasing the cavitation number causes the mixture liquid to experience the cavitation zone for a longer time, thus resulting in higher cavitation and better conversion yield. It has been found that when the C_v number was reduced to near 0.3, it gave the maximum benefits in methyl ester conversion. The chosen configuration (orifice plate with 21 holes of 1 mm diameter, inlet pressure of 2 bar) guaranteed a $C_v = 0.357$ with a flowrate of 23.4 L/min at a velocity of 23.636 m/s (Chuah et al., 2016).

Biodiesel and glycerol streams coming from centrifugation unit are sent into two separate purification units (reported in Figs.S6 and S7). The other units of the biodiesel production are the same as those listed in section (Section 3.1) for this below only the figures are reported.

3.2.2. Case study B2, feedstock = waste cooking oil, hydrodynamic cavitation

In the Case study B2 (as for case study B1), it has been considered to use as raw material the waste cooking oil to reduce the operative costs. In comparison to Case Study A2, a pre-treatment unit has been added to prepare the feedstock before to feed the transesterification unit. Pre-treatment includes esterification of the free fatty acids, a washing with glycerol and methanol recovery. This section is the same already described for the Case Study B1 (see Fig. S4) for that it has not reported here. The remainder of the process is identical to Case Study A2, described in Figs. S5–S7. Table 1 shows the composition of the final products for each considered process. The final products from A1/B1 and A2/B2 had the same composition because theoretically, once the refined oil without free fatty acids is obtained, the downstream units are identical to those in process A1/B1 using virgin vegetable oil

Table 1
Final products obtained from process analysis.

FINAL PRODUCT		
Biodiesel	Case Study A1/B1	Case Study A2/B2
Biodiesel (%)	98.27	96.50
Glycerol (%)	0.156	0.184
Hydrochloric acid (%)	0.002	0.003
Methanol (%)	0.060	0.056
Sodium Chloride (%)	0.005	0.005
Oil (%)	0.920	2.672
Water (%)	0.587	0.588
Flow (kg/h)	909.24	907.43
Glycerol	Case Study A1/B1	Case Study A2/B2
Biodiesel (%)	0.00	0.00
Glycerol (%)	80.04	80.15
Sodium hydroxide (%)	0.028	–
Methanol (%)	0.00	0.056
Sodium Chloride (%)	3.41	2.68
Oil (%)	0.00	0.00
Water (%)	16.52	16.65
Hydrochloric acid	–	0.520
Flow (kg/h)	102.97	99.96

(Zhang et al., 2003), therefore with the same amount of oil (or treated oil) fed to transesterification reactions the same products (in terms of flowrate and composition) were obtained.

It has been chosen to perform other two process analysis related to the HC process. More in details, the effect of inlet pressure to HC system was studied, by varying the pressure in the range 1–3 bar, under the same operative conditions above described. The efficiency of the reaction was near to 83% and 90% for 1 bar and 3 bar, respectively. The results showed that the reduction of HC efficiency caused an almost negligible reduction (about 1%) of the produced biodiesel, more important was the quality of the final product. The percentage of biodiesel was 83.78% and 90.18% for an inlet pressure to HC system of 1 bar and 3 bar, respectively. The purity of the biodiesel was below the standards required for a possible marketing. An improvement of HC efficiency could be obtained for example by increasing of reaction time. These results showed the importance of the efficiency of the HC process, whose experimentation is still at the pilot scale and needs to be implemented at the industrial scale to validate the operative conditions.

3.3. Economic analysis

3.3.1. Definition of the CAPEX and OPEX

The present section reports the results about the life cycle cost analysis (LCC) based on the mass and energy balances obtained by process analysis. In according to ISO 14040 (2006) (Nouredini and Zhu, 1997), the first phase of life cycle cost analysis (LCC) is to define the goal and scope of the study including the description of the product or process system, the function of the operations, the functional unit, the system boundary, data requirements, assumptions and limitations. In this case, the boundary of the system is reported in Fig. 1. The functional unit chosen for the analysis is 1 m³/h of feedstock.

The main item costs considered for the analysis were: (1) equipment cost, (2) raw material purchase, (3) energy cost, (4) labour cost and (5) transport and disposal of solid waste.

LCC are those incurred over the life span of a process system, including costs required to construct, equip and operate the system. For each treatment process, a general, annual cost estimation was developed consisting of the recurring costs (RC), also known as operation and maintenance costs, and the non-recurring costs (NRC), otherwise known as capital costs, converted to an annual cost basis (ISO 14044:2006).

The general equation used for the analysis model is (Dhillon, 2017):

$$\text{Annual LCC} = \text{RC} + \text{NRC} \quad (2)$$

More in details, RC include annual labour costs, operational energy costs and maintenance (repair) cost and purchase cost for the chemicals and disposal costs for the produced waste (OPERating EXPense, OPEX). Non recurring costs (NRC) is the capital investment including the equipment cost, piping, engineering, that are amortized in X years. CAPital Expenditure (CAPEX) has been estimated from the cost of purchasing the equipment (PEC – purchase equipment cost), on the basis of which total direct and indirect costs have been assessed (FCI-fixed Capital Investment) contributing to the determination of the TCI. Equipment costs were obtained from vendors; if quotes were not available for the required plant capacity, then a process cost estimating was used:

$$C_n = C_0 \left(\frac{S_n}{S_0} \right)^x \quad (3)$$

C_n = cost of new equipment, C_0 = cost of existing equipment with pricing available; S_n = size of new equipment, S_0 = size of existing

equipment and X is the exponent depending on type of equipment (Peter et al., 2004). The reference year for the estimation was 2002 and the values have been discounted by using the CEPCI – Chemical Engineering Plant Cost Index (Calculation Methodology for Cost Goals). Total fixed investment is calculated adding equipment erection, piping, instrumentation, buildings, storages, design and engineering, contractor's fee and contingency of 10% of PCE. Additionally, a working capital of 15% of total project capital costs was added to the project capital costs, and then the total was amortized to obtain annual capital costs. Straight line depreciation over 10 years is considered with an index of 7.7.

Table S1 shows the main processing units required for each process.

Table 2 reports the capital costs for the proposed processes including purchase, installation, electrical service, instruments, buildings site development, ancillary buildings, design and engineering, contractors' fee and contingency (Peter et al., 2004).

The variable operating cost (RC) refer to the materials and energy whose usage varies depending on the process can be found in Table 3. The corresponding RC are detailed in Table S2 with their references. For maintenance it has been considered 3% of FCI.

Labour costs has been calculated considering three labour shifts of 8 h, with two operators per shift. The basic cost for worker is 25 €/h. Moreover, it has been added the operating supervision estimated to be 5% of the labour cost.

Financial indicators as payback period (PBP) and Return on Investment (ROI) have been calculated. The PBT is the time required for a project to return the initial investment. It is computed by calculating the cumulative return for each year and comparing it to the investment; the time at which this sum exceeds the investment is the payback time.

ROI (Chen, 2020) is a performance measure used to evaluate the efficiency of an investment or compare the efficiency of a number

of different investments. ROI tries to directly measure the amount of return on a particular investment, relative to the investment's cost. To calculate ROI, the benefit (or return) of an investment is divided by the cost of the investment. The result is expressed as a percentage or a ratio. "Current Value of Investment" refers to the proceeds obtained from the sale of the investment of interest. Because ROI is measured as a percentage, it can be easily compared with returns from other investments, allowing one to measure a variety of types of investments against one another.

3.3.2. LCC results

The life cycle costs for each biodiesel process are summarised in the Figs. 2 and 3.

The total annualized cost (€/m³ of feedstock) can be divided into Capital cost including (including also insurance and taxes of 2% of FCI), chemical for treatment, labour, maintenance and repairs, utilities (chilled water, steam, electricity) and waste management. As seen from Fig. 2, other items have been added: Operating supplies (15% of maintenance), Laboratory charges (10% of labour cost), Plant overhead cost (30% of the total labour cost) and General expenses including the administrative cost (25% of plant overhead cost) and research and development cost (1.45% of annual net treatment cost, NPC). For Case Study A1 and A2, the chemical purchase necessary for the biodiesel production was determined to be the major component of the total annualized cost due to the purchase of feedstock. The raw material cost was about 650 €/m³ of feedstock for the Case Study A1 and A2, instead for the Case study B1 and B2 the material cost was near to 75 €/m³ of treated oil.

Fig. 3 shows the details of the OPEX (€/m³ of feedstock) for each proposed scenarios. It is possible to observe once again that the raw materials had the major incidence on operating cost followed by the labour cost and utilities for Case Study A1 and A2. The feed-

Table 2
Capital costs for the biodiesel production (k€).

	Case study A1	Case study B1	Case study A2	Case study B2
Fixed Capital Investment Cost (FCI)	2510.91	2808.19	2243.70	2540.98
Working capital	376.64	421.23	336.56	381.15
Total Capital Investment Cost (TCI)	2887.55	3229.42	2580.26	2922.13

Table 3
Variable operating parameters (€/m³ of virgin oil or exhaust oil) for biodiesel production.

	Case study A1	Case study B1	Case study A2	Case Study B2
Consumable and raw materials (€/m³ of feedstock)				
Feedstock	603.05	0.00	603.05	0.00
Methanol	33.20	54.19	33.20	54.19
Catalyst	13.91	13.91	10.11	10.11
Water	0.0246	0.0246	0.0246	0.0246
Hydrochloric acid (36%)	1.11	1.11	1.11	1.11
Sodium hydroxide	0.36	0.36	0.36	0.36
Sulfuric acid (96%)	0.00	0.70	0.00	0.70
Glycerol	0.00	4.00	0.00	4.00
Total	651.65	74.29	647.86	70.49
	Case study A1	Case study B1	Case study A2	Case Study B2
Utilities (€/m³ of feedstock)				
Electricity	1.37	1.66	0.86	1.15
Chilled water (5–10 °C)	18.04	39.89	17.23	39.08
Steam (152 °C)	2.30	3.60	2.30	3.60
Total	21.71	45.15	20.39	43.83
	Case study A1	Case study B1	Case study A2	Case Study B2
Other (€/m³ of feedstock)				
Waste Management (Transport and Landfill)	2.19	18.39	2.19	18.39
Maintenance and repairs	9.07	10.14	7.84	8.91
Total	11.26	28.53	10.03	27.3

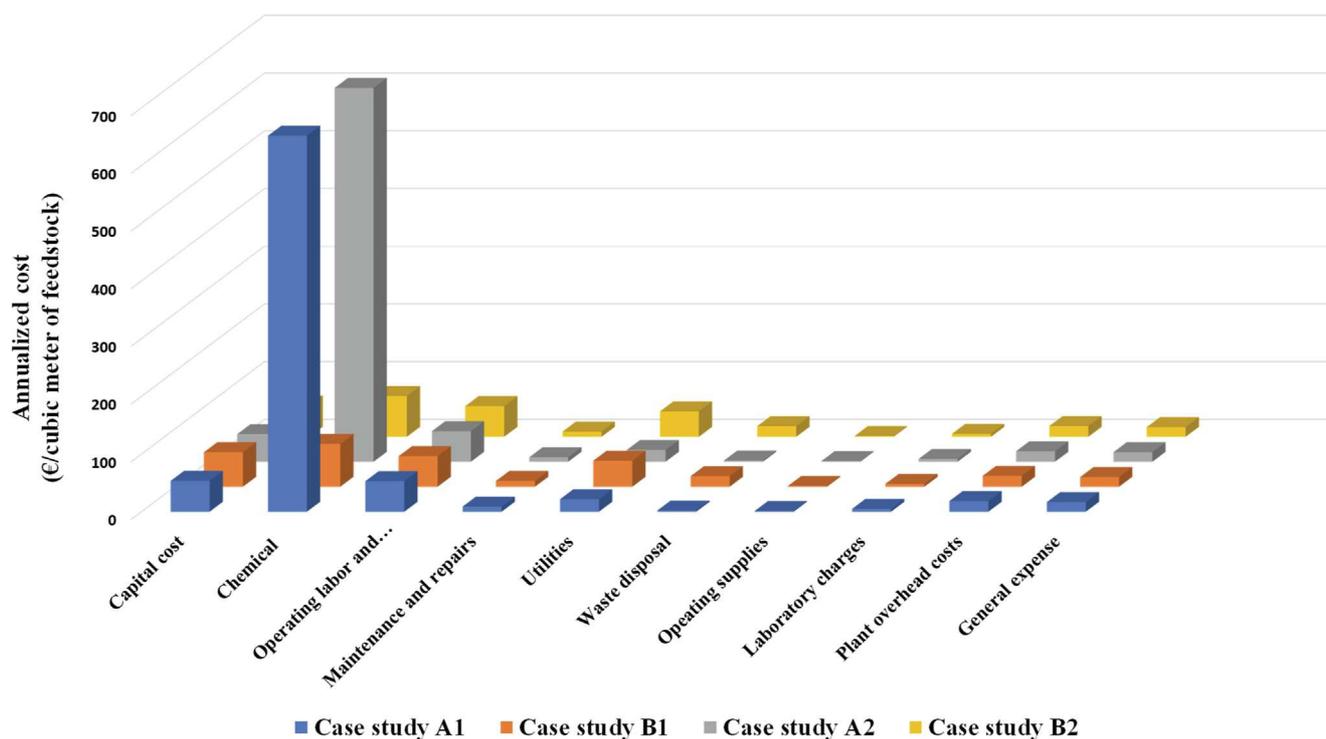


Fig. 2. Total annualized cost (€/m³) for selected process schemes to biodiesel production. Annual plant capacity = 7920 m³ of feedstock, virgin oil (A1 and A2) and exhaust oil (B1 and B2).

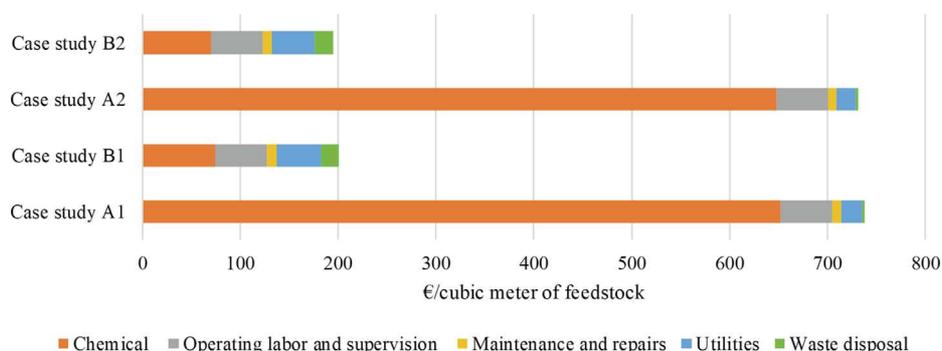


Fig. 3. OPEX (€/cubic meter of feedstock) for selected process to biodiesel production. Annual plant capacity = 7920 m³ of feedstock, virgin oil (A1 and A2) and exhaust oil (B1 and B2).

stock purchase (virgin oil) is around 90% of the total chemical cost for Case Study A1 and A2 instead for Case Study B1 and B2, methanol is around 73% of the total chemical cost due the fact that in these last scenarios methanol is used for the pre-treatment of the exhaust oil before to transesterification reaction.

Regarding to the utilities cost (Fig. S8), Case study A1 and A2 had the lower cost, infact in these situations the consumption of electricity, chilled water and steam was reduced because there was not the pre-treatment of the exhaust oil. The main advantage of the innovative process is related to electricity consumption, actually there is a reduction of around 40% of the energy demand for the reaction section but this impact only for 6% on the total utilities. The main voice is the chilled water, having an impact greater than 80% on the total. The reaction section of the case study A2 and B2 has not the transesterification reactors (R101 and R102) and there is an energy saving related to mixing system. The electric con-

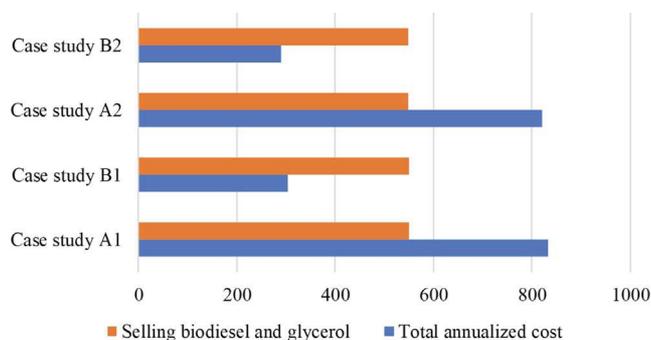


Fig. 4. Total annualized cost and total revenues due to the biodiesel and glycerol selling.

Table 4
Financial parameters calculated for the proposed processes.

	Case Study A1	Case Study B1	Case Study A2	Case Study B2
Net annualized cost (k€/y)	6,597	2,401	6,497	2,300
Revenue (€/y)	4,360	4,360	4,350	4,350
Net profit	–2,237	1,958	–2,147	2,048
PBP	>10 years	2–3 years	>10 years	2–3 years
ROI (%)	n.a.	70.88	n.a.	94.41

sumption for each transesterification reactors has been estimated to be equal to 1.4 kW/m³, for Case Study A2 and B2 this consumption is replaced from electricity energy necessary for the pumping the current into HC system with a pressure of 2 bar (around 0.1 kW). Figure S9 shows the details of the electricity consumption.

3.3.3. Economic feasibility

In this section the economic feasibility of the proposed processes has been reported. For each scenario it has been evaluated the annual treatment cost as already described above and the revenues coming from the selling of biodiesel and glycerol. For biodiesel and glycerol value, it has been considered 0.6 €/kg (Cavallo, 2017) and 0.05 €/kg (Quispe et al., 2013), respectively.

The results of this analysis are shown in Fig. 4.

It is possible to observe that the plant solutions A1 and A2 are not economically feasibility, instead for the Case Study B1 and B2 there is a positive profit for the selling mainly of biodiesel. Glycerol accounts for only 1% of the total revenues. It is clear that with the considered price of selling for biodiesel, investments cannot be made unless oil waste is considered as raw material. These results are confirmed also in Table 4 in which net profit (€/y), payback period and ROI have been calculated for the proposed scenarios. An acceptable economic return can only be considered for Case Study A2 and B2. As regards the traditional and the innovative process with hydrodynamic cavitation, the differences in economic terms is minimal.

A sensitivity analysis has been performed in order to check the feasibility of the process. The following parameters which had the greatest impact on the total operative cost have been changed: feedstock and methanol price as chemicals and chilled water cost as utilities. The other voices have not been considered as they did not affect the final operative costs. For the analysis, it has been assumed a maximum variability of the unit costs for the chemicals (methanol and virgin oil) and utilities (chilled water) of ±20%. The cost for waste cooking oil has been varied between 0.1 and 0.67 €/kg. Scientific literature reports that the purchase cost for waste cooking oil was near 0.17 €/kg (Gholami et al., 2018; West et al., 2008).

The analysis showed that for Case Study A1 and A2 the methanol and chilled water costs were not found to affect the feasibility of the process which was always not economically feasible. Instead the initial price of the feedstock (virgin oil) had a relevant influence: if the price of feedstock was 0.3 €/kg, the net profit was about 400,000 € and 492,670 € for the Case Study A1 and A2, respectively.

For the Case Study B1, the net profit varies between 2,039,534 € and 1,867,379 € for a methanol unit price between 0.30 and 0.45 €/kg, respectively. Net profit varies between 2,019,016 € and 1,892,654 € for a chilled water unit price between 0.26 and 0.40 €/kg, respectively. The process was not economically feasible if it was considered an initial purchase price of the exhausted oil greater than 0.2 €/kg. The same results were obtained for the Case Study B2: the net profit varies between 2,129,697 € and 1,957,542 € for a methanol unit price between 0.30 and 0.45 €/kg, respectively. Net profit varies between 2,106,729 € and 1,982,928 € for a chilled water unit price between 0.26 and 0.40 €/kg, respectively. The process B2 was not economically feasible if it was considered

an initial purchase price of the exhausted oil greater than 0.2 €/kg (Figure S10). It is possible to observe that the process B1 and B2 were much more advantageous than A1 and A2.

4. Conclusions

In this work, a comparison between the traditional and an innovative process for biodiesel production has been performed through a process analysis by using *SuperPro Designer*[®] software. Traditional treatment includes three main sections: transesterification reaction of oil with methanol in the presence of catalysts, purification of biodiesel and purification of glycerol. In the innovative process, as demonstrate by scientific literature, transesterification reactors have been replaced with hydrodynamic cavitation equipment. Several scenarios have been proposed: traditional treatment with soybean oil (Case Study A1) and waste cooking oil (Case Study B1), and innovative process with soybean oil (Case Study A2) and waste cooking oil (Case Study B2). In the two scenarios that used oil waste a pre-treatment unit is introduced before the transesterification reaction, necessary to remove the suspended solid and prepare the raw material for the subsequent operation of biodiesel production.

Economic feasibility of the treatments has been investigated by LCC analysis considering the mass and energy balances obtained from process analysis. This methodology confirmed to be an excellent tool to identify the most sustainable option for the biodiesel production from an economic point of view. LCC showed that the raw materials, mainly due to the purchase of soybean oil, had the major incidence on operating cost followed by the utilities cost. The chemical cost was reduced by 90% in the Case Study B1 and B2 in which waste cooking oil was used as feedstock. Regarding to the utilities cost, Case Study A1 and A2 had the lower cost, in fact in these the pretreatment section was missing. Hydrodynamic cavitation reduces of about 40% the energy consumption with respect to the traditional process. The total treatment costs were: 833 €/t of oil and 820 €/t of treated oil for Case Study A1 and A2, these values were reduced of the 60% for the Case Study B1 and B2. Life cycle cost analysis allows for an economic assessment of different options, therefore enabling decision-makers to make the best overall decision. In the specific case, any effort to increase the use of waste cooking oil as an alternative to soybean oil is seen as a good opportunity to reduce the process cost for biodiesel production. Hydrodynamic cavitation reduces the energy consumption and further development and improvements can be obtained if pre-treatment unit could be not necessary by using hydrodynamic cavitation. This aspect needs further experimental researches that will be the scope of the future scientific activity, in order to investigate the possibility to reduce the process unit cost and to check the quality of biodiesel according to International Standards.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- Ahmed, S., Hassan, M.H., Kalam, M.A., Rahman, S.M., Abedin, J., Shahir, A., 2014. An experimental investigation of biodiesel production, characterization, engine performance, emission and noise of Brassica juncea methyl ester and its blends. *J. Clean. Prod.* 15, 74–81. <https://doi.org/10.1016/j.jclepro.2014.05.019>.
- Ajanovic, A., 2011. Biofuels versus food production: does biofuels production increase food prices?. *Energy* 36, 2070–2076. <https://doi.org/10.1016/j.energy.2010.05.019>.
- Al-Sakkari, E.G., El-Sheltawy, S.T., Soliman, A., Ismail, I., 2018. Transesterification of Low FFA Waste Vegetable Oil using Homogeneous Base Catalyst for Biodiesel Production: Optimization, Kinetics and Product Stability. *J. Adv. Chem. Sci.* 4, 586–592. <https://doi.org/10.30799/jacs.195.18040305>.
- Argus media. <https://www.argusmedia.com/-/media/Files/sample-reports/argus-sulphuric-acid.ashx?la=en&hash=28D8CDEF485998FED5806750D90A916D3F3DED19>. Accessed 7.07.2020.
- Asif, S., Chuah, L.F., Klemes, J.J., Ahmad, M., Akbar, M.M., Lee, K.T., Fatima, F., 2017. Cleaner production of methyl ester from non-edible feedstock by ultrasonic-assisted cavitation system. *J. Clean. Prod.* 161, 1360–1373. <https://doi.org/10.1016/j.jclepro.2017.02.081>.
- ASTM D6751. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.
- Bagal, M.V., Gogate, P.R., 2014. Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. *Ultrason. Sonochem.* 21, 1–14. <https://doi.org/10.1016/j.ultsonch.2013.07.009>.
- Capocelli, M., Prisciandaro, M., Lancia, A., Musmarra, D., 2013. Modeling of cavitation as an advanced wastewater treatment. *Desalin. Water Treat.* 51, 1609–1614. <https://doi.org/10.1080/19443994.2012.705094>.
- Cassman, K.G., Liska, A.J., 2007. Food and fuel for all: realistic or foolish?. *Biofuels, Bioprod Biorefin* 1, 18–23. <https://doi.org/10.1002/bbb.3>.
- Cavallo M., 2017. Prezzi degli oli vegetali e effetti del prezzo del petrolio. <https://www.pricepedia.it/it/magazine/article/2017/12/20/Effetti-prezzo-petrolio-sui-prezzi-biodiesel/>. Accessed 7.03.2020.
- Chen, H., Xie, B., Ma, J., Chen, Y., 2018. Nox emission of biodiesel compared to diesel: higher or lower?. *Appl. Therm. Eng.* 137, 584–593. <https://doi.org/10.1016/j.applthermaleng.2018.04.022>.
- Chen, J. 2020. Return on Investment (ROI). www.investopedia.com/terms/r/returnoninvestment.asp. Accessed 7.03.2020
- Chipurici, P., Vlaicu, A., Calinescu, I., Vinatoru, M., Vasilescu, M., Ignat, N.D., Mason, T.J., 2019. Ultrasonic, hydrodynamic and microwave biodiesel synthesis – a comparative study for continuous process. *Ultrason. Sonochem.* 57, 38–47. <https://doi.org/10.1016/j.ultsonch.2019.05.011>.
- Chitsaz, H., Omidkhan, M., Ghobadian, B., Ardjmand, M., 2018. Optimization of hydrodynamic cavitation process of biodiesel production by response surface methodology. *J. Environ. Chem. Eng.* 6, 2262–2268. <https://doi.org/10.1016/j.jece.2018.02.047>.
- Chuah, L.F., Klemes, J.J., Yusup, S., Bokhari, A., Akbar, M.M., 2017. A review of cleaner intensification technologies in biodiesel production. *J. Clean. Prod.* 146, 181–193. <https://doi.org/10.1016/j.jclepro.2016.05.017>.
- Chuah, L.F., Yusup, S., AbdAziz, A.R., Bokhari, A., Abdullah, M.Z., 2016. Cleaner production of methylester using waste cooking oil derived from palm olein using a hydrodynamic cavitation reactor. *J. Clean. Prod.* 112, 4505–4514. <https://doi.org/10.1016/j.jclepro.2015.06.112>.
- Correa, D.F., Beyer, H.L., Fargione, J.E., Dill, J.D., Possingham, H.P., Hall, S.R.T., Schenk, P.M., 2019. Towards the implementation of sustainable biofuel production system. *Renew. Sust. Energ. Rev.* 107, 250–263. <https://doi.org/10.1016/j.rser.2019.03.005>.
- Crudo, D., Bosco, V., Cavaglià, G., Grillo, G., Mantegna, S., Cravotto, G., 2016. Biodiesel production process intensification using a rotor-stator type generator of hydrodynamic cavitation. *Ultrason. Sonochem.* 33, 220–225. <https://doi.org/10.1016/j.ultsonch.2016.05.001>.
- Dhillon, B.S., 2017. *Life Cycle Costing for Engineers*. CRC Press, New York.
- Diaz-Chavez, R.A., 2011. Assessing biofuels: Aiming for sustainable development or complying with the market? *Energy Policy* 39 (2011), 5763–5769. <https://doi.org/10.1016/j.enpol.2011.03.054>.
- Dismukes, G.C., Carrieri, D., Bennette, N., Ananyev, G.M., Posewitz, M., 2008. Aquatic phototrophs: efficient alternatives to land-based crops for biofuels. *Curr. Opin. Biotechnol.* 19, 235–240. <https://doi.org/10.1016/j.copbio.2008.05.007>.
- Dovi, V.G., Friedler, F., Huisingh, D., Klemes, J.J., 2009. Cleaner energy for sustainable future. *J. Clean. Prod.* 17, 889–895. <https://doi.org/10.1016/j.ultsonch.2016.05.001>.
- Dular, M., Griessler-Bulc, T., Gutierrez-Aguirre, I., Heath, E., Kosjek, T., Krivograd Klemenčič, A., Oder, M., Petkovšek, M., Rački, M., Ravnikar, N., Šarc, B., Širok, A., Zupanc, M., Žitnik, M., Kompare, B., 2018. Use of hydrodynamic cavitation in (waste)water treatment. *Ultrason. Sonochem.* 29, 577–588. <https://doi.org/10.1016/j.ultsonch.2015.10.010>.
- EN 14214. Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods.
- Freedman, B., Pryde, E.H., Mounts, T.L., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.* 61, 1638–1643. <https://doi.org/10.1007/BF02541649>.
- Gagol, M., Przyjazny, A., Boczkaj, G., 2018. Wastewater treatment by means of advanced oxidation processes based on cavitation – a review. *Chem. Eng. J.* 338, 599–627. <https://doi.org/10.1016/j.cej.2018.01.049>.
- Gayal, D., Pandit, A.B., Rathod, V.K., 2013. Optimization of biodiesel production in a hydrodynamic cavitation reactor using used frying oil. *Ultrason. Sonochem.* 20 (1), 322–328. <https://doi.org/10.1016/j.ultsonch.2012.07.009>.
- Gholami, A., Hajinezhad, A., Pourfayaz, F., Ahmadi, M.H., 2018. The effect of hydrodynamic and ultrasonic cavitation on biodiesel production: an exergy analysis approach. *Energy* 160, 478–489. <https://doi.org/10.1016/j.energy.2018.07.008>.
- Goldemberg, J., 2007. Ethanol for a sustainable energy future. *Science* 315, 808–810. <https://doi.org/10.1126/science.1137013>.
- Gomez, L., Steele-King, C., Mc Queen-Mason, S.J., 2008. Sustainable liquid biofuels from biomass: the writing's on the walls. *New Phytol* 178, 473–485. <https://doi.org/10.1111/j.1469-8137.2008.02422.x>.
- Gude V.G., 2018. *Green Chemistry for Sustainable Biofuel Production* CRC Press.
- Günay, M.E., Türker, L., Tapan, L.A., 2019. Significant parameters and technological advancements in biodiesel production systems. *Fuel* 250, 27–41. <https://doi.org/10.1016/j.fuel.2019.03.147>.
- Hass, M.J., McAloon, A.J., Yee, W.C., Foglia, T.A., 2006. A process model to estimate biodiesel production costs. *Bioresour. Technol.* 97 (4), 671–678. <https://doi.org/10.1016/j.biortech.2005.03.039>.
- Hill, J., Nelson, E., Tilman, D., Polasky, S., Tiffany, D., 2006. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proc. Natl. Acad. Sci. USA* 103, 11206–11210. <https://doi.org/10.1073/pnas.0604600103>.
- Hoekman, S.K., Robbins, C., 2012. Review of the effects of biodiesel on NOx emissions. *Fuel Process. Technol.* 96, 237–249. <https://doi.org/10.1016/j.fuproc.2011.12.036>.
- IEA, International Energy Agency, 2010. Sustainable production of second-generation biofuels, Potential and perspectives in major economies and developing countries. Information paper.
- Innocenzi, V., Prisciandaro, M., Vegliò, F., 2018. Effect of the Hydrodynamic cavitation for the treatment of industrial wastewater. *Chem. Eng. Trans.* 67, 529–534. <https://doi.org/10.3303/CET1867089>.
- Innocenzi, V., Prisciandaro, M., Centofanti, M., Vegliò, F., 2019. Comparison of performances of hydrodynamic cavitation in combined treatments based on hydrid induced advanced Fenton process for degradation of azo-dyes. *J. Env. Chem. Eng.* 7 (2019), 103171. <https://doi.org/10.1016/j.jece.2019.103171>.
- ISO 14044:2006. Environmental management -life cycle assessment- requirements and guidelines, 2006.
- Italian market. <https://www.cometea.it/costa-poco/tariffe-vigore/>. Accessed 7.07.2020.
- Jefferson, M., 2008. Accelerating the transition to sustainable energy systems. *Energy Policy* 36, 4116–4125. <https://doi.org/10.1016/j.enpol.2008.06.020>.
- Ladino, J.A., Herrera, J., Malagon, D., Prisciandaro, M., Piemonte, V., Capocelli, M., 2016. Biodiesel production via hydrodynamic cavitation: numerical study of new geometrical arrangements. *Chem. Eng. Trans.* 50, 319–324. <https://doi.org/10.3303/CET1650054>.
- Maddikeri, G.L., Gogate, P.R., Pandit, A.B., 2014. Intensified synthesis of biodiesel using hydrodynamic cavitation reactors based on the interesterification of waste cooking oil. *Fuel* 137, 285–292. <https://doi.org/10.1016/j.fuel.2014.08.013>.
- Marulanda, V.F., 2012. Biodiesel production by supercritical methanol transesterification: process simulation and potential environmental impact assessment. *J. Clean. Prod.* 33, 109–116. <https://doi.org/10.1016/j.jclepro.2012.04.022>.
- Mata, T., Martins, A., Caetano, N.S., 2010. Microalgae for biodiesel production and other applications: a review. *Renew. Sust. Energ. Rev.* 14, 217–232. <https://doi.org/10.1016/j.rser.2009.07.020>.
- Noureddini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. *J. Am. Oil Chem. Soc.* 74, 1457–1463. <https://doi.org/10.1007/s11746-997-0254-2>.
- Peter, M.S., Timmerhaus, K.D., West, R.E., 2004. *Plant design and economics for chemical engineers*. McGraw-Hill Chemical Engineering Series, New York.
- Piemonte, V., Di Paola, L., Iaquaniello, G., Prisciandaro, M., 2016. Biodiesel production from microalgae: ionic liquid process simulation. *J. Clean. Prod.* 111, 62–68. <https://doi.org/10.1016/j.jclepro.2015.07.089>.

- Qiu, Z., 2010. Intensification of liquid-liquid contacting processes. Doctoral dissertation, University of Kansas.
- Quispe, C.A.G., Coronad, C.J.R., Carvalho Jr., J.A., 2013. Glycerol: production, consumption, prices, characterization and new trends in combustion. *Renew. Sust. Ener. Rev.* 27, 475–493. <https://doi.org/10.1016/j.rser.2013.06.017>.
- Van Gerpen, J., 2005. Biodiesel processing and production. *Fuel Proc. Technol.* 86, 1097–1107. <https://doi.org/10.1016/j.fuproc.2004.11.005>.
- Verma, D., Raj, K., Pal, A., Jain, M., 2016. A critical review on production of biodiesel from various feedstocks. *Int. J. Sci. Res. Innov. Std.* 5 (2), 51–58.
- West, A.H., Posarac, D., Ellis, N., 2008. Assessment of four biodiesel production processes using HYSYS.Plant. *Bioresour. Technol* 99 (14), 6587–6601. <https://doi.org/10.1016/j.biortech.2007.11.046>.
- Wu, Z., Tagliapietra, S., Giraudo, A., Martina, K., Cravotto, G., 2019. Harnessing cavitation effects for green process intensification. *Ultrason. Sonochem.* 52, 530–546. <https://doi.org/10.1016/j.ultsonch.2018.12.032>.
- Zhang, Y., Dubè, M.A., McLean, D.D., Kates, M., 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour. Technol* 89, 1–16. [https://doi.org/10.1016/S0960-8524\(03\)00040-3](https://doi.org/10.1016/S0960-8524(03)00040-3).

Supplementary materials

Figures

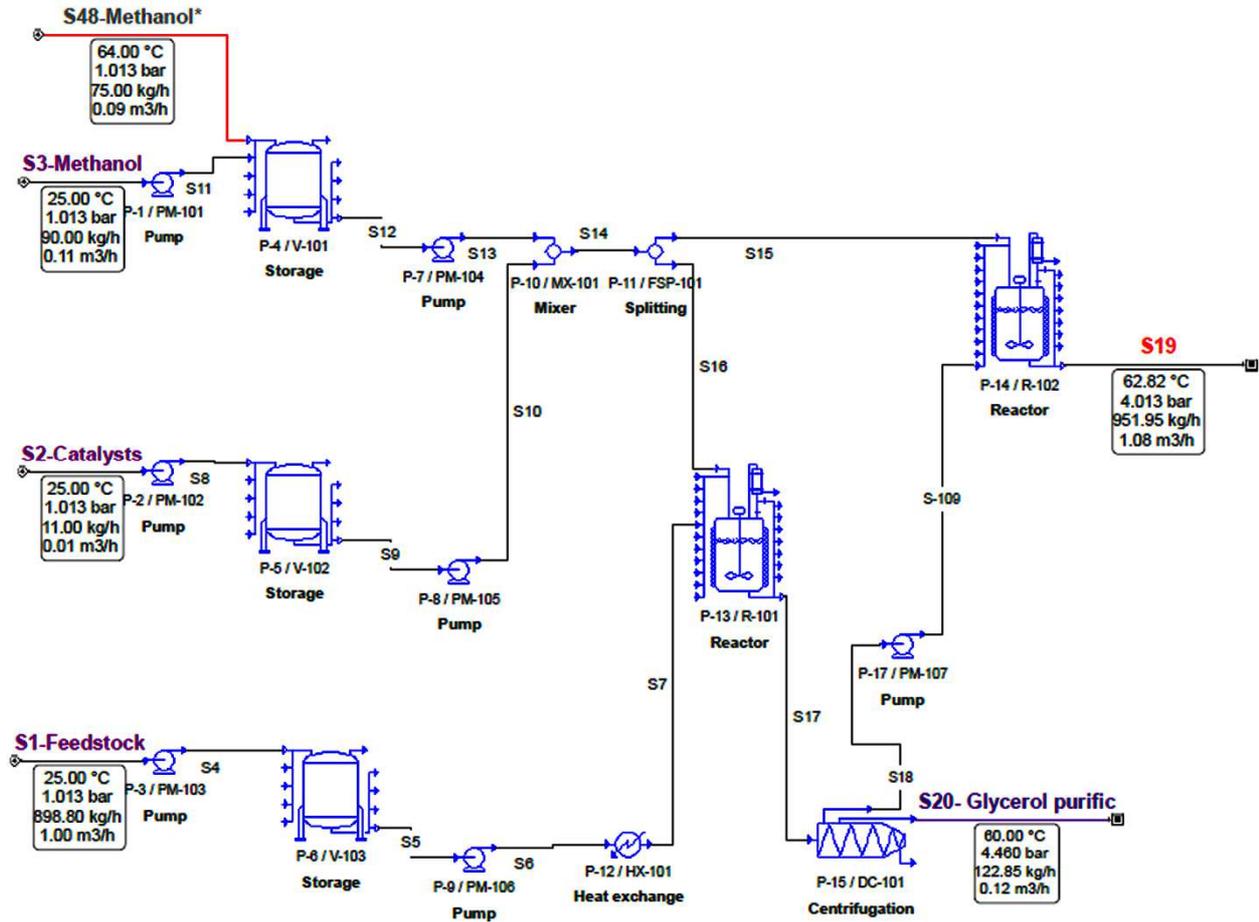


Figure S1: Transesterification reaction section (*methanol from glycerol purification section)

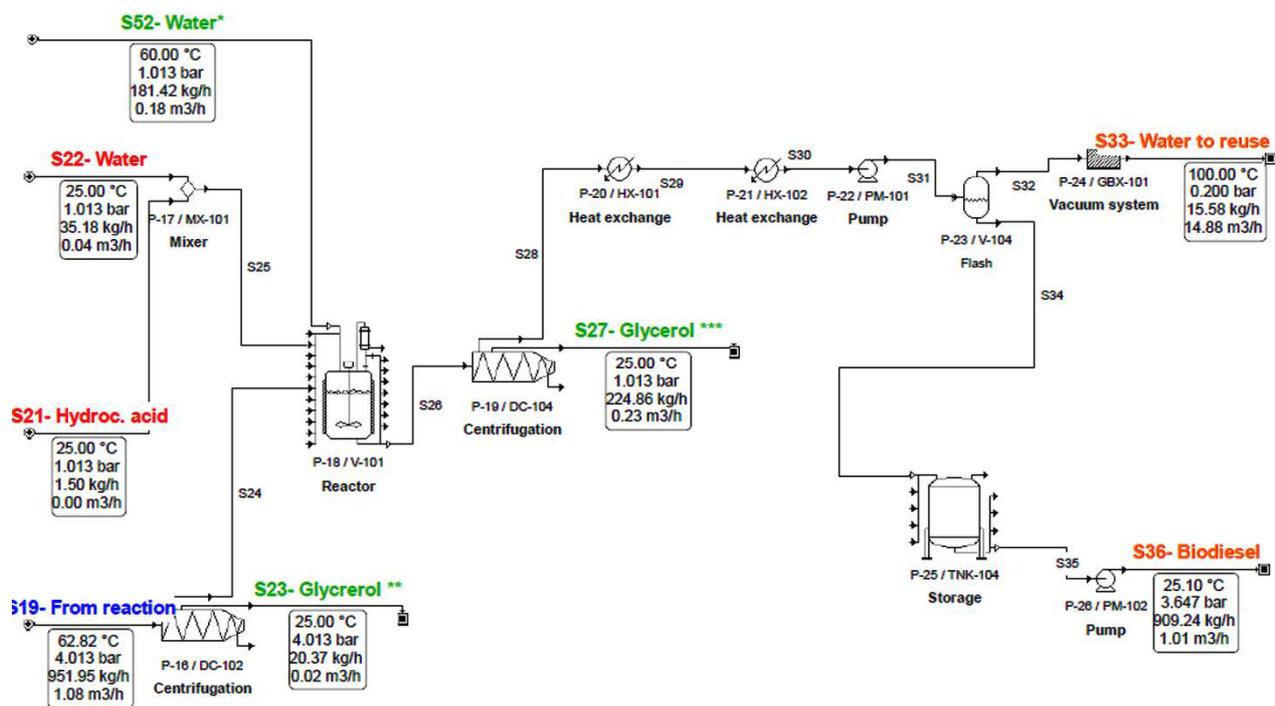


Figure S2: Biodiesel purification section (water* from glycerol purification section, glycerol ** and glycerol *** sent to glycerol purification section, see Fig. S3)

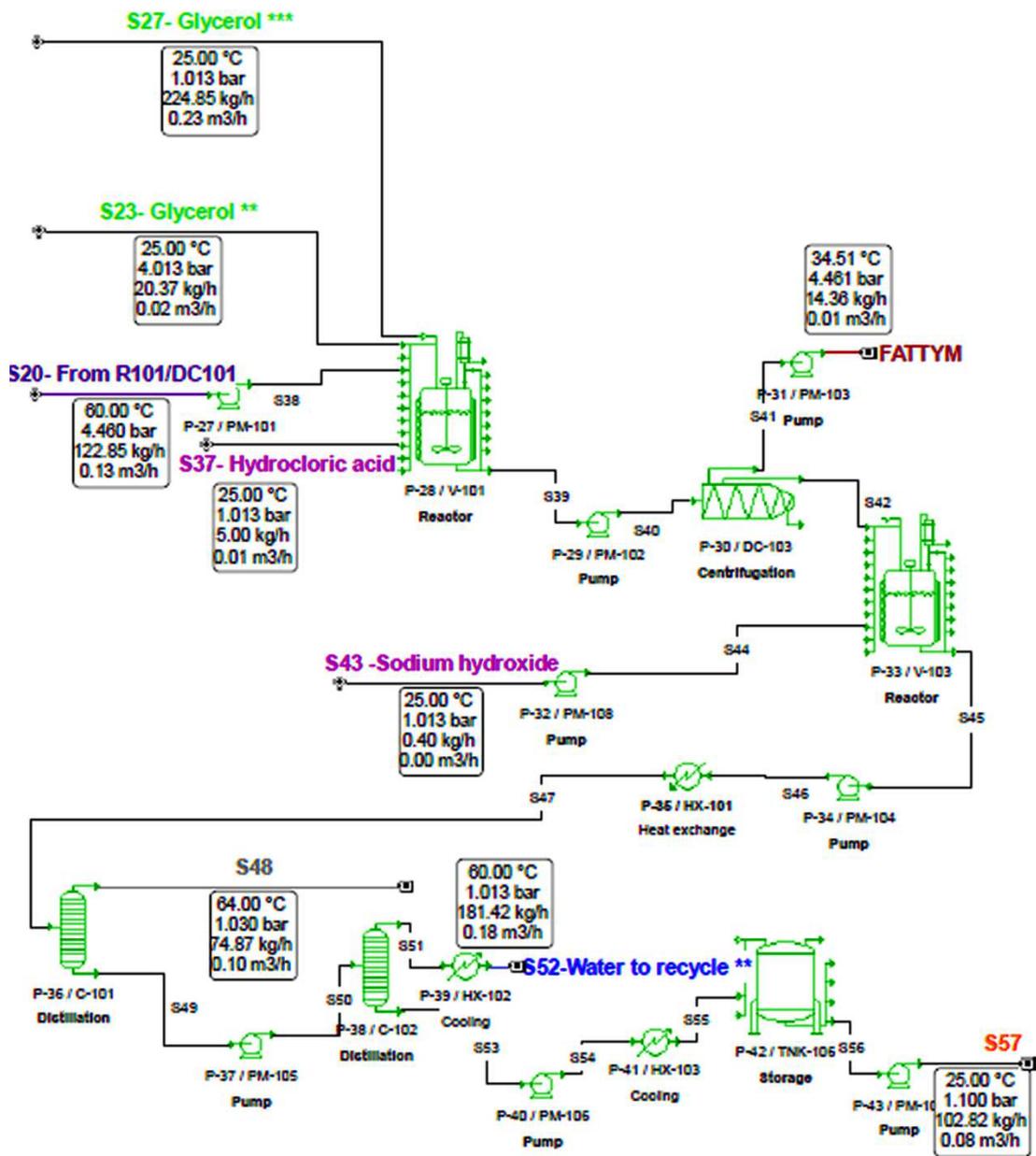


Figure S3: Glycerol purification section (glycerol ** and glycerol *** from biodiesel purification section, see Fig. S2; water to recycle* sent to biodiesel purification section, see Fig. S2; methanol to recycle* sent to transesterification reaction section, see Fig. S1)

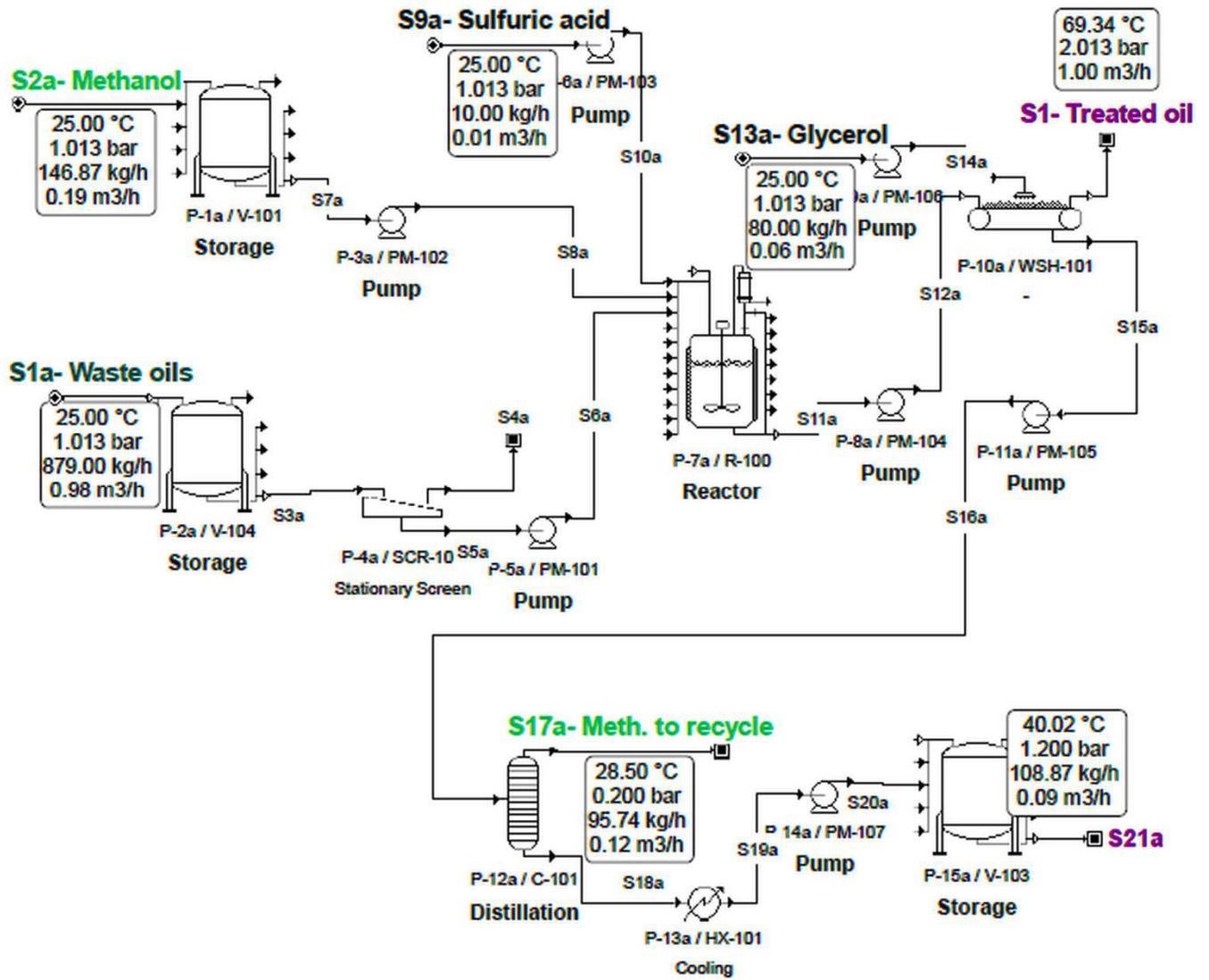


Figure S4: Pre-treatment section for waste cooking oil

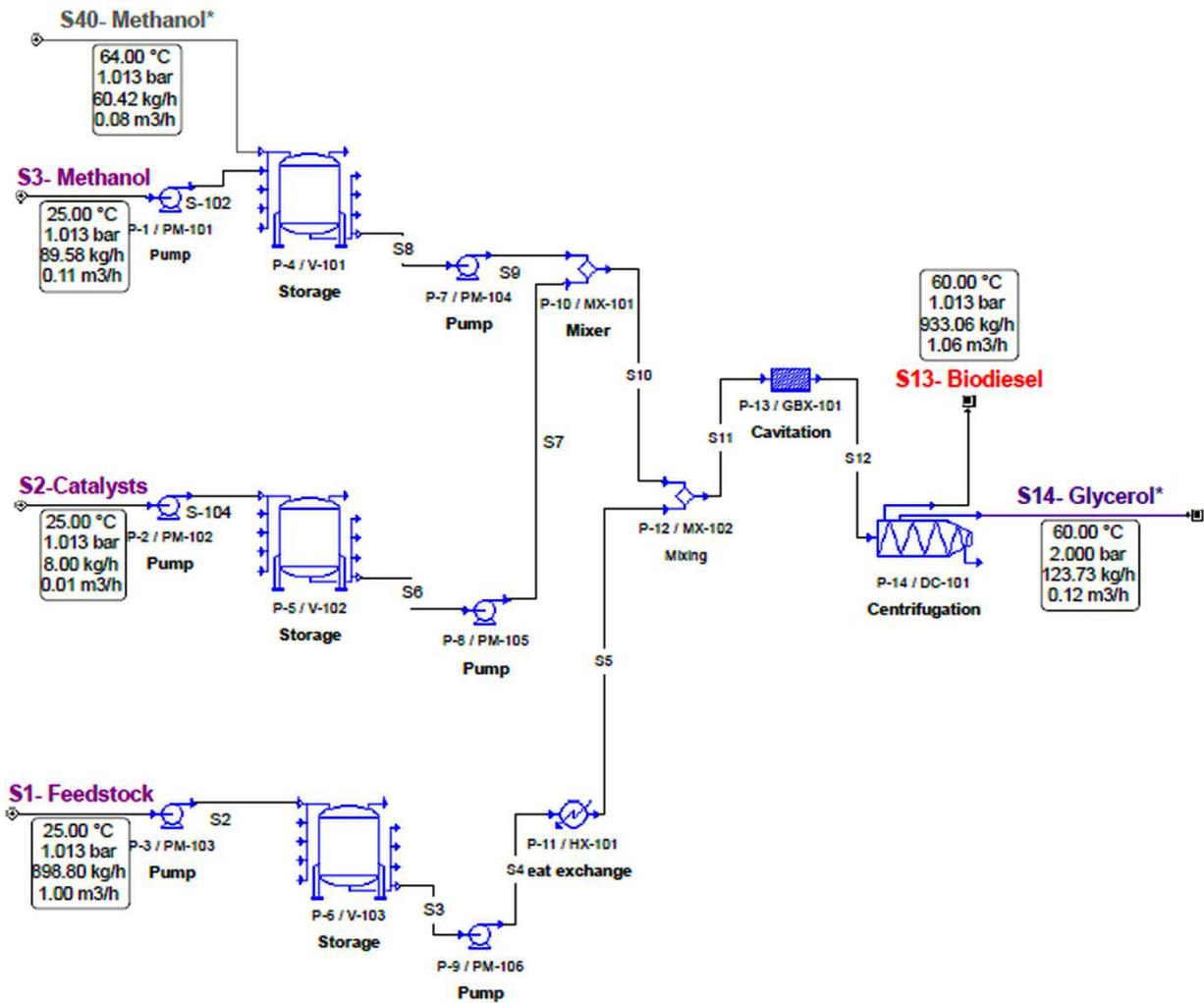


Figure S5: Transesterification reaction section by hydrodynamic cavitation (*methanol from glycerol purification section, see Fig. S7)

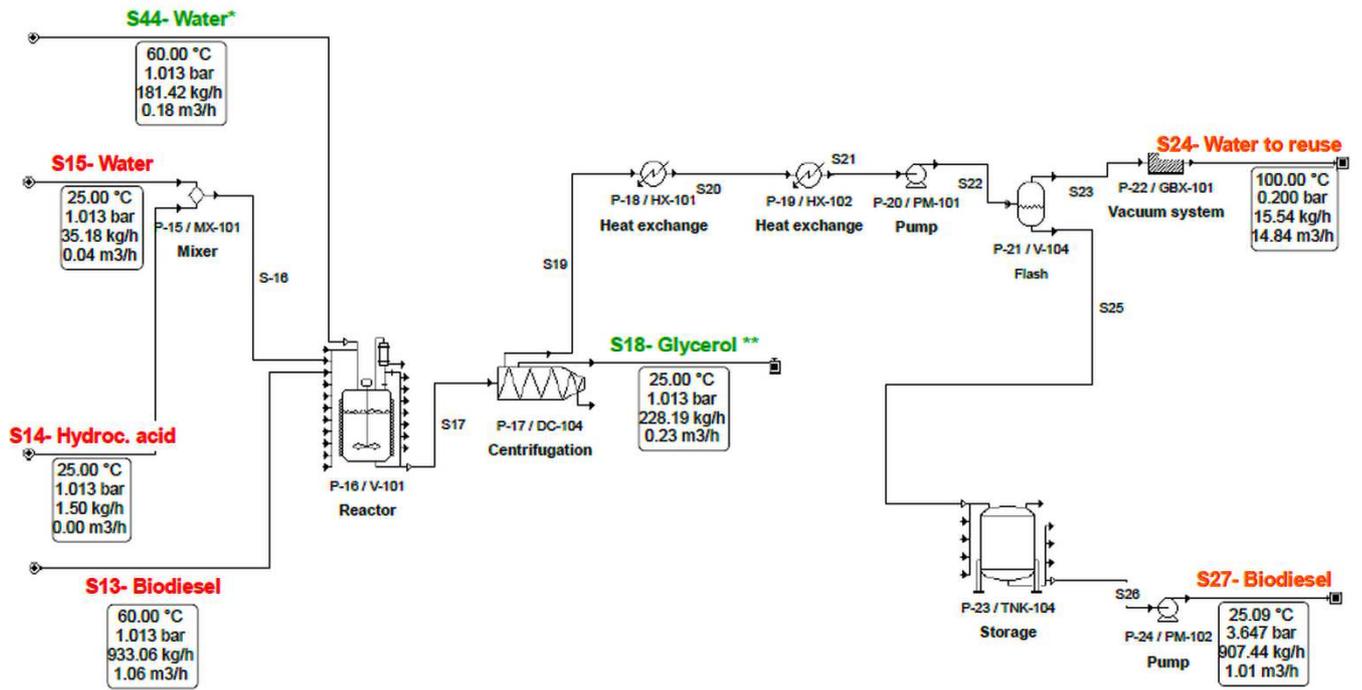


Figure S6: Biodiesel purification section (water* from glycerol purification section, glycerol ** is sent to glycerol purification section)

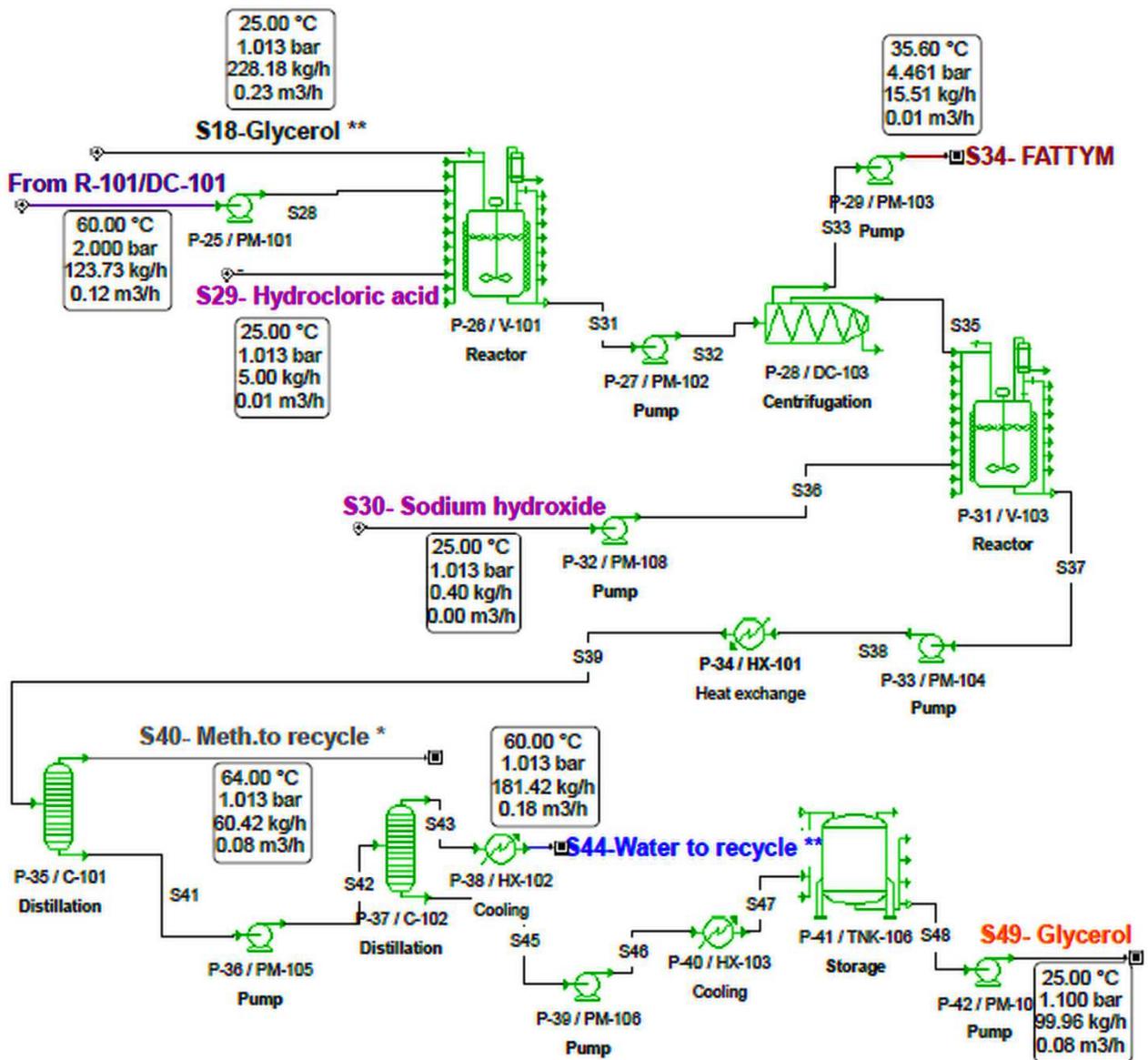


Figure S7: Glycerol purification section (glycerol ** from biodiesel purification section, see Fig.S6; water to recycle* sent to biodiesel purification section, see Fig. S6; methanol to recycle* sent to transesterification reaction section, see Fig.S5)

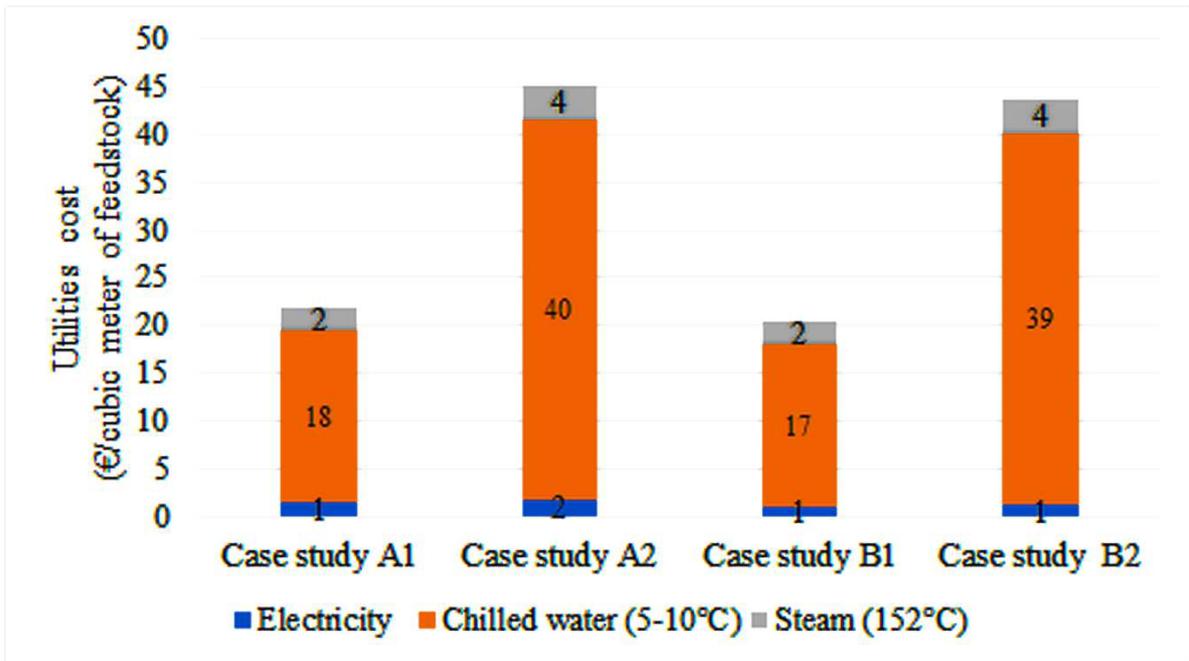


Figure S8: Annualized costs for utilities (€/cubic meter of feedstock) selected process to biodiesel production. Annual plant capacity = 7920 m³ of feedstock, virgin oil (A1 and B1) and exhaust oil (A2 and B2)

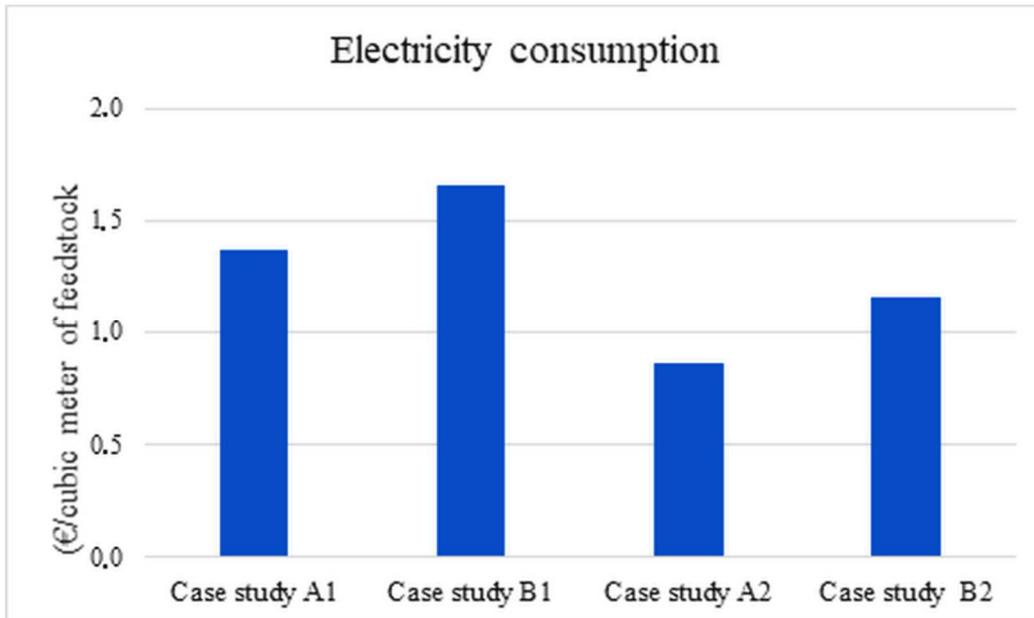


Figure S9: Electricity consumption (€/cubic meter of feedstock) for selected process to biodiesel production. Annual plant capacity = 7920 m³ of feedstock, virgin oil (A1 and A2) and exhaust oil (B1 and B2)

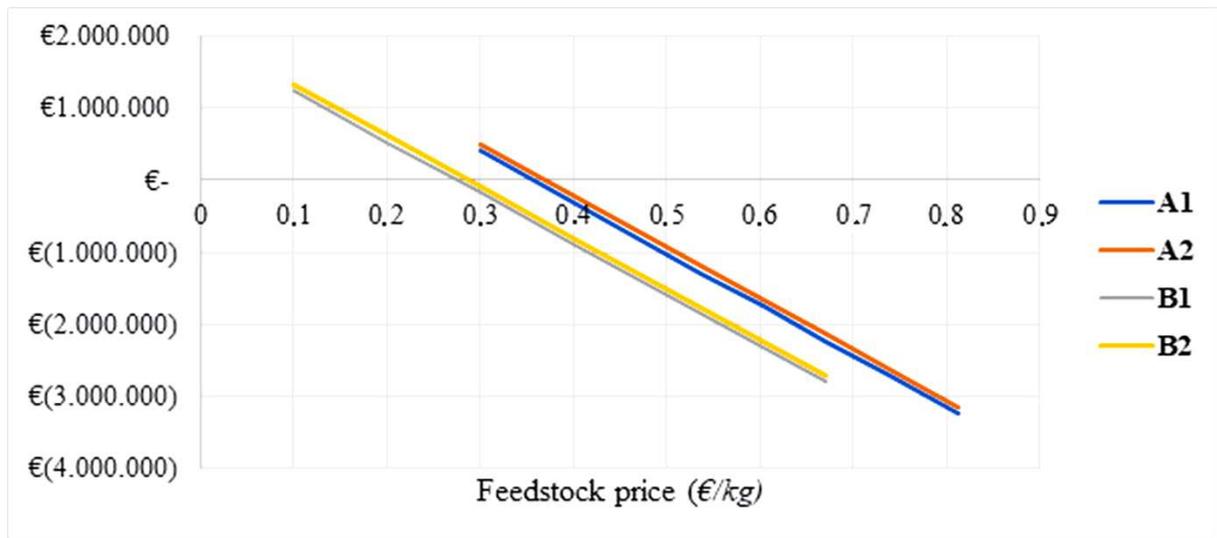


Figure S10: Annual net profit (€) as a function of the initial price of feedstock (€/kg). Virgin oil for A1 and B1; Exhausted oil for A2 and B2.

Tables

Pre-treatment section for Case Study B1 and B2				
Unit	Size (D x H), m	T, °C	P, bar	€
<i>P-1a/V-101</i>	0.44 x 1.33	25°C	1.013	2800
<i>P-2a/V-104</i>	0.77 x 2.31	25°C	1.013	1000
<i>P-4a/SCR-10</i>		25°C	1.013	1000
<i>P-7a/R-100</i>	0.87 x 2.173	70°C	1.013	13000
<i>P-10a/WSH -101</i>		68°C	2.026	10000
<i>P-12a/C-101</i>	0.77 x 2.80 Stages = 7	64.75°C	0.2	30000
<i>P-15a/V-103</i>	0.347 x 1.040	40.02 °C	1.2	700

Transesterification reaction for Case Study A1 and B1				
Unit	Size (D x H, m; A, m²)	T, °C	P, bar	€
<i>P-4/V-101</i>	1.286 x 3.858	42.77	1.013	17300
<i>P-5/V -102</i>	0.946 x 2.839	25.07	1.013	10000
<i>P-6/ V-103</i>	2.569 x 7.706	25.00	1.013	60200
<i>P-12/HX-101</i>	0.11	60.00	4.460	3500
<i>P-13/R101</i>	0.934 x 2.334	64.74	4.460	15300
<i>P-15/ DC-101</i>		64.74	4.460	45000
<i>P-14/R -102</i>	0.903 x 2.257	62.82	4.013	14400

Transesterification reaction for Case Study A2 and B2				
Unit	Size (D x H, m; A, m²)	T, °C	P, bar	€
<i>P-4/V-101</i>	1.246 x 3.738	42.77	1.013	17300
<i>P-5/V -102</i>	0.851 x 2.552	25.07	1.013	10000
<i>P-6/ V-103</i>	2.569 x 7.706	25.00	1.013	60200
<i>P-11/HX-101</i>	0.11	60.00	2.00	3500
<i>P-13/GBX-101</i>		60.00	2.00	20000
<i>P-14/ DC-101</i>		60.00	2.00	45000

Biodiesel purification for Case Study A1 and B1				
Unit	Size (D x H, m; A, m²)	T, °C	P, bar	€
<i>P-16/ DC-102</i>		62.82	4.013	44000
<i>P-18/V-101</i>	1.404 x 0.562	36.00	1.013	6200
<i>P-19/DC - 104</i>		36.00	1.013	45000
<i>P-20/HX-101</i>	0.269	95.42	1.013	6200
<i>P-21/HX-102</i>	0.206	101.67	1.013	5200
<i>P- 23/V-104</i>	0.803 x 3.212	41.24	0.2	20000
<i>P-25/TNK-104</i>	2.380 x 7.141	25	0.2	20900

<i>Biodiesel purification for Case Study A2 and B2</i>				
<i>Unit</i>	<i>Size (D x H, m; A, m²)</i>	<i>T, °C</i>	<i>P, bar</i>	<i>€</i>
<i>P-16/V-101</i>	1.404 x 0.562	36.00	1.013	6200
<i>P-17/DC - 104</i>		36.00	1.013	45000
<i>P-18/HX-101</i>	0.269	95.42	1.013	6200
<i>P-19/HX-102</i>	0.206	101.67	1.013	5200
<i>P- 21/V-104</i>	0.803 x 3.212	41.24	0.2	20000
<i>P-23/TNK-104</i>	2.380 x 7.141	25	0.2	20900

<i>Glycerol purification for Case Study A1 and B1</i>				
<i>Unit</i>	<i>Size (D x H, m; A, m²)</i>	<i>T, °C</i>	<i>P, bar</i>	<i>€</i>
<i>P-28/V-101</i>	0.457 x 1.143	33.3	1.013	8500
<i>P-30/DC-103</i>		33.3	4.46	34000
<i>P-33/V-103</i>	0.452 x 1.131	34.43	1.013	8500
<i>P-36/HX-101</i>	0.30	80.56	4.46	6600
<i>P-36/C-101</i>	0.60 x 4.800	80.56	0.20	52500
<i>P-38/C-102</i>	0.60 x 4.800	100.50	1.013	52500
<i>P-39/HX-102</i>	0.08			3400
<i>P-41/HX-103</i>	0.42	25	4.46	8200
<i>P-42/TNK-106</i>	1.818 x 5.455	25	1.013	24300

<i>Glycerol purification for Case Study A2 and B2</i>				
<i>Unit</i>	<i>Size (D x H, m; A, m²)</i>	<i>T, °C</i>	<i>P, bar</i>	<i>€</i>
<i>P-26/V-101</i>	0.45 x 1.124	33.3	1.013	8500
<i>P-28/DC-103</i>		33.3	4.46	34000
<i>P-31/V-103</i>	0.44x 1.109	34.43	1.013	8500
<i>P-34/HX-101</i>	0.26	80.56	4.46	6100
<i>P-35/C-101</i>	0.60 x 4.800	80.56	0.20	52500
<i>P-37/C-102</i>	0.60 x 4.800	100.50	1.013	52500
<i>P-38/HX-102</i>	0.08			3400
<i>P-40/HX-103</i>	0.42	25	4.46	8200
<i>P-41/TNK-106</i>	1.803 x 5.410	25	1.013	24300

Table S1: List and quotation of the main equipment

	Price (€/kg)	Source
<i>Virgin oil</i>	0.67	(Zhang et al., 2003)
<i>Exhaust oil</i>	0.00	Assumption
<i>Methanol</i>	0.37	(Zhang et al., 2003)
<i>Water</i>	0.0007	(Italian market)
<i>Hydrochloric acid (37%)</i>	0.17	(Zhang et al., 2003)
<i>Sodium hydroxide</i>	0.91	(Zhang et al., 2003)
<i>Sulfuric acid (96%)</i>	0.07	(Argus media)

Table S2: Prices of chemicals used for the LCC analysis

	Price (€/unit)	Unit	Note
<i>Electricity</i>	0.15	kWh	Italian market. Average (day/night) electricity price
<i>Chilled water</i>	0.33	t	SuperPro Database
<i>Steam</i>	10	t	SuperPro Database
<i>Disposal cost</i>	0.15	kg	Assumption Dangerous material

Table S3: Utilities prices and costs of waste disposal and transport