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**DOI:**

[10.1016/j.jclepro.2019.118073](https://doi.org/10.1016/j.jclepro.2019.118073)

**Document Version**

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

**Citation for published version (APA):**

Dimian, A. C., & Kiss, A. A. (2019). Eco-efficient processes for biodiesel production from waste lipids. *Journal of Cleaner Production*, 239, [118073]. <https://doi.org/10.1016/j.jclepro.2019.118073>

**Published in:**

Journal of Cleaner Production

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# Eco-efficient processes for biodiesel production from waste lipids

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## Keywords

FFA treatment; green catalysis; integrated design; process intensification; reactive distillation

## Highlights

- New integrated processes developed for biodiesel production from waste fatty sources
- Effective combination of esterification and transesterification by reactive separations
- Glycerolysis of high FFA feedstock coupled with hetero-catalyzed transesterification

## Abstract

The paper proposes innovative eco-efficient processes for converting waste lipid feedstock with up to 35% free fatty acids into biodiesel. Free fatty acids pre-treatment is a key issue, which can be handled by esterification with methanol or glycerol, using hetero- or homogeneous catalyst. The integration with the transesterification stage is possible using methods based on process intensification and heterogeneous catalysis. Three integrated continuous processes are investigated. The first performs the esterification with methanol by reactive absorption and superacid solid catalyst, followed by transesterification by reactive distillation with alkali catalyst. The second method applies the esterification with glycerol at high temperature, coupled with transesterification by heterogeneous catalyst in a variable residence-time plug-flow reactor. The third alternative replaces the second reaction stage with vacuum distillation. In all cases, biodiesel fulfills the specifications of D6751 and EN14214 norms. This result is obtained by kinetic simulation of reactors including free fatty acids esterification and glycerides transesterification. A techno-economic analysis pinpoints the pros and cons of each process. The first process is suited for low free fatty acids content, as used cooking oils. The second and third processes can be applied for higher content of free fatty acids, such as animal fats and greases. Particularly the third process can deliver biodiesel of highest quality, conforming to the cold soak filtration test.

## 1 **1. Introduction**

2 Biodiesel keeps a prominent place among the renewable biofuels, being a key product of  
3 biorefineries based on the oleo-chemicals platform (Kiss et al., 2016). According to UFOP,  
4 the global biodiesel production reached about 34 million tons in 2016. European Union is the  
5 largest biodiesel producer with 12.6 million tons (37% of total), having key producers such as  
6 Germany (3.1), France (2.0), Spain (1.6), The Netherlands (1.2) and Italy (1). United States,  
7 Brazil and Argentina produced 6.2, 3.3 and 2.7 million tons, respectively. Asia produced 5.4  
8 million tons, with key contributors such as Indonesia (3.15), Thailand (1.16) and Singapore  
9 (1). China had a modest production of only 0.44 million tons, but it has a very large potential.  
10 Biodiesel includes fatty acid methyl esters (FAME) and hydrogenated vegetable oil (HVO).  
11 The main resources today are crops of vegetable oils, from which palm oil (37%), soybean oil  
12 (27%) and rapeseed oil (20%), followed by used cooking oils (UCO) (10%), animal fat (7%)  
13 and others (5%). Rapeseed is about 48% from feedstock, but the share of UCO and fats raises  
14 to 18%. In Germany the use of UCO for biodiesel in 2017 was 1.5 million tons (about half of  
15 biodiesel production), which is more than the domestic available rapeseed oil (UFOP, 2017).  
16 This work focuses on the valorization of UCO together with waste fats resulting from other  
17 food processing, such as poultry and animal fat (tallow, lard). There are several major reasons  
18 to promote UCO as a key resource that goes beyond its today share: 1) it avoids pollution of  
19 soil and water by wastes that spoil the environment; 2) it is sustained by a positive public  
20 opinion of clean production, converting waste into products; and 3) it avoids the food vs fuel  
21 controversy. As low-cost feedstock (about half the price of original oil), waste lipids are very  
22 economically attractive and more sustainable (Macombe et al., 2013). The problem with using  
23 UCO and fats as feedstock is that they have various origin and composition, contain variable  
24 fraction of free fatty acids (FFA) and contaminants. Processing waste feedstock into biodiesel  
25 requires effective pre-treatment methods that are eco-efficient and preserve the environment  
26 against pollution. Employing strong acids and bases should be limited or avoided, while the  
27 substantial amounts of water used should be recycled. Using solid catalysts for reactions and  
28 adsorption media for purification may greatly simplify the flowsheet and save energy. Process  
29 intensification techniques (Chuah et al., 2017) are also useful and should be considered for a  
30 cleaner production of biodiesel, for example by reactive separations (Kiss, 2014).  
31 Integrating new methods in the design of more eco-efficient processes for converting waste  
32 lipids into biodiesel is the goal of this paper. A plant capacity of 20 ktpy is considered, and an  
33 upper limit of 15 %wt FFA is assumed when treating UCO, while max. 35 %wt FFA is used  
34 when dealing with animal fats or trap (brown) grease.

1 Many papers explored the use of UCO, animal fats and waste lipids for manufacturing  
2 biodiesel, most of them handling physical and chemical aspects regarding the feedstock  
3 pretreatment and the conversion to biodiesel by various means. Comprehensive papers and  
4 reviews are available, covering topics such as: technical aspects of production and analysis of  
5 biodiesel from UCO (Enweremadu and Mbarawa, 2009); technologies for UCO conversion  
6 (Math et al., 2010); biodiesel production, properties, and flexible feedstock (Moser, 2009);  
7 biodiesel production from high FFA feedstock (Atadashi et al., 2012); conversion of  
8 slaughterhouse and poultry farm animal fats and wastes to biodiesel (Chakraborty et al.,  
9 2014); intensification approaches for biodiesel synthesis from UCO (Maddikeri et al., 2012);  
10 sustainable biodiesel production by waste-oil biodiesel utilization (Hajjari et al., 2017); and a  
11 handbook on biodiesel (Knothe et al., 2010).

12 From the large number of papers, only one refers directly to the full process design and  
13 simulation. Zhang et al. (2003a, 2003b) considered a plant capacity of 8,000 tpa with  
14 feedstock containing 6% FFA. The paper claimed that the *acid-catalyzed* transesterification  
15 using UCO proved to be techno-economically viable, but to the best of our knowledge this  
16 has not happened so far in the industrial practice, where the alkali-based process remains the  
17 most employed. The paper also contains several drawbacks regarding the technology and  
18 computer simulation. The plant has a simple black-box unit hence the biodiesel specifications  
19 cannot be guaranteed. The plant is designed with unreacted oil recycle, involving deep  
20 vacuum distillation of FAME operating in unrealistic conditions.

21 The waste lipids (WL) feedstock for biodiesel can be characterized by the *fatty acid profiles*.  
22 Table 1 displays typical compositions for UCO, tallow, poultry fat and lard, as well as for  
23 palm and sunflower oils whose blends are used the most used as cooking oils. The  
24 composition is lumped in five categories: C16:0 (palmitic), C18:0 (stearic), C18:1 (oleic),  
25 C18:2 (linoleic), and C18:3 (linolenic). The palmitic category includes all saturated species up  
26 to C16:0, while oleic category includes all single double bond species. The applicability of  
27 feedstock for biodiesel manufacturing may be characterized by USI index (unsaturated to  
28 saturated fatty acids ratio). Feedstock with high content in saturated fatty acids (palm and  
29 tallow) has USI close to 1. Hence the cetane number (which reflects the combustion properties  
30 including NO<sub>x</sub>, PM, HC and CO) has high values, but problems may rise during the cold  
31 weather. Sunflower oil has most unsaturated TG and is therefore better suited for colder  
32 weather, but this profile is unfavorable from the viewpoint of oxidation stability and storage.

33 The FFA content of waste lipids is very variable, and a distinction may be made between UCO and  
34 animal fats. UCO has an FFA content of 2-10%, the lower bound being typical for countries with

1 rigorous public health rules, e.g. 3% in The Netherlands (Venkatesh et al., 2014). For animal fats  
2 and trap grease residues, the FFA content is typically larger than 15 %wt (Tu et al., 2017). This  
3 large variation is a challenge when designing biodiesel plants processing waste lipids, being in  
4 contrast with processes handling vegetable crops oils of almost constant quality. Also, during the  
5 cooking process the oil composition suffers a significant but unpredictable variation because of  
6 degradation reactions. In general, the saturation degree increases, which affects negatively the  
7 viscosity (Knothe and Steidley, 2009). Systematic testing of the feedstock is needed before FFA  
8 treatment. The plant should have certain flexibility in terms of FFA processing, but also in the  
9 transesterification stage. Alternatively, in view of maintaining the operation conditions, blends of  
10 feedstock may be envisaged (waste fats and vegetable oils), adapted to local market conditions.  
11 Based on the fatty acid profile, a *design of biodiesel properties* may be undertaken for a specific  
12 application by considering only five fundamental fatty acids, as indicated in Table 1 (Knothe,  
13 2008, 2010). The cetane number varies in the series of C18 FAME as following: stearate (101),  
14 oleate (56), linoleate (38) and linolenate (22.7). Hence the interest is maximizing the content in  
15 saturated esters (which also improve stability to oxidation). But in case of the melting point (which  
16 translates into cold weather properties) the C18 variation is: 39, -19.5, -35 and -52 °C. Hence more  
17 unsaturated esters are preferred for cold weather usage. Design of biodiesel properties should find  
18 the best compromise, and this is the case when the feedstock has 60-70 % wt oleic acid esters.

19

## 20 **2. Approach and originality**

21 This paper provides innovative conceptual design of integrated processes for converting waste  
22 lipid feedstock into biodiesel. A plant capacity of 20 ktpy is considered. The feedstock can be  
23 UCO with an upper limit of 15 %wt FFA, as well as animal fats, oils and (trap) greases  
24 (FOG), while max. 35 %wt FFA is assumed.

25 A key issue is the FFA pre-treatment stage. This is handled by esterification with methanol or  
26 glycerol. It is shown that the esterification with methanol by reactive absorption using  
27 superacid solid catalyst (ion-exchange resin Amberlyst-15, thermally stable up to 150°C) is  
28 particularly effective offering flexibility up to FFA 15 %wt just by adjusting the operation  
29 conditions (e.g. amount of methanol or column's pressure). A second alternative, which can  
30 be applied for handling FOG feedstock, is the autocatalytic esterification with glycerol at high  
31 temperature, compatible the transesterification employing solid base catalysts.

32 The process synthesis approach used in this work handles the integration of three stages: pre-  
33 treatment, transesterification and post-treatment. Using a suitable catalyst plays an essential  
34 role in technology. The final goal of the design is the fulfillment of quality specifications of

1 biodiesel, as defined by the norms EN14214 and ASTM D6751, which was upgraded in 2008  
2 to include the cold soak filtration test (Van Gerpen, 2017a).

3 A distinct feature of this paper is the use of detailed kinetic modeling for simulating chemical  
4 reactors, both for FFA esterification and transesterification, such that the final product  
5 respects the quality specifications required by the norms. This approach regards particularly  
6 the “bound-glycerol” that includes residual TG, DG, MG, and free glycerol, as well as the  
7 “acid value” due to the residual FFA. For this reason, the process design adopts as general  
8 strategy a two-stage transesterification with intermediate glycerol removal which guarantees  
9 the fulfillment of specifications. When applying only one-stage transesterification - by  
10 heterogeneous catalyst and very high conversion - the vacuum distillation is applied in view  
11 of obtaining high-quality biodiesel that satisfies the cold-soak test. The selection of the  
12 operation parameters (pressure, temperature profile, reflux ratio, bottom flowrate and  
13 composition) and the column’s design considers the risk of product degradation and the use of  
14 an appropriate utility for heating.

15 Several design alternatives emerge that are discerned both by the FFA pre-treatment method  
16 as well as by the catalyst employed in the transesterification stage. The flowsheets of these  
17 process alternatives are original, and to the best of our knowledge have not been proposed so  
18 far in the literature.

19 **Process 1** uses homogeneous alkali catalyst (current standard) for transesterification, with  
20 intermediate glycerol removal that ensures the biodiesel specifications at the reaction stage.  
21 The best FFA pre-treatment method is esterification with methanol in a continuous reactive  
22 absorption setup using a superacid ion-exchange catalyst. The transesterification stage uses a  
23 CSTR-PFR tandem, followed by a reactive distillation (RD) for the second stage.

24 **Process 2** employs as FFA pre-treatment stage the esterification with glycerol at 250 °C. This  
25 approach allows direct coupling with transesterification using a heterogeneous base catalyst at  
26 high temperature. An innovative reactor design offers a large flexibility in operation, by a  
27 variable-time construction and easy catalyst replacement. The result is a compact equipment  
28 and energy efficient process.

29 **Process 3** is based on similar conceptual ideas, but it uses separation by vacuum distillation  
30 for recycling unconverted material and delivering high-quality product. By suppressing the  
31 second trans-esterification stage, the flowsheet becomes even simpler. Attention is given to  
32 the simulation and design of the biodiesel distillation, by respecting the temperature constraint  
33 of the reboiler bellow 280 °C. The need of recycling substantial amounts of FAME and mono-

1 glycerides is highlighted. This process has a good potential for application dealing with high  
2 FFA feedstock.

3 With respect to post-treatment, this work highlights the post-processing method suitable for  
4 each alternative. Water washing is favored when dealing with alkali catalysis, while dry wash  
5 treating of biodiesel by heterogeneous catalysis is perfectly suitable. In addition, the glycerol  
6 co-product is of high purity. The economic evaluation indicates that the capital costs are  
7 equivalent for the three processes, although for different reasons. The energy requirements  
8 and CO<sub>2</sub> emissions are low. Suitable recommendations are formulated for process selection.

9

### 10 **3. Process design and simulation**

11 This section provides details about the property models required for simulation, the reaction  
12 schemes and kinetics, as well as characteristics of the feedstock (waste lipids).

13

#### 14 **3.1 Physical property models**

15 The physical properties required for simulation and the binary interaction parameters were  
16 available for pure components in the Aspen Plus v9.0 database, while the other interaction  
17 parameters were estimated using UNIFAC – Dortmund modified group contribution method  
18 (Gmehling et al., 2002). In the case of methanol-water separation there is only one liquid  
19 (aqueous) phase possible, while for the liquid-liquid separation by decanting, the UNIFAC-  
20 Dortmund model was applied.

21

#### 22 **3.2 Reaction scheme and kinetics**

23 This section provides the reaction schemes for the FFA pre-treatment and transesterification  
24 of triglycerides, along with the pseudo-homogeneous and heterogeneous kinetics.

25

##### 26 **3.2.1 FFA pre-treatment**

27 The free fatty acids (FFA) pretreatment step relies on two methods. The first consists of  
28 esterification with methanol:



30 The acid-type catalyst may be a mineral acid, mostly sulfuric acid, or heterogeneous, usually  
31 ion-exchange resins. This topic was recently analysed by Chai et al. (2014) including kinetic  
32 aspects. In this study we prefer the use of heterogeneous catalysis. Kinetic data for using  
33 Amberlyst 15 resin were published by Steingeweg and Gmehling (2003). They studied this

1 reaction in a laboratory column equipped with structured packing Katapak-SP. The model  
2 considers the reversible reaction:



4 Two kinetic models were proposed: pseudo-homogeneous and LHHW heterogeneous. The  
5 rate equation for the pseudo-homogeneous model is:

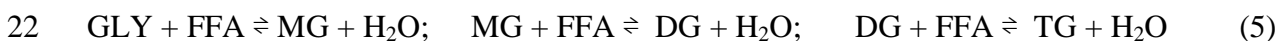
$$6 r_{Ac} = -dN_{Ac}/dt = m_{cat} \times (k_1 a_{Ac} a_{Al} - k_{-1} a_E a_W) \quad (3)$$

7 The concentrations are expressed in terms of activities, which in turn are given by the molar  
8 fractions multiplied by activity coefficients. The LHHW model considers the adsorption of  
9 different species on heterogeneous catalyst surface. In this case Steinigeweg and Gmehling  
10 (2003) demonstrate that only the sorbtion of water is of significance. Accordingly, the well-  
11 known LHHW rate expression can be simplified to the following equation:

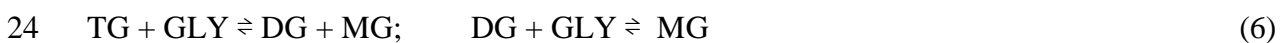
$$12 r_{Ac} = -dN_{Ac}/dt = m_{cat} \times (k_1 a_{Ac} a_{Al} / (K_S a_W)^2 - k_{-1} a_E / (K_S a_W)) \quad (4)$$

13 in which  $K_S$  is a sorbtion constant. Table 2 presents the parameters of the model. According  
14 the above reference the homogeneous model gives a slight overestimation of the reaction rate  
15 by 10-15%. Note that Aspen Plus cannot consider LHHW kinetics in a reactive distillation  
16 process but can well include power-law kinetics. Accordingly, equation (4) may be applied.  
17 However, the initial feed should contain some water to avoid numerical problems because of  
18 the hyperbolic form of the equation (4).

19 The second FFA esterification method employs glycerol, this time a heavy alcohol. The FFAs  
20 are converted in glycerides that join the flow sent to transesterification. First MGs are formed,  
21 further converted to di- and triglycerides:



23 After water removal by evaporation, the TG and DG are converted back to MG:



25 The reaction can be catalyzed by strong mineral acids, as well as by some heavy metal salts.  
26 Recently, Tu et al. (2017) found that at temperatures over 200 °C the reaction becomes  
27 autocatalytic. They reported first-order kinetics with  $k=1.445 \text{ h}^{-1}$  at 230 °C and activation  
28 energy  $E_a=69.14 \text{ kJ/mol}$ . Accordingly, the pre-exponential factor is  $k=2.18 \times 10^7 \text{ h}^{-1}$ .

29

### 30 **3.2.2 Transesterification of triglycerides**

31 The chemistry of the transesterification with methanol involves several reactions that convert  
32 triglycerides (TG), diglycerides (DG), and monoglycerides (MG) to fatty acid methyl esters  
33 (FAME) and glycerol (GLY), as follows:





4

5 The free fatty acids (FFA) pretreatment step relies on the esterification with methanol:



7 The reaction medium by transesterification is actually a very fine dispersion consisting of  
 8 two-liquid phases. Because of vigorous agitation in the first minutes of contact and the  
 9 formation of tension-active species (mono- and di-glycerides), the liquid mixture may be  
 10 considered as pseudo-homogeneous emulsion. Therefore, the mass transfer did not influence  
 11 the process kinetics. Moreover, the kinetic data used in this work (Bambase et al., 2007;  
 12 Allain et al., 2016) were obtained by using this realistic assumption. For the same reasons, the  
 13 reactive distillation columns are simulated by using VLE and not VLLE. Property constant  
 14 estimation system (PCES) was used to generate the parameters of the thermophysical models  
 15 of tri- di- and mono-glycerides that were missing from the Aspen Plus database.

16

17 ***Kinetics for transesterification by homogeneous catalysis.*** For the homogeneous catalysis it  
 18 is appropriate to apply the detailed kinetic model of Bambase et al. (2007) who studied the  
 19 trans-esterification of sunflower with NaOH catalyst 0.5 %wt/oil. The kinetic parameters are  
 20 summarized in Table 3. The equilibrium constants indicate that the first and third reactions are  
 21 strongly oriented to the formation of products, while for the second reaction is more balanced,  
 22 with the result of controlling the final biodiesel composition.

23 A question may rise if the above model is compatible with the fatty acid profiles of the UCO  
 24 and fats and if conceivable differences in the kinetic behavior of species would affect the  
 25 results. This issue was found indeed to be important in heterogeneous catalysis (Dimian et al.,  
 26 2010) resulting in significant difference in the triglycerides conversion and the product  
 27 specifications (Dimian and Rothenberg, 2016). However, when dealing with homogeneous  
 28 catalysis in well-mixed reactors such differences are improbable, since the steric and bond  
 29 effects should not play a role. The composition of initial oil and final product are identical in  
 30 term of fatty acid composition, which is a good indication that there are no noteworthy  
 31 differences in the reaction rate of species (Chang and Liu, 2010).

32 A key merit of the kinetic model from Bambase et al. (2007) is the ability of predicting the  
 33 formation of a significant amount of MG vs DG in the final product, as indicated by the

1 EN14214 norm (0.80 vs. 0.20 %wt). Other models that might be employed (Nurreddini, 1997;  
2 Vincente, 2005) have the drawback of predicting the formation of more DG than MG. Likozar  
3 and Levec (2014) developed a comprehensive analysis of transesterification by alkali catalyst,  
4 and determined by regression the kinetic parameters (pre-exponential factors and activation  
5 energy) of the individual fatty acid species involved (e.g. stearic, oleic, linoleic, linolenic).  
6 When combined with the *fragment-based approach* for estimating thermophysical properties  
7 of fatty acids and derived molecules (Zong et al., 2010), this method would allow the  
8 prediction of key biodiesel properties (density, viscosity, flash point, cetane number) based on  
9 the initial feedstock composition only (Chang and Liu, 2010). However, the kinetic  
10 parameters listed by Likozar and Levec (2014) have not been validated against other  
11 experimental researches. In addition, the kinetic modelling based on species raises another  
12 problem, the property estimation of so many molecular species. Thus, the model of Bambase  
13 et al. (2007) is considered suitable for designing a reaction system that can realistically  
14 achieve the required product quality.

15  
16 ***Kinetics for transesterification by heterogeneous catalysis.*** This work considers the zinc  
17 aluminate catalyst developed by the French company AXENS. Table 4 gives the kinetic  
18 parameters adapted from Allain et al. (2016). A correction was necessary, since the industrial  
19 reactors employ cylindrical pellets of 3.0 mm, while the lab reactor used grains of 0.4 mm. It  
20 was assumed considering an overall efficiency of 0.25 that multiplies the pre-exponential  
21 factors of the original rate equations. The activation energy is set equal for forward and back  
22 reactions, as the global thermal effect of reaction is practically zero. This approach was  
23 founded suitable for describing the behavior of industrial reactors dealing with rapeseed-oil  
24 type feedstock (Dimian and Rothenberg, 2016). The detailed kinetic models presented have  
25 been implemented in Aspen Plus v9.0 by taking the oleic acid as base molecule for the  
26 glycerides and the fatty acid methyl ester (FAME). Property constant estimation system  
27 (PCES) was used to generate the parameters of the thermo-physical models of the tri- di- and  
28 mono-glycerides that were missing from the Aspen Plus database.

29

### 30 **3.3 Technology issues**

31 Figure 1 displays a block diagram for manufacturing biodiesel from waste lipids. After  
32 washing with hot water to remove soluble impurities and filtering, the feedstock is submitted  
33 to degumming with hydrophosphoric acid. Additional treatment with chelating agents or  
34 adsorbents may be considered for feedstock containing long-chain triglycerides over C20. The

1 feedstock is then sent to storage in view of blending and FFA treatment. The processing steps  
 2 include free fatty acid (FFA) pre-treatment, transesterification and post-treatment, briefly  
 3 examined. This section handles also constraints and design decisions that have been  
 4 considered for developing the integrated processes proposed in this paper.

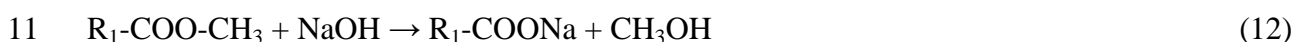
5

### 6 **3.3.1 FFA pre-treatment**

7 The lipid feedstock may contain variable FFA amounts that should be removed or converted  
 8 to esters before transesterification. Soaps are formed by reaction of FFA with alkali catalyst:



10 Another undesired reaction is the saponification of dissolved ester in the glycerol phase:



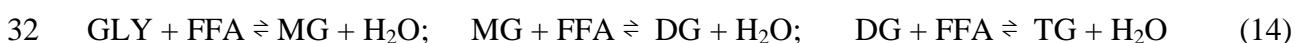
12 The soaps that cause foaming can be removed by filtering, although the reconversion to FFA  
 13 by treatment with mineral acid is the preferred method:



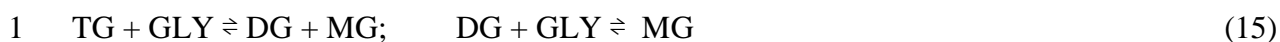
15 The target of FFA reduction in industry is below 2 mg KOH/g or 0.5-1 % with respect to oil.  
 16 The water content should be below 0.1 % wt, but better below 500 ppm. For an FFA range of  
 17 1-2 %wt the problem is solved usually by increasing the amount of base catalyst for trans-  
 18 esterification. When the FFA amount exceeds 2 % wt the oil pre-treatment is compulsory. This  
 19 can follow two methods: caustic stripping or esterification with suitable alcohol. By the first  
 20 method the FFA are converted in soaps by alkali treatment followed by removal. By the  
 21 second method the FFA are transformed to esters that remain in the biodiesel. This is more  
 22 advantageous from an economical viewpoint.

23 When methanol is used for transesterification, FFAs are converted directly in FAME. The  
 24 amount of chemicals and pre-treatment time may be determined based on FFA analysis. The  
 25 recommendation by US-NREL agency is 20:1 methanol-to-FFA molar ratio and 5% wt.  
 26 H<sub>2</sub>SO<sub>4</sub>-to FFA, as well as 2 hours reaction time (Van Gerpen et al., 2004). Chai et al. (2014)  
 27 re-examined this rule and found that it works well at higher FFA content (above 15 %wt.), but  
 28 for lower FFA content - as encountered with UCO - the methanol-to- FFA molar ratio should  
 29 be increased to 40:1 and the catalyst amount to 10 %wt to FFA, for temperatures of 55-65 °C.

30 When glycerol is employed as alcohol for esterification, the FFA is converted in glycerides  
 31 that are then transesterified. First MGs are formed, further converted to di- and triglycerides:



33 After water removal by evaporation, the TG and DG are converted back to MG:



2 The esterification with glycerol takes place at higher temperatures (over 150 °C) but normal  
3 pressure. The water is easily removed by evaporation. The presence of mono-glycerides has a  
4 positive effect on an increased solubility of methanol in the oil phase and the stabilization of the  
5 liquid-liquid dispersion. This method is particularly suitable for treating fats, oils and greases  
6 (FOG) feedstock with high FFA content, over 15 %wt (Wang et al., 2012). Both  
7 homogeneous and heterogeneous catalysts have been considered. Venkatesh et al. (2014)  
8 found that by treatment with 3 %wt. H<sub>2</sub>SO<sub>4</sub> at 150 °C the FFA content of industrial FOG  
9 drops by 90% in less than 2 hours in a batch reactor. On the contrary, at the same temperature  
10 using sulfated zirconia catalyst needs much more time. Felizardo et al. (2011) used Zn acetate  
11 at temperatures in the range of 180-230 °C and glycerol excess of 4 to 65%. The best  
12 conditions were with 0.1 %wt catalyst at 220 °C, 10 % glycerol excess and 500 rpm stirring  
13 rate, when the FFA conversion was 94.7 % in 60 minutes; while 120 minutes were necessary  
14 without catalyst, for the same result.

15 At temperatures over 200 °C the esterification with glycerol becomes autocatalytic. Tu et al.  
16 (2017) found that this may be successfully applied for treating FOG with 30% FFA to reduce  
17 it to 1%. At 1:1 molar ratio, the optimal conditions in a batch reactor were 230 °C and 150  
18 minutes. The important result for this study is that FFA pre-treatment may be compatible with  
19 the transesterification by heterogeneous catalyst that takes place at the same temperature  
20 level. The result is significant flowsheet simplification and energy saving.

21

### 22 **3.3.2 Transesterification**

23 In the second stage, the FFA-free stream is sent to the main processing stage, the trans-  
24 esterification with methanol to produce FAME, using hetero- or homogeneous base catalysts.  
25 The reaction must run practically at full conversion aiming for the lowest possible amounts in  
26 MG and DG. The European EN 14421 norm limits the content of TG to 0.2 %wt, DG 0.2  
27 %wt and MG 0.8 %wt. In the US ASTM standard D6751 these requirements are lumped into  
28 a single specification, the 'bound glycerol' that must be below 0.2 %wt. This specification is  
29 considered the most important (Van Gerpen, 2004) and it is essential for ensuring a high-  
30 quality biodiesel, avoiding the formation of solid deposits harmful for engine and emissions.  
31 Yet, norm D6751 is not enough to avoid the occurrence of some sediments that may occur  
32 from storage in variable weather conditions. This phenomenon is due to the presence of sterol  
33 glucosides and saturated MG not removed after transesterification, which can interact at  
34 longer time during storage and form solid sediments (Van Gerpen, 2004). Sterols can be

1 found in vegetable oils (rapeseed, canola) but their presence is even higher in animal fats. The  
2 presence of such contaminants may be detected by the *cold soak filtration test* (CSFT).  
3 The final biodiesel composition results from three parallel-consecutive equilibrium reactions  
4 involving saturated and unsaturated long-chain alkyl molecules. The best method to obtain  
5 high quality biodiesel is fulfilling the biodiesel specifications at the reaction stage.  
6 Using a large excess of methanol would allow in principle achieving very high conversions,  
7 in a single reactor, but in practice this approach is confronted with two drawbacks. Firstly, it  
8 increases the size of vessels and the energy consumption. These latter may be estimated from  
9 the vaporization energy (1.2 MJ/kg methanol) and the cost of energy (15 \$/GJ) at 15 \$/t  
10 biodiesel for 100% methanol excess. Secondly, a large methanol excess does not guarantee  
11 the fulfillment of specifications. More methanol leads to the solubilization of glycerol in the  
12 FAME phase promoting the formation of mono-glycerides by the back reaction, such that  
13 more mono-glycerides are formed (Bambase et al., 2007). More suitable is the intermediate  
14 glycerol removal (Dimian and Bildea, 2008), which leads to a two-step reaction process, a  
15 method largely adopted in industry (Haas et al., 2006; Stiefel and Dassori, 2009; Air Liquid /  
16 Lurgi, 2017). An excess of methanol of 6:1 molar ratio is considered in general optimal. In the  
17 two-reactor sequence a split in the ratio of 70 to 30 % was found optimal. Distillation under  
18 slight vacuum is necessary to recycle the excess of methanol. Note that low methanol content  
19 allows better separation of FAME and glycerol phases.

20

### 21 **3.3.3 Post-processing**

22 The resulting raw biodiesel and glycerol streams are sent to post-processing that is essentially  
23 a purification step aiming to remove the soaps and residual catalyst, as well as to correct the  
24 content of methanol and glycerol below the required limits, both in biodiesel and the glycerol  
25 by-product. Purification may be done by water washing, dry-wash and distillation.

26 The *wet-wash* scheme consists of removing the contaminants by extraction with water. The  
27 operation is energy-intensive implying neutralizations, waste water treatment, methanol  
28 distillation and glycerol drying. This scheme is adopted in conventional processes using alkali  
29 catalyst. Most of the soaps are captured in biodiesel, while most of the catalyst remains in  
30 glycerol. This method is effective for achieving the glycerol and methanol specs.

31 The *dry-wash* method applies ion-exchange resins or adsorbents for removing contaminants  
32 (Yawn, 2013). After several cycles the resin is regenerated, or the adsorbent dumped as solid  
33 waste. This approach is popular among small producers, as it avoids the drawback of waste-  
34 water treatment. Dry-wash makes use of adsorbents (Magnesol<sup>®</sup> and silica) or ion-exchange

1 resin (Amberlite BD10 and Purolite PD 206). The resins can remove efficiently soap, glycerol  
2 and catalyst, but not methanol (Faccini et al., 2011). The action mechanism is based on ion  
3 exchange, filtration, adsorption and soap-glycerol interaction (Van Gerpen, 2010). The  
4 specific consumption is in the range of 800-1800 L/kg resin, while the washing rate is 3 bed  
5 volumes per hour. The cost of resin and of regeneration may result finally in a cost of 2-5  
6 \$/gallon or 5-13 \$/ton biodiesel (Kotrba, 2014).

7 Water-washing is more efficient than dry-wash, namely for higher content of contaminants  
8 (Van Gerpen, 2017b) and it is more appropriate when using alkali transesterification at larger  
9 scale. But in general, this method is penalized by the availability of water treatment facility.  
10 When solid catalysts are employed, the cost of purification is drastically reduced since the  
11 soap amount is low and there is no catalyst to remove. Hence dry wash is suitable and regards  
12 only glycerol reduction from the raw biodiesel.

13 *High vacuum distillation* of biodiesel has emerged recently as an advanced method to answer  
14 the higher quality requirements for biodiesel. However, the use of this costly technology must  
15 consider careful design constraints, as described in a later section.

16

## 17 **4. Results and discussion**

18 This section provides the main results for the FFA pre-treatment and the three integrated  
19 processes proposed, as well as their economic evaluation and comparison of performance.

20

### 21 **4.1 FFA pre-treatment**

22 The FFA pre-treatment can be carried out in a batch process (by esterification methanol or  
23 glycerol) or in a continuous process (by esterification methanol), as follows.

24

#### 25 **4.1.1 Batch process**

26 *FFA reduction by esterification with methanol.* Figure 2 presents the flowsheet of  
27 esterification with methanol. Oil and methanol are put in contact in an autoclave with 5 %wt  
28 sulfuric acid-to-FFA catalyst under vigorous stirring. This comprises of reaction vessel with  
29 heating jacket or heat exchanger, centrifugal separator (Tricanter, Flottweg company, 2008),  
30 methanol distillation tower, and oil dryer. The broken line means discontinuous operation,  
31 while the rest of the plant is operated continuously. A batch converts a feed of 2,500 kg/h  
32 with 10 %wt FFA. The refined oil ensures 4 hours of continuous operation, equivalent to  
33 10,000 kg (or 11,000 L) oil inventory. Taking oleic acid as base molecule, the batch contains  
34 9,000 kg (10.16 kmol) trioleine, 1,000 kg (3.54 kmol) oleic acid, and 3,398 kg (106.2 kmol)

1 methanol in order to ensure a methanol to FFA molar ratio of 30:1. To this 50 kg sulfuric acid  
2 is added; or 5 %wt. The total mixture volume is 15.5 m<sup>3</sup> hence considering a filling factor of  
3 0.8 the required vessel volume is 20 m<sup>3</sup>. Flexibility in operation can be achieved by playing  
4 on temperature, acid concentration and methanol amount. Thus, for achieving a target of 0.5%  
5 FFA the reaction time can be estimated from the plots presented by Chai et al. (2014) at 90  
6 min (at 55 °C) and 60 min (at 65 °C), the maximum allocated time being 2 hours. Next, the  
7 batch content is treated with Ca(OH)<sub>2</sub> solution for neutralization. Then oil, aqueous methanol  
8 and solid CaSO<sub>4</sub> are separated by centrifugation and decanting filtering. Finally, the moisture  
9 is reduced to 500 ppm by vacuum drying, while methanol is distilled and recycled.

10  
11 **FFA reduction by esterification with glycerol.** The esterification with glycerol is much  
12 simpler than with methanol. The reaction can run in a batch autoclave at 230-240 °C (heated  
13 with Dowtherm) using a molar ratio 1:1 for a reaction time of about 150 minutes. The reaction  
14 can be performed also in a PFR continuous device with variable residence time (Dimian and  
15 Rothenberg, 2016), as shown in a subsequent section. This method will be applied in the  
16 processes 2 and 3, as described later.

#### 17 18 **4.1.2 Continuous process by FFA esterification with methanol**

19 Figure 3 presents a continuous process employing reactive absorption (RA) and hetero-  
20 geneous catalysis. The key advantage is that catalyst neutralization and removal is no longer  
21 needed, which otherwise involved costly operations. The esterification of fatty acids with  
22 heterogeneous catalysts was investigated in studies regarding the design and simulation  
23 (Omota et al., 2003), catalyst synthesis (Kiss et al., 2006), alcohols (Grecea et al., 2012), and  
24 reactive separation processes (Kiss and Bildea, 2012). Kiss (2009) reported the application of  
25 RA by esterification of fatty acids with methanol when heterogeneous catalyst is employed.

26 The simulation implemented here in Aspen Plus considers a feedstock of 2,525 kg/h with  
27 2,250 kg/h triolein and 250 kg/h oleic acid as well as 25 kg/h water. The oil stream enters the  
28 column at the top, in counter-current with 500 kg/h methanol vapor produced in a stand-alone  
29 pressure vessel. Large excess methanol is necessary for reaction and to ensure proper  
30 liquid/vapor traffic over the internals. Kinetic data are available from the paper of  
31 Steinigeweg and Gmehling (2003), see equations (3) and (4) as well as Table 2. They studied  
32 this reaction in a laboratory column equipped with structured packing Katapak-SP in which  
33 ion-exchange resin catalyst Amberlyst-15 was inserted.

1 Katapak-SP is compatible with Mellapak structured packing, both commercialized by Sulzer  
2 ChemTech, for which hydraulic parameters are available in Aspen Plus. Physical data for  
3 catalyst has been retrieved from the technical brochure regarding the superacid Amberlyst™  
4 15WET manufactured by DOW Chemical: particle size 0.6-0.85 mm, bulk density 770 g/L,  
5 void fraction 0.4, surface area 56 m<sup>2</sup>/g and maximum operating temperature 120 °C.  
6 For the operations involving methanol/water mixture separation, the selected thermodynamic  
7 model was Wilson with parameters from the Aspen Plus database. Suitable results have been  
8 obtained with a column of 15 theoretical stages and catalyst holdup of 6 kg per stage, in total  
9 90 kg/h catalyst, using the heterogenous kinetic model (Table 2). Considering a column  
10 diameter of 0.42 m and HETP 0.6 m the hydraulic computation in Aspen Plus with Mellapak  
11 750 Y from Sulzer gives a volumetric holdup of 15 L. Accordingly, the mass holdup of  
12 catalyst per stage is  $0.77 \times (1-0.4) \times 15 = 6.9$  kg, which is 15% more than the actual value of 6  
13 kg considered in simulation. The operation is at ~80% of the maximum capacity. With a  
14 column pressure of 2.3 bar, top feed temperature at 95 °C and using methanol superheated at  
15 108 °C, the temperature profile is almost constant at 107 °C, resulting in FFA conversion  
16 exceeding 99%. Note that the homogeneous model results in a column design with the same  
17 sizing but operating at lower pressure of 1.5 bar. The temperature profile drops by 8°C. Thus,  
18 the column's pressure is a key variable for controlling the process faced with disturbances in  
19 FFA content, as well as by catalyst deactivation.

20 The refined oil leaving the RD column with some methanol is suitable for transesterification.  
21 Water resulting from esterification with the excess methanol goes out as top vapor, being fed  
22 directly to the methanol distillation column operating at nearly atmospheric pressure. The  
23 column has 12 stages and is equipped with Pall rings (16 mm, ceramic). A molar reflux ratio  
24 of 1.0 ensures over 99.6% methanol recovery. Methanol is sent back to the RD column. The  
25 bottom stream is sent to wastewater treatment.

26 Table 2 presents sizing elements of the RD setup. Both columns have a diameter of 0.4 m,  
27 except the stripping part of the methanol distillation tower (reduced to 0.3 m due to lower V/L  
28 traffic). By comparing the two methods, the following differences may be noted:

- 29 • The amount of methanol is 3400 kg in batch treatment, but only 2,000 kg for 4 h operation  
30 in reactive absorption. The energy for methanol recycling is higher in the first case, but if  
31 one considers the ion-exchange regeneration the energy usage might be similar.
- 32 • The neutralization with Ca(OH)<sub>2</sub> gives waste water to be treated and CaSO<sub>4</sub> that should be  
33 landfilled. In contrast, the ion-exchange resin can be used on long-runs (months) without  
34 wastewater and with easy regeneration. The exhausted resin is also in much less amount.



1 • The stainless-steel batch reactor is an expensive piece of equipment, to which the tricanter  
2 and dryer must be added.

3 • The reactive absorption is a standard piece of process equipment. In addition, the  
4 methanol distillation may be integrated with the transesterification process.

5 Consequently, the reactive absorption should be more advantageous than the batch treatment.  
6 (this will be checked later by the economic analysis). Table 6 presents the simulation results  
7 regarding the RA design flexibility with respect to FFA variability, considering feedstock  
8 with 10 and 15 %wt FFA. In the first case the residual FFA is 0.42 % (below the 0.5% norm),  
9 while in the second case the FFA is under 1% (still acceptable). The amount of methanol and  
10 the operating conditions can be controlled. As the reaction takes place in liquid phase,  
11 increasing the pressure can ensure a higher flexibility. If the pressure is raised to 3 bar it is  
12 possible to treat a 20 %wt FFA feedstock to less than 0.2 %wt. This result indicates that RA  
13 exhibits a large flexibility ensuring that a large variety of feedstock (UCO and animal fats)  
14 can be treated directly for FFA reduction.

## 16 4.2 Integrated process design

17 The integrated process combines the pre-treatment, transesterification and purification stages.  
18 The design of the reaction section is based on detailed kinetic modeling of reactors. The goal  
19 is to match the biodiesel quality specs after the reaction stage, thus avoiding the use energy-  
20 demanding separations such as vacuum distillation. The content in TG, DG, and MG should  
21 be limited to 0.2, 0.2 and 0.8 %wt, respectively, and to 0.25 %wt as total glycerine (see  
22 EN14214). The norms restrict the methanol, free glycerol and water content to under 0.2, 0.02  
23 and 0.05 %wt, respectively. Another important specification is the *acid value*, which is max  
24 0.80 mg KOH/g in D6751 norm and 0.50 mg KOH/g in EN 14214. The last value is  
25 equivalent with 0.25 %wt or 2500 ppm, taking the oleic acid as reference molecule. Thus, this  
26 specification sets the FFA conversion target in the FFA pre-treatment process.

27 Further, the impurities of alkali and earth alkali metals are limited to 5 ppm each, while  
28 phosphorous to 10 ppm. The methanol specification in biodiesel and glycerol can be fulfilled  
29 by vacuum evaporation, although with different parameters. The recovered methanol is  
30 recycled back such to obtain a material balance closed to stoichiometry. For other  
31 specifications, the dry-wash purification method can be applied.

### 33 4.2.1 Process 1: Homogenous catalysis process

34 The application of reactive distillation (RD) as process intensification for transesterification

1 was proposed by He and Thompson (2006). RD is usually applied by reactions controlled by  
2 chemical equilibrium when the product formation is enhanced by separation. In this case both  
3 product and reactant remain in the stream leaving the column at bottom. The intensification  
4 effect is not caused by separation but by creating a large excess of methanol, controlled by the  
5 energy injected in reboiler. In addition, the stages behave as a series of CSTRs. It was found  
6 that a RD scheme with pre-reactors (CSTR and PFR) is advantageous. The simulation of such  
7 process in a single stage showed that fulfilling the end-product specs is not possible, since the  
8 presence of large amounts of glycerol on the RD column stages combined with the counter-  
9 current methanol flow tend to reform MG and DG by the reverse reactions. Hence the  
10 removal of glycerol before applying reactive distillation is mandatory.

11 The property model for transesterification is based on ideal assumption, due to large  
12 differences in the boiling points and no molecular interactions. For the liquid-liquid  
13 separation by decanting, the UNIFAC-Dortmund model was applied. Figure 4 shows the  
14 process flowsheet simulated with Aspen Plus v9.0, while Table 7 presents the key results in  
15 term of progress of transesterification. Firstly, the 2,500 kg/h feedstock containing 10% FFA  
16 is treated in the RA column FFA-RD following the procedure described before. The  
17 conversion of FFA to methyl ester is over 99%. Further, the resulting stream is submitted to  
18 transesterification. The reaction starts in a small CSTR (500 L volume, 5 minutes residence  
19 time) operated at 70 °C and 3 bar and provided with intensive agitation to develop a stable  
20 dispersion. Methanol enters on inventory control to keep an inlet molar ratio methanol to oil  
21 at 6:1 when methanol recycle is added. TG conversion is 26.2 %, while DG and MG are  
22 formed in amounts of 67 and 32 kg/h and help sustaining the liquid-liquid dispersion in the  
23 PFR-type device. Then the reaction continues in a tubular reactor. A *multi-tubular serpentine*  
24 device is suitable (Dimian and Rothenberg, 2016) provided with *static mixers* (Sulzer, 2018a).  
25 From a practical viewpoint, the reactor construction consists of 14 tubes of 0.25 m diameter  
26 and 2.5 m length, giving a total volume of 1.717 m<sup>3</sup>. The residence time is 20 minutes while  
27 the conversion rises to 84.5 %. The amounts of MG and DG are an order of magnitude higher  
28 than required by end-product specs, so even if the conversion is pushed to over 99% the specs  
29 cannot be met. Glycerol removal is required to push the equilibrium-controlled conversion.  
30 After cooling and neutralization, glycerol separation takes place by gravity decantation or  
31 centrifugation. The oil phase is submitted to a second transesterification. The ester stream  
32 enters the RD top stage. It contains 2,010 kg/h ester and 413 kg/h TG, 36 kg/h DG and 63  
33 kg/h MG. This stream contains a fair amount of methanol (286 kg/h), but this is insufficient  
34 for converting the remaining glycerides to the low limits fixed by specifications. A larger

1 amount of methanol is recycled to the reaction space by the internal reflux, in turn controlled  
2 by the reboiler duty. A duty of 250 kW creates an internal methanol recycle of ~300 kg/h.  
3 The addition of a small catalyst amount might be necessary. The RD column has 14 reactive  
4 stages provided with Sulzer structured packing (Sulzer, 2018b). A reactive volume of 10 L  
5 was assumed in simulation (checked later by hydraulic computation). The top pressure is at  
6 1.8 bars, which results in a temperature of 87.2 °C that rises to 91 °C in the reactive zone. The  
7 ester leaves the column at 140 °C (at 2 bar pressure and some methanol content). The total  
8 packing height is 7.5 m, giving a HETP of 0.535 m. The total reaction volume is of 1.038 m<sup>3</sup>.  
9 Rigorous hydraulic calculation performed in Aspen Plus gives for Sulzer BX packing a  
10 holdup of 10 L (at 0.4 m diameter and above HETP), the operating point being at 60% from  
11 flooding. Sulzer CY packing (at 0.42 m diameter) gives a higher holdup of 14 L at 80% from  
12 the maximum capacity. Using the Sulzer CY packing ensures better flexibility in operation.  
13 Figure 5 shows the flow rates profile of the species on the RD column stages. A sharp drop on  
14 the top stages is noticed, but with an asymptotic trend to the bottom. The RD behaves as a  
15 series of small reactors. In this way, the bottom product reaches a composition that fulfils the  
16 specifications term of glycerides. Hydraulic computation confirms that the total residence  
17 time is 16 min. Thus, employing RD shows high efficiency although the reaction rate is very  
18 low due to approaching equilibrium, confirming the statement of He and Thompson (2006).  
19 After reaction completion, the bottom stream from RD joins the glycerol streams from D-1  
20 forming the stream named FAME. This stream containing about 80% ester, 11% methanol  
21 and 7% Glycerol is sent to the top of the *reboiled stripping* column (DIST) for methanol  
22 recovery. This column receives also the vapor methanol stream from the FFA-RD column.  
23 The methanol distillation takes place under vacuum at 0.3 bar. Twelve theoretical stages  
24 ensure quantitative recovery of excess methanol, which is recycled. The methanol-free ester  
25 stream is sent to the separation of glycerol and biodiesel by decantation or centrifugation. The  
26 raw biodiesel is already in specs, except the glycerol amount which can be further reduced by  
27 dry-wash. The raw glycerol that has over 98% purity with methanol and salt as impurities is  
28 sent to purification. This may employ dry wash or wet wash (preferred) by state-of-the-art  
29 methods that were presented in a previous section. Table 8 presents a summary of the sizing  
30 of reactive distillation and methanol recovery columns.  
31 In terms of efficiency, the conversion of triglycerides in FAME, DG and MG is over 99.9%  
32 while the FAME yield including FFA is 99.99%. The raw biodiesel is already in the specs  
33 mentioned above. Namely the MG content, can be finely adjusted by means of the reboiler  
34 duty. Thus, considering the water- and catalyst-free biodiesel for 325 kW reboiler duty the

1 FAME content is 98.9 %wt while TG, DG and MG are 0.08, 0.13 and 0.72 %wt, the rest  
2 being methanol, glycerol and unreacted FFA.

3

#### 4 **4.2.2 Process 2: Heterogeneous catalysis process**

5 Heterogeneous catalysis brings major advantages over homogeneous catalysis, by dropping  
6 operations involving water. A key benefit is obtaining high-purity glycerol as valuable by-  
7 product. But the key problem is the availability of a robust and cost-competitive catalyst. The  
8 French company AXENS developed the Esterfip<sup>TM</sup> process based on a zinc aluminate catalyst  
9 used in a process for esters production from oils (Stern et al., 1999) or for the preparation of  
10 alcohol esters from triglycerides and alcohols (Bazer-Bachi et al., 2011). Despite intensive  
11 research, this catalyst remains the only one that proved active and robust in industrial  
12 operation. Details about technology can be found in patents (Bourney et al., 2005) and papers  
13 (Bloch et al., 2008) published by researchers from FPI. The preferred operating conditions are  
14 pressure of 40-70 bar, temperatures of 190-220 °C, liquid hourly space velocity (LHSV) of  
15 0.5-1 h<sup>-1</sup>, and MeOH:oil weight ratio 0.3:0.5. The catalyst consists of extrudates of 3 mm  
16 diameter. The reaction takes place in two steps, with intermediate conversion of 90-93%.

17 A drawback of heterogeneous catalysis is that the reactor should be sufficiently oversized for  
18 dealing with the feedstock variability, the presence of impurities, and catalyst deactivation. To  
19 overcome these drawbacks, Dimian and Rothenberg (2016) proposed a novel design ensuring  
20 variable residence-time and easy catalyst replacement. The reaction device illustrated in the  
21 Figure 6 consists of a serpentine-type PFR assembled as vertical tubular segments filled with  
22 solid catalyst. A switching valve system is employed to connect or bypass the reaction tubes,  
23 and to easily replace the catalyst, all these without shutting down the reactor. As methanol and  
24 oil streams are pumped at high pressure, the mixing of reactants is realized by a static device  
25 exploiting the kinetic energy of flows. Heating and cooling tubular elements are provided for  
26 thermal conditioning before and after reaction. Energy savings are obtained by a FEHE built-  
27 in unit. Employing liquid thermal agent (Dowtherm) is convenient for small scale or mobile  
28 units. This reaction set-up allows adjusting the residence time to the feedstock type and to the  
29 catalyst activity by varying the number of the active tubes. Smaller catalyst grain can be used,  
30 resulting in a faster reaction rate by reducing the external and internal diffusion effects. In  
31 addition, a significant catalyst saving is obtained.

32 Figure 7 displays the flowsheet of a process including FFA pre-treatment by esterification  
33 with glycerol followed by transesterification using a solid catalyst. The plant is designed for a  
34 capacity of 2,500 kg/h feedstock containing variable FFA amounts (20 %wt FFA is used in

1 this example). The simulation considers oleic acid and its glycerides as key components. The  
2 stream FFA-OIL is sent to FFA reduction by esterification with glycerol after preheating by  
3 the units FEHE-1 and H-1. The reaction takes place in the tubular reactor FFA-GLY provided  
4 with heating by Dowtherm. A reaction time of 150 minutes using a molar ratio GLY:FFA of  
5 1:1 was found optimal by Tu et al. (2017), the FFA conversion being 90%. In this project we  
6 aim 99% conversion and therefore the temperature is raised to 250 °C. An amount of 500 kg/h  
7 glycerol is used. The simulation of a PFR by kinetic modelling indicates that this conversion  
8 is achieved in 1.72 hours and reactor volume of 7.85 m<sup>3</sup>. Note that the conversion of FFA by  
9 esterification should be high enough to comply with the quality specifications, expressed as  
10 acid value. Considering oleic acid as reference molecule the FFA conversion should be at  
11 least 0.988 at 20 %wt, and 0.992 at 35 %wt oil content. This requirement is accomplished by  
12 the above described reactor design.

13 After pressure reduction at 1.1 bar, the cleaned oil is dried by flash evaporation. Using the hot  
14 effluent for feedstock preheating in the unit FEHE-1 results in energy savings of 70%.  
15 Further, the oil and methanol are pumped at 40 bar (at 0.3 weight-ratio) and homogenized in a  
16 static mixer. The mixture is then heated up to 200 °C after passing through the FEHE-2 unit  
17 and the heater HX-2. Conditioned mixture enters the first reactor R-1 (an adiabatic PFR  
18 operating at constant temperature as the thermal effect is negligible). The design of R-1 aims  
19 to reach a conversion of TG close to 90-93%. The hot outlet cooled in counter-current with  
20 the feed is sent to flash evaporator (FL-1) after pressure reduction to 2 bar. Lower methanol  
21 amount makes phase separation easier. After cooling at 35 °C the liquid mixture is sent to the  
22 glycerol removal in the decanter (D-1).

23 The process continues in the second transesterification reactor R-2, by remixing ester and  
24 recovered methanol, and rising the pressure and temperature to the previous values. After the  
25 reactor R-2, the conversion should be over 99.7 % to meet the biodiesel specifications. After  
26 heat recovery by the unit FEHE-3 the reactor outlet stream is sent to the stripping column  
27 DIST, provided with 4 theoretical stages and operates under vacuum at 0.3 bar. The top  
28 distillate delivers methanol to be recycled to the transesterification reactors. Methanol  
29 recovery of 99.5 % is necessary for enhancing the glycerol separation and for reducing the  
30 methanol content in product below 0.2 %wt. The final separation takes place in unit D-2,  
31 which delivers raw biodiesel that complies with the specs, except glycerol set by phase  
32 equilibrium. Gravity driven separators D-1 and D-2 can be replaced by centrifuges.

33 Table 9 presents the main elements regarding the reactor sizing (note that each reactor  
34 employs two serpentine-type modules). Figure 8 shows the concentration profiles of key

1 species. The methanol flowrate reduces from 294.2 to 286.2 kg/hr in R-2 (but not shown in  
2 Figure 8-right, as it is out of the scale). The plot is typical for consecutive / parallel reactions,  
3 in which DG and MG are intermediates. Although the TG conversion in the first reactor  
4 reaches 93%, the concentrations of DG and MG are higher than end-product specs by an order  
5 of magnitude. Hence the need for using a second reactor is obvious. The residence (spatial)  
6 times are similar in both reactors, about 1 hour. The flow superficial velocity (a key parameter  
7 for ensuring good mass transfer) is about 3 mm/s, in agreement with best practice of liquid-  
8 phase reactors. The results prove that kinetic modeling offers a realistic description of the  
9 transesterification reaction in industrial conditions (Bloch et al., 2008).

10 The efficiency of this process is excellent as can be expressed as follows:

- 11 - TG conversion 99.98%, full quantitative FAME yield with reference to oil and FFA
- 12 - Raw biodiesel: FAME content 99.41, MR 0.017, DG 0.013, MG 0.28, GL 0.032, FFA  
13 0.18 all in %wt.

#### 15 **4.2.3 Process 3: Heterogeneous catalysis and vacuum distillation**

16 In this alternative, the 2nd reaction stage is suppressed and replaced by a vacuum distillation  
17 of the FAME stream obtained from R-1. The goal here is realizing an advanced purification of  
18 the top product to match the requirements of EN 14241 and D6751 standards. As drawback of  
19 biodiesel distillation, a loss in material of 3-10 % was noted (Van Gerpen, 2012), which  
20 clearly affects the profitability. The reboiler temperature must be limited to avoid thermal  
21 biodiesel degradation. Below 270 °C the degradation should be negligible (Lin et al., 2013).  
22 The limit may be raised to 300 °C but not exceeding 20 minutes. The vacuum should be fitted  
23 to this requirement.

24 Figure 9 presents the process flowsheet, in which the esterification with glycerol is handled as  
25 described in the previous process while the transesterification is carried out in a single PFR by  
26 using heterogeneous catalysis at 210 °C and 40 bar. In a first attempt the oil has 20 %wt FFA,  
27 which is further raised to 35 %wt to explore the process flexibility. The thermodynamic  
28 model is ideal, except the liquid-liquid separation where the UNIFAC-Dortmund method was  
29 applied. The methanol-to-oil weight-ratio is 0.3 (750/2,500 kg/h). The conversion of TG in  
30 the reactor is pushed to over 98% in order to minimize the recycle to the reactor, but also to  
31 ensure feasible temperatures by vacuum distillation. The profile of species flowrates in the  
32 catalytic reactor is similar to Figure 8, left. A large amount of MG is still present in the stream  
33 after reaction, about 7 to 8 % with respect to FAME ester, formed by FFA esterification in the  
34 pre-treatment step, as well as the unconverted FFA from the pre-treatment stage. The

1 methanol is recovered for the most part in the flash FL-1, followed by the separation of raw  
2 glycerol in the decanter D-1, from which high purity glycerol is obtained by the evaporation.  
3 The FAME stream is then submitted to distillation after preheating. The methanol flows from  
4 flash separation, glycerol purification and FAME distillation are gathered in a recycle stream.  
5 The vacuum distillation aims to reduce the amount of glycerides in biodiesel (top distillate),  
6 namely MG, far below the specifications of above mentioned norms. This is possible because  
7 of large volatility differences between the methyl esters and the corresponding glycerides. The  
8 reboiler temperature should be kept below 300 °C, better under 270 °C. Vacuum distillation is  
9 a suitable purification method, if some precautions are taken. The column's pressure should  
10 be selected such to operation costs by considering the temperature constraints. In this case a  
11 pressure of 0.1 bar is suitable.

12 The separation of FAME versus glycerides needs only 6 theoretical stages. The bottom  
13 temperature may be limited by allowing a suitable amount of FAME to be recycled. The top  
14 temperature may be controlled by means of the condenser duty that determines also the vapor  
15 distillate flow and composition. In this way it is possible to recover 99.9% of the methanol  
16 with only very limited amount of FAME losses (under 0.05%). The mass reflux of 1,500 kg/h  
17 or molar reflux ratio of 0.77 ensure a wide operation range of internals. The simulation shows  
18 that the column operates correctly (80 to 90% from flooding) if structured packing is used, as  
19 Sulzer BX or BX Plus, but not random packing or sieve trays. The column sizing leads to a  
20 1.0 m diameter and total packing height 3.0 m, while the pressure drop is only 0.076 bar. The  
21 reboiler temperature is kept below 280 °C. The heating can be done with organic thermal  
22 fluid, as Dowtherm Q that works well up to 330 °C at 3.4 bar (Dimian et al., 2014). This may  
23 be used in close cycle for heating other high temperature units, namely the chemical reactors.  
24 The use of high temperature raises the problem of energy usage which can be reduced  
25 significantly by heat integration. FEHE units are used to take advantage of the hot reactor  
26 outlet, as shown in Figure 7 and Figure 9. Hot biodiesel distillate can be used to drive the  
27 glycerol evaporator. Further options can be explored by applying Pinch technology, but this is  
28 outside the goal of this research.

29 The efficiency of this process is excellent delivering a quantitative FAME yield. The quality  
30 of the final product surpasses the required specifications: over 99.6 % wt FAME and only few  
31 ppm of glycerides. The residual acid content is 1400 ppm by 20 %wt initial FFA and 1950  
32 ppm by 35 % wt, by keeping the same operation parameters. The methanol is below 0.20 % wt,  
33 and only the glycerol amount needs a slight correction by dry-wash.

34

### 1 **4.3 Economic evaluation**

2 Before detailing the economic analysis, note that the three processes were optimized with  
3 respect to units' sizing and the energy use but aiming to offer also an operational flexibility.  
4 The key optimization parameters, as temperatures, methanol/oil ratio and catalyst amount  
5 were selected in the optimal range. The reactors were sized to cope with the specifications,  
6 while the flexibility may be obtained by the adjustment of temperature. The distillation  
7 columns have been oversized by about 30% as number of stages. The heat integration  
8 opportunities have been identified by running the Energy Analyzer tool in Aspen Plus. Thus,  
9 in the Process 1 that works at lower temperature, the heat integration possibilities are limited,  
10 as it may be seen from the duties of units presented in Figure 1. On the contrary, the heat  
11 integration is compulsory in Process 2 and 3, where it was implemented by means of FEHE  
12 units. Table 5, Table 8, and Table 9 present the sizing elements of the key units.

13 Table 10 summarizes the economic evaluation of all processes, which lists the capital costs in  
14 terms of Purchased Cost of Equipment (PCE) and Installed Cost (IC) of the key equipment  
15 items, as calculated using Aspen Process Economic Analyzer. The values correspond to  
16 individual flowsheet items, lumped as reactors, separators, heat exchangers and pumps.  
17 Process 1 (employing RD) has the lowest cost, about 20% of the other two processes which  
18 have similar costs. The cost of reactors is higher, but the separators and heat exchangers cost  
19 much less, while the cost of pumps is negligible. Process 2 and 3 use similar techniques in  
20 pre-treatment and reaction, but Process 3 uses a demanding separation (high temperature  
21 vacuum distillation) whose cost is compensated by the simplification of the reaction section.

22 A complete evaluation should consider the cost of purification that leads to similar quality of  
23 the products. Process 1 needs more capital and energy cost for purification due to the need to  
24 remove soaps and catalyst from both biodiesel and glycerol. Water washing is recommended,  
25 but it involves higher equipment and energy costs. The purification of Process 2 and 3 is  
26 much cheaper. The overall result is that all three processes have similar investment costs. The  
27 selection depends on the availability of catalyst, Process 1 being the most convenient. When  
28 heterogeneous catalyst is selected, Process 3 is recommended as it delivers a better quality of  
29 biodiesel, and it is also more capable to treat feedstock of high FFA content.

30 Table 11 presents the key performance indicators in terms of utility requirements and costs,  
31 heating duties, specific energy usage, and CO<sub>2</sub> emissions. Despite very different flowsheets  
32 and operation conditions, the processes have similar performance. As Process 1 works at low  
33 to moderate temperatures and pressures, the energy usage is low. The situation changes if wet  
34 washing (which is energy-intensive) is selected for purification. Process 2 and 3 (employing



1 heterogeneous catalysis) work at higher temperature but show moderate energy usage due to  
2 energy integration. The utility cost in Process 2 is somewhat higher because of the electricity  
3 involved in high pressure pumping. Despite using energy intensive vacuum distillation,  
4 Process 3 has low energy use and moderate utility cost.

5

## 6 **5. Conclusions**

7 This study showed that converting waste lipids to biodiesel by integrated eco-efficient pro-  
8 cesses is profitable for biofuel manufacturers while being environmentally friendly. Many  
9 researchers explored this topic from the viewpoint of chemistry and technology, but this study  
10 is the first to provide an integrated analysis of process design issues, including the recent  
11 progress in reaction and separation methods. The results are based on rigorous simulations  
12 employing detailed kinetic modeling of reactors for both esterification and transesterification,  
13 in view of fulfilling the biodiesel specifications, namely the *bound glycerol* and the *acid*  
14 *value*. Using reactive separations and heterogeneous catalysis leads to significant savings in  
15 resources, energy and equipment. The main conclusions drawn are summarized as follows:

- 16 • The esterification with methanol by reactive absorption using solid catalysts  
17 (superacid ion-exchange resins) is suitable for feedstock pre-treatment of low and  
18 moderate FFA content (<15 %wt) such as UCO. This method is cost-effective as  
19 equipment and energy, and more beneficial than batch treatment, by avoiding  
20 neutralization, distillation and drying.
- 21 • The esterification with glycerol can be performed even without catalyst (working at  
22 250 °C and over 1.5 hours reaction time), being suitable for pre-treating high FFA  
23 feedstock (>15 %wt). The higher temperature is compatible with the trans-  
24 esterification using heterogeneous base catalyst.
- 25 • Process 1 (suitable for a feedstock below 15 %wt FFA) handles the FFA pre-treatment  
26 by reactive absorption and the transesterification by homogeneous alkali catalysis. RA  
27 reduces the FFA content below 0.5 %wt. The reaction setup for transesterification is  
28 built-up from a CSTR and PFR leading to a conversion of up to 92%. After glycerol  
29 removal, a reactive distillation unit is used to reach biodiesel quality specifications.  
30 This process shows the lowest investment cost regarding the pre-treatment and  
31 processing stages.
- 32 • Process 2 may reduce the high FFA feedstock up to 35 %wt by autocatalytic  
33 esterification with glycerol at 250 °C in a plug-flow reactor and conversion around

1 99%. The resulting mono- and di-glycerides enter directly the transesterification stage  
2 that employs solid catalyst operating at high pressure (35-40 bar) and temperature  
3 (190-220 °C). A two-stage reaction with intermediate glycerol separation is used. A  
4 new reactor design is applied (multi-tubular reactor with variable residence time and  
5 easy catalyst change). Despite high temperatures in reactors low energy use is  
6 achieved by heat integration.

- 7 • Process 3 is similar to the second one, but the 2nd transesterification stage is replaced  
8 by vacuum distillation. The first reaction stage runs at 98% TG conversion, but the  
9 amount of mono-glycerides is substantial, due to the pre-treatment stage. Vacuum  
10 distillation (operated at 0.1 bar) plays a key role by recycling the monoglycerides to  
11 transesterification. The design is constrained by keeping the reboiler temperature  
12 below 280 °C to avoid thermal degradation. This condition is realized by ensuring a  
13 suitable amount of FAME in the bottom stream recycled to reactor. Low energy  
14 consumption is achieved by heat integration.
- 15 • Economic analysis shows an advantage of Process 1 in terms of capital investment and  
16 utility consumption for the pre-treatment and processing stage, but the overall benefit  
17 is less when considering the purification, as the alkali catalysis implies higher costs of  
18 materials / energy than processes using solid catalysts (Process 2 & 3). Also, high  
19 purity glycerol is obtained by heterogeneous catalysis, which brings a substantial  
20 credit for the biodiesel price. Among them, Process 3 leads to highest quality biodiesel  
21 that largely fulfils the EN14214 and CSFT standards.
- 22 • The selection of technology depends on the available catalyst and the FFA amount in  
23 feedstock. Process 1 is more suitable for low FFA feedstock, while Process 2 and 3 are  
24 convenient for high FFA feedstock while moving away from the constraints and  
25 drawbacks of using homogeneous catalyst, but with a more demanding technology.

26 The proposed integrated biodiesel production processes allow the eco-efficient conversion of  
27 cheap waste lipids into valuable biofuels, by using advanced technologies and catalysts.

## 28 **Acknowledgement**

29 Financial support of the European Commission through the European Regional Development  
30 Fund and of the Romanian state budget, under the grant agreement 155/25.11.2016 (Project  
31 POC P-37-449, acronym ASPIRE) is gratefully acknowledged. AAK gratefully acknowledges  
32 the Royal Society Wolfson Research Merit Award.

34

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- 23

1 **Tables**

2

3 **Table 1.** Fatty acid profile of some vegetable oil and waste lipids\*

Fatty acid	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Ratio US	CN	PP
Formula	16:0	C18:0	C18:1	C18:2	C18:3	-	-	°C
Palm	40-47	3-6	52-65	6-12	-	1.1	55	6 to10
Rapeseed	4	2	58-60	9-23	1-13	15.7	48-55	-9 to 3
Sunflower	3-8	1-6	14-43	44-74	-	10.1	54-58	-3 to 3
Soybean	11	4	21-24	49-53	7-8	5.7	48-52	0
UCO	5-20	5-30	50-70	10-20	-	1.9	54-60	-3 - 3
Tallow	27-44	25-37	9-34	14-50	26-50	1.0	60-62	9 - 13
Poultry fat	23	6	43	20	8	2.4	-	-
Lard	21	18	39	21	1	1.6	-	-

4 **\*Note:** Data collected from various sources (Knothe et al., 2008, 2010; Rohmans et al., 2012)

5

6

7 **Table 2.** Kinetic parameters for FFA esterification with methanol using Amberlyst-15 catalyst  
8 (Steingeweg and Gmehling, 2003)

Parameters	$K_i$	$E_{ai}$	$k_i$	$E_{ai}$
Units	kg/kmol/s	kJ/mol	kg/kmol/s	kJ/mol
Esterification, $i=1$	$9.116 \times 10^5$	68.71	$3.18 \times 10^6$	72.23
Hydrolysis, $i=-1$	$1.498 \times 10^4$	64.66	$3.55 \times 10^5$	71.9
Sorption constant $K_S$	None	-	2.77	-

9

10

11 **Table 3.** Kinetic parameters by transesterification with alkali catalyst (Bambase et al., 2007)

		$k_1$	$k_{-1}$	$k_2$	$k_{-2}$	$k_3$	$k_{-3}$
$k_{0,i}$	L/mol/s	$2.40 \times 10^6$	$1.68 \times 10^3$	$1.91 \times 10^8$	$2.92 \times 10^6$	$4.07 \times 10^2$	$1.04 \times 10^6$
$E_{a,i}$	J/mol	58,771	44,953	67,181	58,215	30,026	46,033
$k$ (50°C)	L/mol/min	0.0451	0.0054	0.1565	0.0674	0.3404	0.0224
$K_{eq}$ (50°C)		8.346		2.323		15.218	
$k$ (60°C)	L/mol/min	0.087	0.009	0.332	0.129	0.476	0.037
$K_{eq}$ (60°C)		9.741		2.568		12.724	

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**Table 4.** Kinetic parameters by transesterification with heterogeneous catalyst (adapted from Allain et al., 2016)

	Reaction	$k_0$ / [ $\text{m}^6\text{kg-cat/kmol/s}$ ]	$E_a$ / [ $\text{kJ/mol}$ ]	$K_{eq}$
1	TG+MeOH $\rightleftharpoons$ DG+FAME	3.15	64.6	51.2
2	DG+MeOH $\rightleftharpoons$ MG+FAME	$2.22 \times 10^{-3}$	31.8	53.1
3	MG+MeOH $\rightleftharpoons$ GLY+FAME	$3.18 \times 10^{-5}$	17.0	12.2

**Table 5.** Sizing of reactive absorption and distillation columns

Parameter	Unit	Reactive absorption	MeOH distillation
Packing	-	Katapak SP	Pall 16 mm
Pressure, top – bottom	bar	2.3-2.34	1.2-1.22
Temperature, top – bottom	°C	114.8 – 105.2	67 – 101
Theoretical stages/feed	-	15	11/7
Column diameter	m	0.42	0.40/0.32
HETP	m	0.6	0.5
Sections	-	2	1
Flooding	%	82	81/80
Holdup	L	15	1.2
Height packing / total	m	9	4
$Q_{\text{cond}} / Q_{\text{reb}}$	kW	0 / 0	225 / 115

**Table 6.** FFA reduction by reactive absorption with heterogeneous catalyst

		FFA 10 %wt in feedstock			FFA 15 %wt in feedstock		
		Feed	Bottom	Top	Feed	Bottom	Top
Flowrate							
Triglycerides	kg/h	2,250	2,250	0	2,125	2,125	0
FFA	kg/h	250	10.73	0.05	375	23.71	0.07
Ester	kg/h	0	255.83	0.14	0	375.64	0.17
Methanol	kg/h	500	60.10	401.64	500	62.28	381.54
Water	kg/h	0	0.03	21.49	0	0.05	31.54
Total	kg/h	3000	2,576.69	423.31	3,000	2,586.68	413.32
FFA	% wt	10	0.42		15	0.92	
FFA reduction	%		95.71			93.68	

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2 **Table 7.** Evolution of mass flow rates of species after reactors (values in kg/h)

	<b>Feed</b>	<b>CSTR</b>	<b>PFR</b>	<b>RD</b>
Triglycerides	2,250	1,844	413	1
FFA	250	2.5	2.5	2.5
Methanol	500	439	283	38
FAME	-	567	2,010	2,496
Glycerol	-	50	195	61
Diglycerides	-	68	36	3
Monoglycerides	-	32	63	13
Conversion %	-	26.2	83.5	99.9

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5 **Table 8.** Sizing elements of the reactive distillation and methanol recovery units

<b>Parameter</b>	<b>Unit</b>	<b>Reactive distillation</b>	<b>MeOH recovery</b>
Packing	-	CY	Pall 25 mm
Pressure, top - bottom	bar	1.8 – 1.94	0.3 – 0.35
Temperature, top – bottom	°C	87 - 142	46 – 140
Stages/ feed	-	14 /1	12/ 1
Column diameter	m	0.42	0.5
HETP	m	0.535	0.5
Sections	-	1	1
Flooding	%	80	75
Holdup	litre	10 (Max. 15.7)	1.35
Height packing / total	m	7.5	1.5 / 2.5
$Q_{\text{cond}} / Q_{\text{reb}}$	kW	200 / 50	0 / 245

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9 **Table 9.** Design parameters of multi-tubular reactors for transesterification by heterogeneous  
10 catalysis

Reactor	Tube diameter	Length	Serpentines	Volume	Residence time	Superficial velocity
	$D_t$	$L$	$N_s$	$V_R$	$t_R$	$w_s$
	m	m	-	m <sup>3</sup>	sec	mm/s
R-1	0.3	70	2	9.9	3,703	18.9
R-2	0.3	70	2	9.9	4,318	15.0

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1 **Table 10.** Economic evaluation comparison of integrated processes for biodiesel production  
 2 (n.b. abbreviations refer to flowsheets in Figure 4, Figure 7, and Figure 9)

Process 1	PCE	IC	Process 2	PCE	IC	Process 3	PCE	IC
<b>Reactors</b>			<b>Reactors</b>			<b>Reactors</b>		
FFA-RD	25	150	FFA-GLY	59	119	FFA-GLY	59	119
CSTR	64	205	R-1	72	193	R-1	79	203
PFR	25	117	R-2	72	192			
RDIST	43	238						
Total	157	711	Total	203	504	Total	138	322
<b>Separators</b>			<b>Separators</b>			<b>Separators</b>		
D-1	18	106	FL-1	25	106	FL-1	25	106
D-2	16	119	D-1	15	97	D-1	15	97
DIST	69	277	D-2	15	97	DIST-BD	86	477
			DIST	72	314	EVAP-1	15	104
			DRYER	18	134	DRYER	18	134
Total	103	502	Total	145	748	Total	159	917
<b>Exchangers</b>			<b>Exchangers</b>			<b>Exchangers</b>		
COND	9	59	HX-1	11	69	FEHE-1	10	66
H-3	10	59	HX-2	11	69	FEHE-2	11	69
COOL-1	10	61	HX-4	15	83	HX-1	13	82
COOL-2	10	61	HX-5	9	66	HX-2	16	88
H-1	10	64	HX-6	13	70	HX-3	28	128
AC-1	10	60	AC-1	9	59	HX-4	8	46
H-2	13	80	AC-2	10	61	HX-5	8	49
			AC-4	11	62	AC-1	11	62
			B2	13	82	AC-2	9	59
			B4	10	66	COOL-1	9	59
Total	71	443		112	688	Total	123	708
<b>Pumps</b>			<b>Pumps</b>			<b>Pumps</b>		
P-1			P-1	52	80	P-1	52	79
			P-2	52	80	P-2	52	80
			P-3	51	82	P-3	4	32
Total	4	27	Total	155	242	Total	109	192
Total costs (k\$)	335	1,683		614	2,181		529	2,139

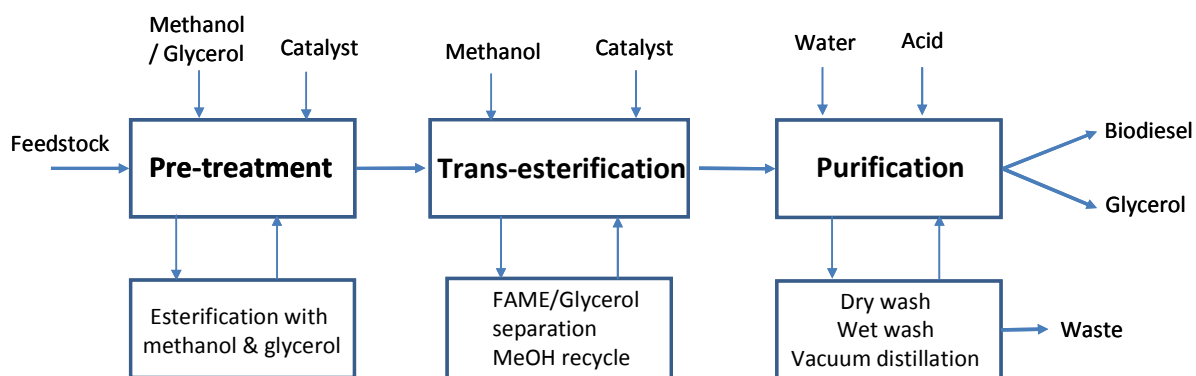
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4 **Table 11.** Key performance indicators for integrated processes for biodiesel production

KPI	Unit	Process 1	Process 2	Process 3
Utility cost	USD/year	125,162	247,980	159,461
Utility requirements	kW	1,413	1,556	1,162
Heating duty	kW	697	827	663
Specific energy use	kWh/t	278.8	330.8	265.2
CO2 emissions	kg/h	165	196	183
Specific CO2 emissions	kg/t	66	78.4	73.2

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- 2 **Figure captions**
- 3
- 4 **Figure 1.** Block diagram for biodiesel manufacturing from waste lipids
- 5
- 6 **Figure 2.** FFA esterification with methanol by batch treatment and H<sub>2</sub>SO<sub>4</sub> catalyst
- 7
- 8 **Figure 3.** FFA esterification with methanol by reactive absorption
- 9
- 10 **Figure 4.** Process 1 - FFA esterification with methanol by reactive absorption and
- 11 transesterification by reactive distillation and homogeneous catalysis
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- 22 second (right) catalytic reactor
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- 25 vacuum distillation
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**Figure 1.** Block diagram for biodiesel manufacturing from waste lipids

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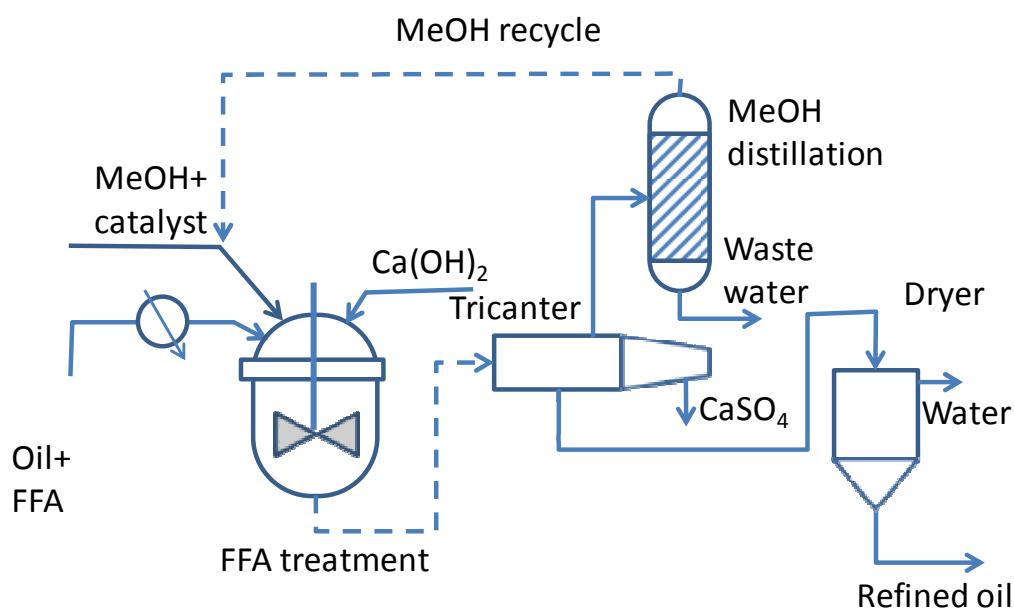
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**Figure 2.** FFA esterification with methanol by batch treatment and  $H_2SO_4$  catalyst

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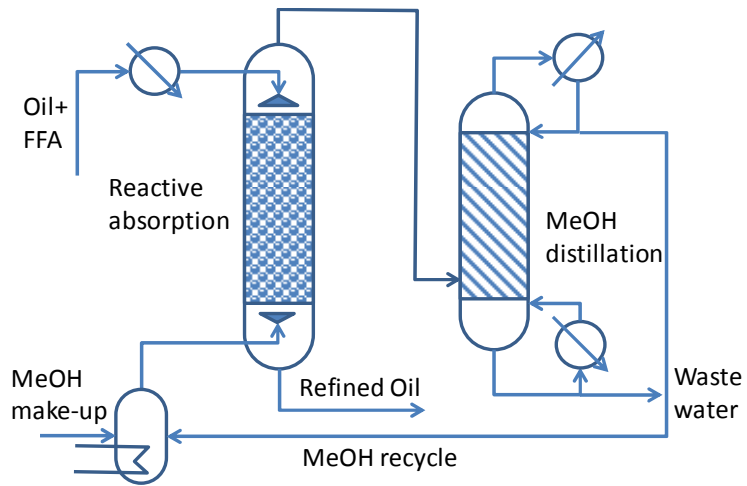


Figure 3. FFA esterification with methanol by reactive absorption

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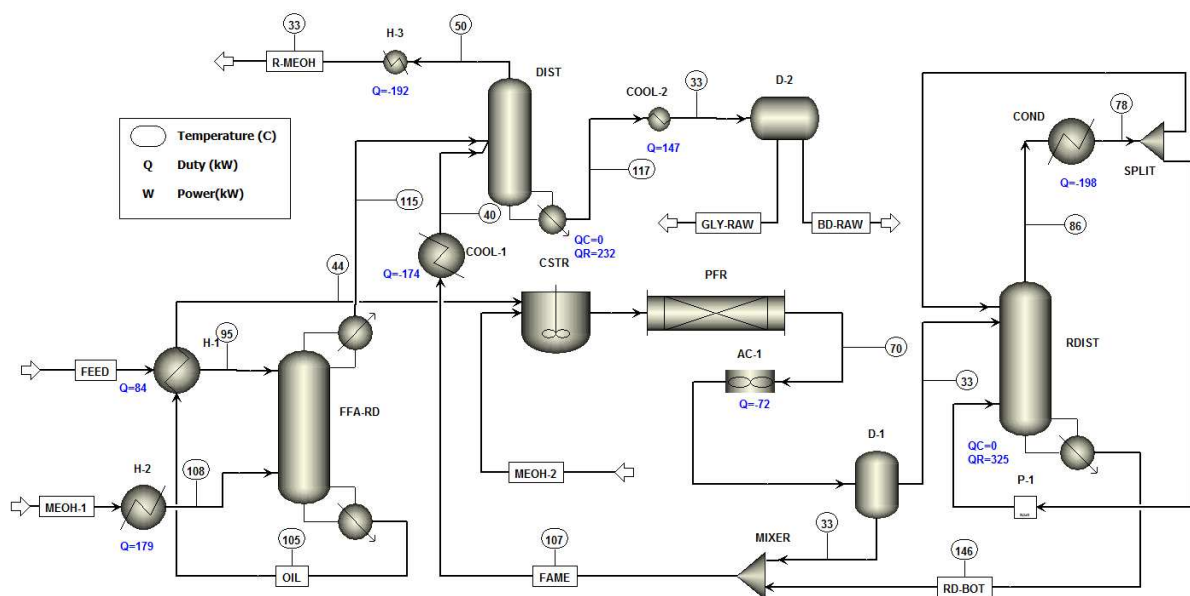


Figure 4. Process 1 - FFA esterification with methanol by reactive absorption and transesterification by reactive distillation and homogeneous catalysis

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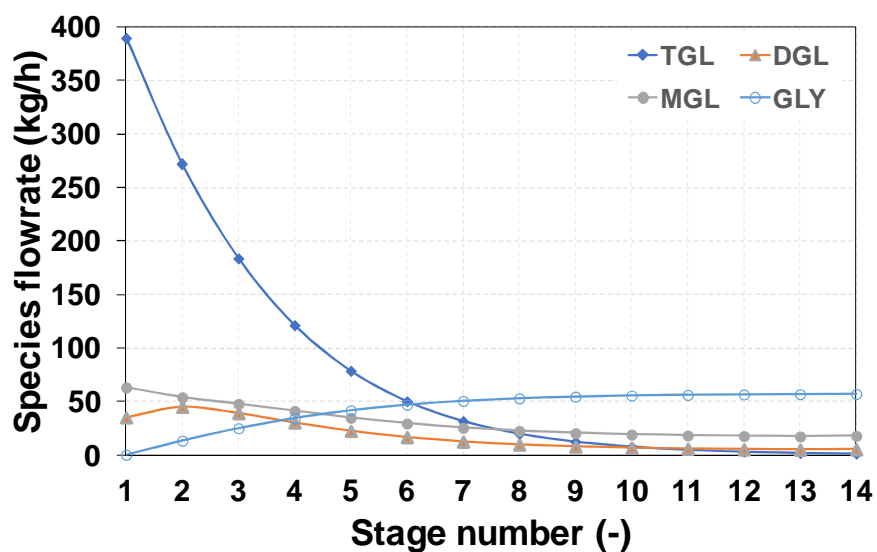


Figure 5. Flow rates of glycerides and glycerol in a reactive distillation column

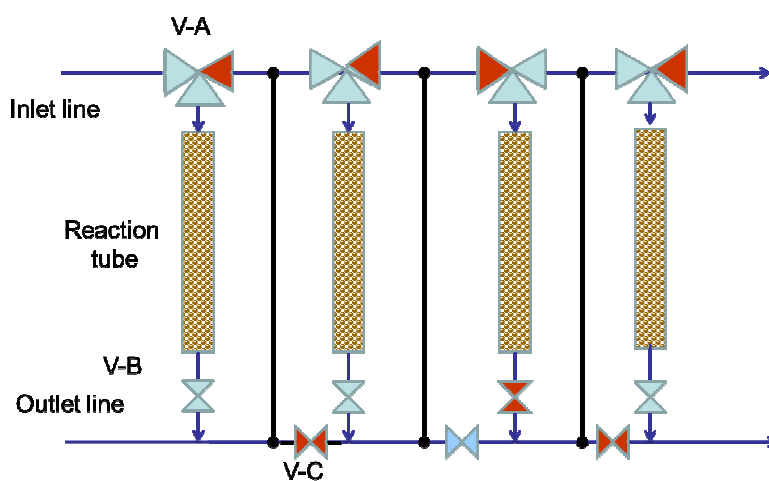


Figure 6. Variable-time reaction device for liquid-phase catalytic reactions with switching valve system for varying the residence time and easy-change of catalyst

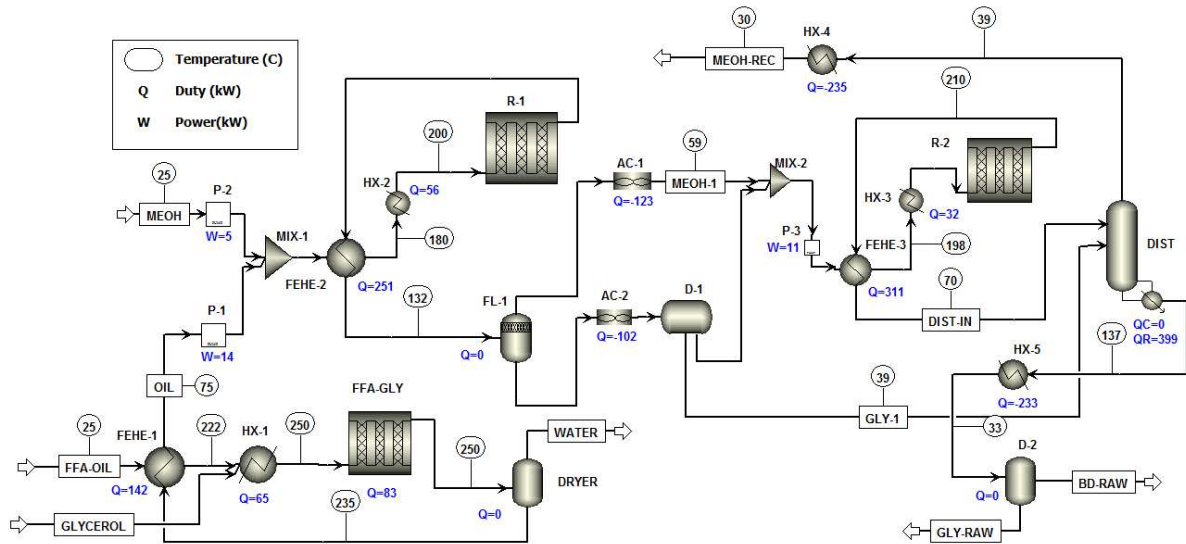


Figure 7. Process 2 - FFA esterification with methanol and transesterification by heterogeneous catalysis

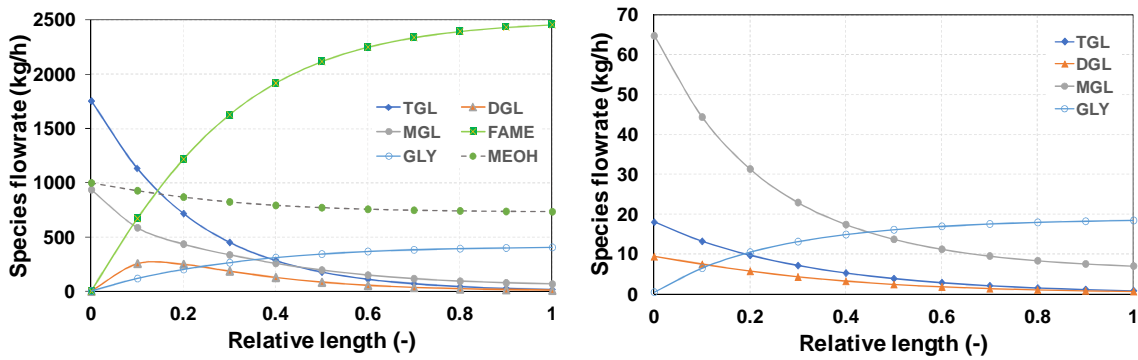
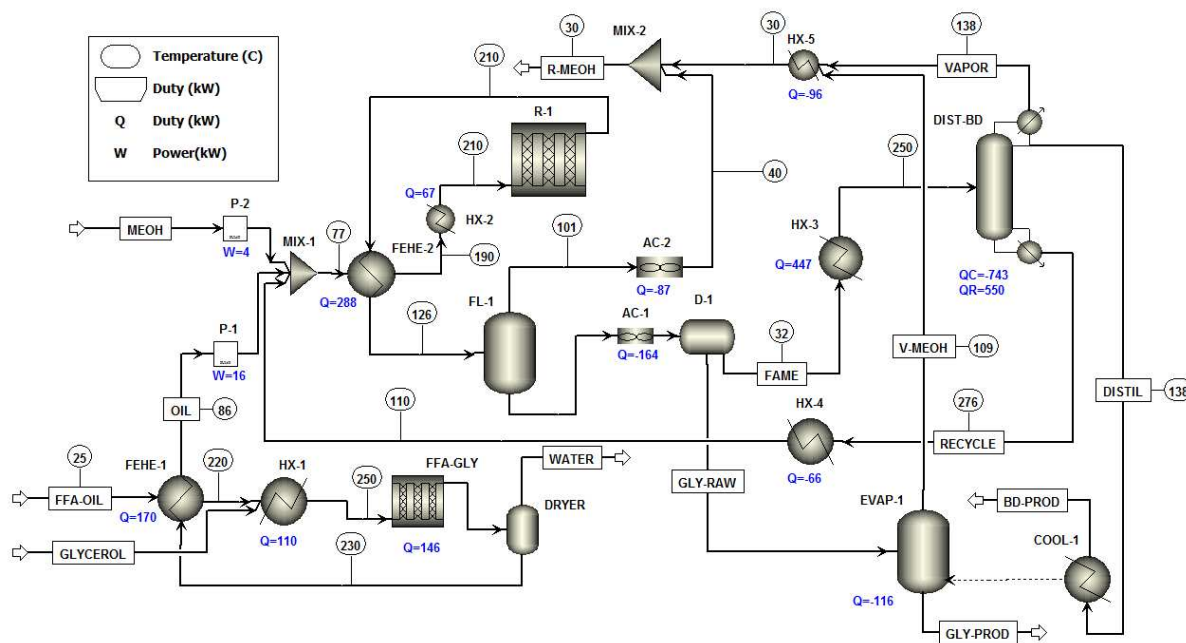


Figure 8. Profiles of glycerides mass fractions along the reactor bed, in the first (left) and second (right) catalytic reactor



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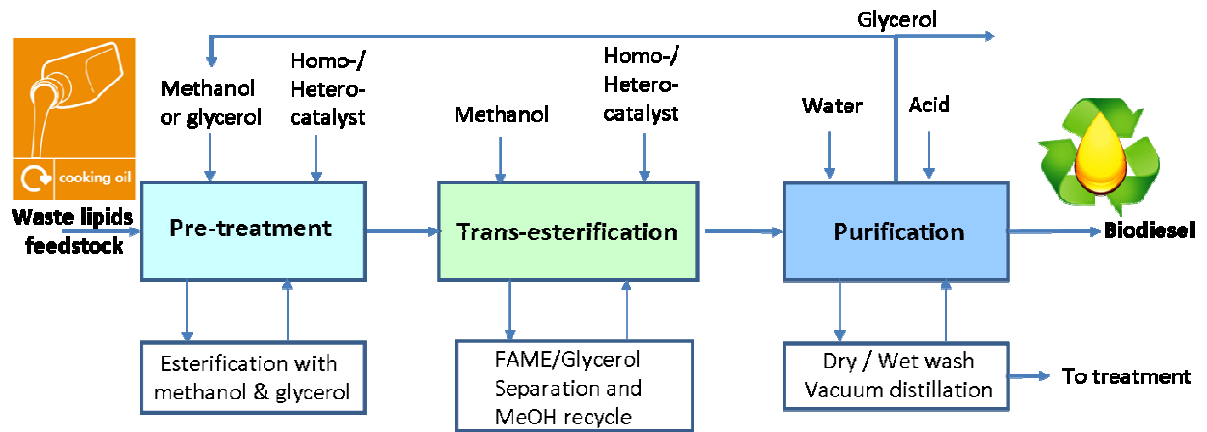
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3 **Figure 9.** Process 3 - FFA esterification, transesterification by heterogenous catalysis, and

4 vacuum distillation of the FAME

1 **Graphical abstract**

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