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Hydrated metal salt pretreatment and alkali catalyzed reactive distillation: A two-step production of waste cooking oil biodiesel

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ABSTRACT

In this work, a novel method was proposed for the conversion of waste cooking oil into biodiesel. A two-step approach based on a pretreatment with $AlCl_3 \bullet 6H_2O$ to convert FFA into the relevant methyl esters, followed by the complete transesterification of glycerides, under KOH catalysis in a reactive distillation column, was considered. The pretreatment with $AlCl_3 \bullet 6H_2O$ allowed to obtain two different phases: an oily phase, rich in FAME and triacylglycerols and with a very limited content of water (100 ppm), and residual FFA (1 mg_{KOH}/g_{oil}), and a methanol phase, in which most of the catalyst, water and monoacylglycerols were dissolved in. The esterified stream was characterized by its composition and used to obtain new kinetic parameters to be used in the setting of the reactive distillation. The reactive distillation column was proved to be efficient in obtaining a biodiesel stream with a purity requirement conform to the EN14214 standards. The transesterification step was characterized by a specific heating requirement of 701.3 kJ per kg of biodiesel produced.

1. Introduction

Under the influence of the French Government, interested in developing energy independence actions for its African colonies, Rudolf Diesel ran his engine on peanut oil during the World Exposition held in Paris in 1900. The interest in vegetable oils quickly faded since their kinematic viscosity is, in general, one order of magnitude higher than petro-derived fuels, causing poor fuel atomization and engine operational problems [1]. The problem was solved in 1937 with the publication of a patent that introduced the reaction between vegetable oils and a low molecular weight alcohol, bringing de facto to the first reference of biodiesel synthesis [2]. Nevertheless, the full development of the petrochemical industry nullified the development of biodiesel facilities until a few decades ago when the priority in reducing the greenhouse gases (GHG) emissions arouse a new wave of interest in the definition of cost-effective biodiesel production routes.

According to preliminary estimates from the European Environment Agency, referring to the EU-27, in 2019, transport GHG emission further increased by 0.8 % after a 0.9 % increase registered in 2018. These projections anticipate that the transport sector is unlikely to contribute in achieving the climate neutrality by 2050 [3]. In 2011, White Papers stated that the EU's overall goal is to reduce the greenhouse gases emissions from transport by 2050 to 60 % below the one in 1990, and, by 2030, the reduction was set to 20 % below the 2008 level [4]. Considering that urban transport contributes by a quarter of the CO_2 emissions from the transport sector, biofuels play an important role in achieving the ambitious reduction targets.

Biodiesel contributed with a world production of 41 billion L in 2019 with Europe being the largest producer with 38 % of the global output [5]. EU's key feedstock is rapeseed oil while the American continent is dominated by the use of soybeans. It is worth noticing that in Germany, the EU's biggest biodiesel producer, the share of biodiesel produced by waste cooking oils (WCO) exceeded the rapeseed oil-based one in 2016.

This consideration brings to one of the most discussed issues in the biodiesel research community: the feedstock selection. Due to the food versus fuel debate, edible crop-based biodiesel has been discouraged, and the selection of alternative feedstocks has found very high interest in both academia and industry. As reported by Gülşen et al. [6] and

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confirmed by several authors [7–10], the price of the feedstock represents 80-85 % of the total biodiesel cost. The cost of waste cooking oils is 2-3 times lower than the cost of vegetable oils [11], setting a clear direction from where the optimization of biodiesel production should begin. The use of WCO has also the benefit of reduction of the oil residue that is poured down the drain at domestic level resulting in pipes clogging, sewer overflow, high wastewater treatment costs, and environmental issues [12]. Despite the economic and environmental benefits, the use of WCO presents some challenges, mainly related to the presence of free fatty acids (FFA) formed during the frying process by hydrolysis of the triacylglycerols in the oil and the food moisture. The presence of FFA influences the choice of the biodiesel production route and, in particular, the type of catalyst that can be used. Biodiesel is produced by the triacylglycerols transesterification reaction with a low-molecular-weight alcohol. This reaction can be catalyzed by both acid and alkali, but it was highlighted that alkali-catalyzed transesterification reactions can achieve a higher yield in short reaction time and under mild conditions [13]. However, FFA are saponified in presence of alkali catalysts, reducing the overall yield of the reaction and increasing the amount of catalyst required. A limit value of FFA of 1 % w/w was suggested by different researchers to economically perform transesterification reactions using an alkaline catalyst [14–16]. In order to combine the convenience to operate with cost-competitive feedstocks and the high reaction yields achievable with alkali catalysts, a two-step process is normally recommended. In the first step, the FFA are esterified through an acid-catalyzed process. In the second step, the esterified feedstock is converted into biodiesel through alkali catalyzed transesterification. Different catalysts and different operating conditions have been explored in the literature to increase the competitiveness of the whole process. For example, Corro et al. [17] developed a two-step process where the FFA are esterified using a heterogeneous SiO_2 pretreated with hydrofluoric acid catalyst. The activity of the catalyst remained unchanged for 10 consecutive batches. The authors performed the second step with a traditional NaOH-based catalysis. Other authors focused on the optimization of the reaction conditions using homogeneous catalysts in both steps [18–20]. The two-step catalytic conversion process was recently reviewed by Thoai et al. [21]. The authors concluded that the two-step process has proven to be superior to the one-step alternative in terms of conversion, biodiesel yield, smoother reaction conditions, amount of alcohol and catalyst requirement. Moreover, the excessive cost of heterogeneous catalysts may negatively affect the biodiesel production cost.

Besides the choice of the feedstock and the definition of the reaction steps, the synthesis of the separation unit is essential to reach a biodiesel purity that meets the market requirements. Low-quality biodiesel can indeed compromise the engine performance and complicate its storage and transportation [22]. As recently reviewed by Bateni et al. [23], biodiesel purification techniques can be classified as: equilibrium-based (distillation, extraction), affinity-based (adsorption, ion exchange), membrane-based, and reaction-based (reactive distillation, membrane bioreactor). Among all the possible methods, reactive distillation (RD) represents an intensified process alternative where reaction and separation are carried out in the same equipment, leading to operative and capital cost reductions quantified between 15-80 % respect to conventional set-ups [24]. RD has reached the industrial application for reactions where the maximum conversion is limited by chemical equilibrium like esterification, transesterification, hydrogenation of aromatics, etherification, hydrolysis, hydrodesulfurization, isobutylene, and ethylbenzene production [24, 25]. Based on these premises, biodiesel production can also benefit from the application of reactive distillation.

Kiss et al. [26] considered RD for the esterification of a waste raw material composed of 100 % FFA (dodecanoic acid) with methanol using a solid acid catalyst. The authors highlighted that a shorter reaction time, a limited excess of alcohol, lower capital cost, and no further separation steps were achieved compared to conventional processes. Later, their configuration was improved by heat integration, and the controllability of the system was proved [27]. Cossio-Vargas et al. [28] used the same principles to produce biodiesel from a mixture of oleic, linoleic, and dodecanoic acids with a homogeneous catalyst and methanol. Their main contribution regards the exploration of thermally coupled reactive distillation alternatives, but it is not reported a correspondence between the feed composition chosen and a real case. Other studies [29, 30] considered RD for the heterogeneous and homogeneous alkali and acid transesterification of soybean oil with methanol modeling the feed using a single triacylglycerol as a model molecule. More recently, Perez-Cisneros [31] presented a two-step RD process where the first column performs the esterification reaction using a heterogeneous acid catalyst while the second one is dedicated to the transesterification reaction with a heterogeneous alkali catalyst.

Starting from the consideration that waste cooking oil, two-step process, and reactive distillation have the potential to reduce the biodiesel production cost, this work explores the combination of these three elements introducing the following novelties:

1 Waste cooking oil without any preliminary treatments like dehydration or deacidification was used for the experiments
2 Differently from studies based on pure triglycerides or synthetic acid samples, the kinetic parameters were obtained experimentally using WCO
3 A two-step process composed of homogeneous esterification followed by an RD for the homogeneous alkali transesterification was used.
4 The economic potential of the solution was evaluated.

2. Material and methods

All chemical reagents used were of analytical grade and used without any purifications or treatments. Methyl esters were identified by gas chromatography-mass spectroscopy (GC-MS, Perking Elmer Clarus 500). Quantitative determinations were performed using a Varian 3800 GC-FID. FAMEs were quantified using methyl heptadecanoate as an internal standard, while mono-, di- and triglycerides were derivatized with pyridine and N-methyl-N-trimethylsyliltrifluoroacetamide (MSTFA) and quantified using a calibration curve determined using 1,2,3-tricaproyilglycerol (tricaprin) as a standard. Both instruments had cold on-column injectors with an HP-5MS capillary column (30 m; Ø 0.32 mm; 0.25 μm film).

Metal analysis (Na, K, Mg, Ca, Al, S e P) of WCO, oily, and methanolic phases obtained from the esterification process were carried out using a 7000X ICP-MS instrument (Agilent Technologies). 0.5 g of sample was mineralized in 9 mL of HCl (37 wt. %), 3 mL of HNO_3 (67 wt. %), 4 mL of H_2O_2 (50 wt. %) for 2 h at 503 K using a Milestone START E microwave oven. The mineralized samples were solubilized into 100 mL of Milli-Q water (0.6 $\mu S^2\ m^{-2}\ \Omega$), filtered, and analyzed.

Water content was determined according to the ISO 11465 method [32].

Saponification number (SN) was determined according to the procedure ISO 3657 [33].

Ashes were determined by weighing the residue obtained after about 100 g sample stayed in the oven at 550 °C for 3 h. All experiments were conducted in triplicate, allowing the average value and the standard deviations to be obtained. The mean value for each parameter was eventually reported, with a relevant variability that did not exceed the 5%.

2.1. FFA content determination

Free fatty acids content was determined by titrating 2 g of sample dissolved in 50 mL of diethyl-ether-to-ethanol solution (1:1 v:v) using 0.1 N KOH solution and phenolphthalein as indicator. Results were reported as milligrams of KOH to neutralize 1 g of oil (mg KOH g^{-1}).

2.2. Characterization of the waste cooking oil

Waste cooking oil (WCO) was collected by GF Energy, S.A. Kiffisias 56, P.C. 15125 Maroussi, Athens, Greece. The sample was characterized in terms of water content (ppm), acid value (mg KOH g^{-1}), FAMEs, mono-, di- and triacylglycerols (wt%), and ashes (ppm).

2.3. Free fatty acid profile and determination of average molecular weight

50 mg oil were dissolved in 2 mL toluene, 2 ml methanol, and 0.01 ml concentrated H_2SO_4. The reactor was then placed into an ultrasonic bath at 70 °C for 5 h. After this treatment, 1 mL of 1000 ppm methyl heptadecanoate-toluene solution was added as an internal standard, and 1μL of the resulting solution was analyzed gas-chromatographically.

The average molecular weight (AMW) was determined according to the following equation:

$$\mathrm{AMW} = \frac{\Sigma A_i \ MW_i}{\Sigma A_i} \tag{1}$$

where A_i and MW_i are the area and molecular weight of FFAs, respectively.

2.4. Pretreatment of WCO with aluminum chloride hexahydrate

In a typical reaction, 1.05 g $AlCl_3 \bullet 6H_2O$ was dissolved into 100 g of methanol in a 500 mL Pyrex reactor. Then, 300 g WCO were added to reach the final weight ratio of oil-to-methanol equal to 3:1 and a molar ratio catalyst to FFAs of 10%. The reactor was closed and placed into a thermostatic bath for 2 h at 70 °C under agitation using a magnetic stirrer. At the end of the process the system was cooled and allowed to be separated into i) a methanolic layer in which the catalyst is dissolved and ii) an oily phase. The two layers were separated, weighed, and analyzed in terms of: methanol content (gas-chromatographic determination), water (loss of weight at 105 °C after 24 h), ashes, metals, residual acidity, FAME, mono-, di- and triglycerides contents were eventually determined. Finally, reactive conditions were optimized: catalyst loaded (5, 7 and 10% mol with respect to the starting FFAs) and reaction time (2, 4, 8 and 16 h) were investigated.

2.5. Transesterification of pretreated oil with methanol

The transesterification reaction was carried out in a 20 mL glass reactor equipped with a silicone septum which allowed sampling throughout the reaction without interrupting the agitation and heating of the reactive system. The experimental setup is reported in Fig. S1 of the Supplementary material. 10.8 g of the oily phase obtained from the pretreatment with $AlCl_3 \bullet 6H_2O$, were introduced into the reactor with 1.0 g of fresh methanol. The system was closed and placed into a thermostatic oil bath at 40, 60 and 70 °C, and magnetically stirred (400 rpm). Temperature range was defined knowing that the maximum yield is expected in the range 60-75 °C [34]. Then, a previously prepared methanol solution of KOH (84 mg in 0.5 g of methanol) was introduced via syringe into the reactor to obtain a final alcohol-to-oil molar ratio of 6:1 and a catalyst loading of 0.83 wt% with respect to the mass of oil. Samples (0.5 mL) were up-taken after 0, 1, 2.5, 5, 10, 15, 30, 60, 120, 240, and 480 minutes, and transferred into vials, in which 0.05 g glacial acetic acid was previously weighed to immediately quench the transesterification. Then, methanol was evaporated, and the residual oil was analyzed gas-chromatographically for FAME using methyl heptadecanoate as internal standard, while mono-, di- and triacylglycerols were determined with respect to tricaprin.

2.6. Kinetic modeling

The transesterification of triacylglycerols (TAG) to produce biodiesel (FAME) is defined as a set of three consecutive and reversible reactions, as seen in Fig. 1. In this case, TAG first reacts with methanol (MeOH) to produce diacylglycerols (DAG), which reacts with another molecule of methanol producing monoacylglycerols (MAG). MAG will finally release one mole of glycerol (Gly) when reacting with methanol. Each reaction forms one mole of FAME. The forward and reverse reactions occur at different reaction rates with their corresponding rate constants ($k_{\pm i}$) and follow the second-order overall kinetics [35, 36].

Based on these assumptions, the rate expressions for the concentration of each substance were evaluated according to Eqs. 2-7:

$$\frac{d[TAG]}{dt} = -k_1[TAG][MeOH] + k_{-1}[DAG][FAME] \tag{2}$$

$$\frac{d[DAG]}{dt} = k_1[TAG][MeOH] - k_{-1}[DAG][FAME] - k_2[DAG][MeOH] + k_{-2}[MAG][FAME] \tag{3}$$

$$\frac{d[MAG]}{dt} = k_2[DAG][MeOH] - k_{-2}[MAG][FAME] - k_3[MAG][MeOH] + k_{-3}[Gly][FAME] \tag{4}$$

$$\frac{d[FAME]}{dt} = (k_1[TAG] + k_2[DAG] + k_3[MAG])[MeOH] - (k_{-1}[DAG] + k_{-2}[MAG] + k_{-3}[Gly])[FAME] \tag{5}$$

$$\frac{d[Gly]}{dt} = k_3[MAG][MeOH] - k_{-3}[Gly][FAME] \tag{6}$$

$$\frac{d[MeOH]}{dt} = (k_{-1}[DAG] + k_{-2}[MAG] + k_{-3}[Gly])[FAME] - (k_1[TAG] + k_2[DAG] + k_3[MAG])[MeOH] \tag{7}$$

The software Matlab v9.6 (MathWorks, Inc.) was used to solve the differential equations and to obtain the kinetic parameters based on the experimental data of components concentrations as a function of the reaction time. The kinetic parameters were obtained at 40, 60 and 70 °C by minimizing the normalized objective function (OF) reported in Eq. 8.

$$OF = \sum_{j=1}^{N_c} \sum_{i=1}^{N_p} \left(\frac{C_{model\ i,j} - C_{experimental\ i,j}}{\max\left(C_{experimental,\ j}\right)} \right)^2 \tag{8}$$

Where N_c is the number of components and N_p the number of experimental points.

From the kinetic parameters at different temperatures, the temperature dependence of the reaction rate constant was established through the Arrhenius equation, given by:

$$k_i = A\exp - E_a/RT \tag{9}$$

Where E_a is the activation energy, R is the universal gas constant, A is the pre-exponential factor, and T is the reaction temperature.

2.7. Process simulation

The RD process was simulated using the software Aspen Plus V11 considering a flowrate of pretreated oil of 1484 kg h^{-1}. The rigorous stage-by-stage RadFrac model with rate-based calculation type was used to describe the coexistence of reaction and phase transfer. The UNIFAC (Dortmund modified) was set as a thermodynamic method according to the study of Kuramochi et al. [22] that investigated vapor-liquid equilibrium (VLE) and liquid-liquid equilibria (LLE) of several binary and ternary mixture, including the VLE of methanol-biodiesel and methanol-glycerol mixtures, the LLE of water-biodiesel, methanol-biodiesel-glycerol, and methanol-water-biodiesel mixtures and compared the results with those predicted by several methods derived from the UNIFAC approach. They reported that the Dortmund modified UNIFAC was the most appropriate one to model the VLE and LLE of

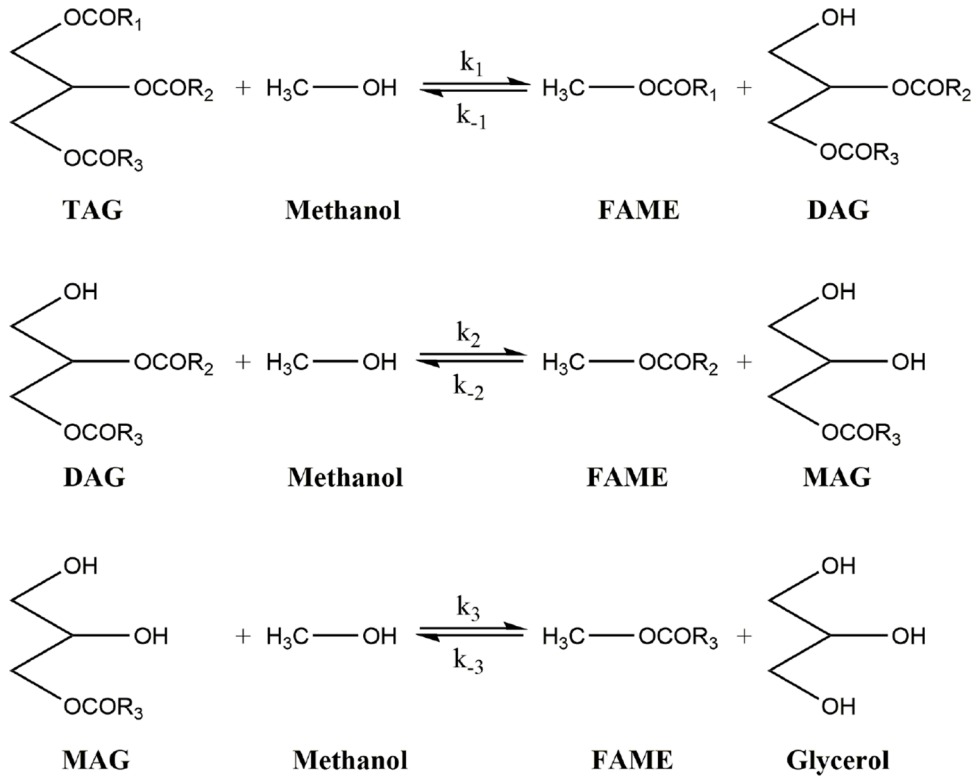

Fig. 1. Reaction scheme of the transesterification of TAG. R1, R2 and R3 are the linear fatty acid chains present in the triacylglycerols.

methanol-soybean biodiesel and methanol-glycerol mixtures. Moreover, Dortmund modified UNIFAC allows the prediction of water solubility in biodiesel, which represents an important information in the design of the biodiesel purification process. Other works on biodiesel production through RD have also successfully applied the UNIFAC model [26-28, 37, 38].

Stage efficiency was assumed to be equal to 1, and pressure drops in the column were neglected. The RD column was considered equipped with a kettle reboiler and a fixed tube overhead condenser. The plant is assumed to operate 8000 h y^{-1}. The capital costs (CC) were estimated through Aspen Economic Analyzer, and they are annualized assuming a linear depreciation over 10 years of lifetime. The operating costs (OC) were evaluated based on the utility consumption associated to the reboiler and condenser duty.

3. Analysis of the results

3.1. Process step 1: WCO pre-treatment for the direct esterification of FFAs into methyl esters

The chemical parameters of the starting WCO feedstock and the pretreated oil are reported in Table 1. The acidity (FFA) of this sample was 8.05 $mg_{KOH}/g_{oil,}$ whereas the water content was 701 ppm. The profile of FFAs was gas-chromatographically determined and the results obtained are reported in Table 2.

Due to the initially higher content of FFA, this sample resulted unsuitable to be converted into biodiesel through a direct alkaline transesterification and the pretreatment was necessary. A pretreatment process based on the use of direct esterification with methanol conducted under $AlCl_3 \bullet 6H_2O$ catalysis was considered [39]. The effects of the catalyst loaded, and the reaction time were investigated with the aim to determine the best experimental conditions required for an efficient conversion of initial FFAs into the corresponding methyl-esters. In detail, a molar ratio catalyst to FFAs of 5, 7 and 10% were tested. The results are shown in Fig. 2.

Table 1
Water content, acid value, FAMEs, mono-, di- and triacylglycerols, ashes, and metal content of the raw WCO and pretreated oil.

Chemical composition	Waste cooking oil	Pretreated Oil
Water content (ppm)	701 ± 8	100 ± 6
Acid value (mg KOH g^{-1})	8.05 ± 0.04	1.05 ± 0.03
FAMEs (wt%)	Traces	3.5 ± 0.2
Monoacylglycerols (wt%)	0.8 ± 0.1	0
Diacylglycerols (wt%)	3.9 ± 0.1	2.8 ± 0.1
Triacylglycerols (wt%)	90.9 ± 0.3	93.2 ± 0.4
SN	194 ± 1	190 ± 1
Ashes (ppm)	100 ± 11	< 2
Metal content		
Na (ppm)	<0.1	<0.1
K (ppm)	<0.1	<0.1
Ca (ppm)	13.3 ± 0.2	<0.1
Mg (ppm)	9.2 ± 0.3	<0.1
P (ppm)	<0.1	<0.1
S (ppm)	<0.1	<0.1

Table 2
Free fatty acids composition of the waste cooking oil.

Free fatty acids	[wt%]
Myristic acid (C14:0)	0.2 ± 0.05
Myristoleic acid (C14:1)	-
Palmitic acid (C16:0)	12.4 ± 0.2
Palmitoleic acid (C16:1)	0.4 ± 0.1
Stearic acid (C18:0)	3.9 ± 0.1
Oleic acid (C18:1)	45.6 ± 0.4
Linoleic acid (C18:2)	37.5 ± 0.3
AMW (g/mole)	277.9

The amount of the catalyst loaded has a remarkable effect on the esterification process. Using 10%mol of catalyst with respect to the starting FFAs, a residual acidity of 1.05 mg KOH/g was obtained after only 4 h of reaction. Even using 7 % mol of $AlCl_36H_2O$ made possible to

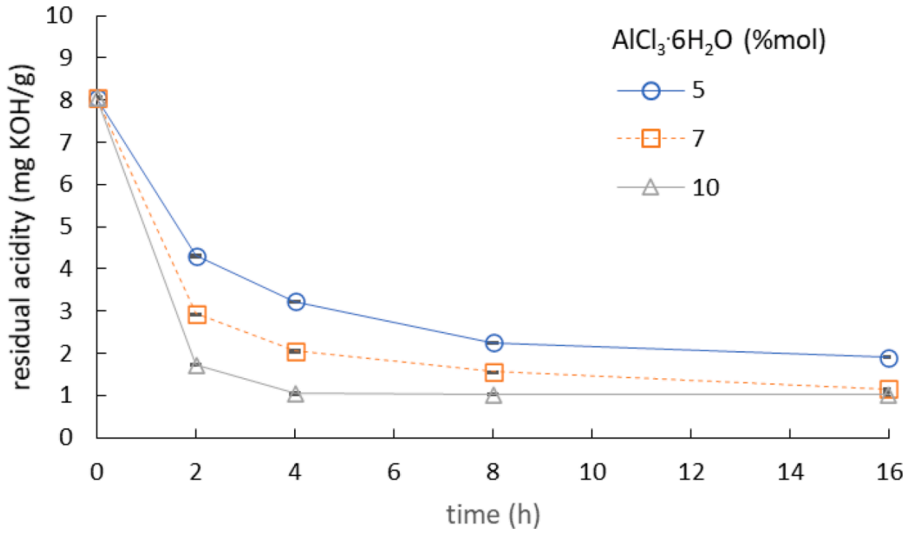

Fig. 2. Effects of the catalyst loading and of the reaction time in the esterification of WCO with methanol using $AlCl_3 6H_2O$ as a catalyst (oil:methanol = 3:1 by weight, 70 °C).

obtain a residual acidity of 1.11 mg KOH/g by extending the reaction time to 8 h. On the other hand, when the catalyst amount was 5 % mol, the residual acidity was 1.92 mg KOH/g after 16 h at 70 °C.

After the reaction, two distinguished homogeneous phases were obtained. On the top, a methanol phase was collected and analyzed. Most of the starting catalyst (> 95 %) was found to be solubilized into the solution, as well as most of the water produced from direct esterification (> 98 %). Whereas, on the bottom, an oily phase with 7 % of methanol was recovered. Part of this oily phase was evaporated to remove methanol and to be fully characterized. The results are reported in Table 1. The oily phase recovered after such a pretreatment, contained a very reduced amount of FFA and water, whereas FAME derived from direct esterification was mostly recovered. In addition, monoacylglycerols, ashes, and metals in general were absent, because they were preferentially solubilized into the methanol phase. Based on this composition profile, the pretreated oil resulted to be ready for alkali catalyzed transesterification without any further treatment. As highlighted by di Bitonto and Pastore [39], the use of $AlCl_3 \bullet 6H_2O$ represents a very promising alternative to the traditional acid-catalyzed pretreatment process based on the use of sulfuric acid. In fact, when sulfuric acid is used to promote direct esterification, partial dissolution of the catalyst into the oily phase occurs, and the pretreated oil needs to be washed before being transesterified under alkaline conditions.

3.2. Process step 2: homogeneous transesterification of the pretreated WCO with KOH

In order to design the RD for the transesterification step, it is necessary to evaluate the kinetic parameters for the reaction reported in Fig. 1.

3.2.1. Kinetic study

For comparison purposes, in agreement with the WCO characterization reported in Table 2, the kinetic parameters were obtained assuming that the WCO was composed of an equal amount of oleic and linoleic. Data were obtained with alcohol-to-oil molar ratio of 6:1 and a KOH loading of 0.83 wt. % with respect to the mass of oil. Raw experimental data and data treatment are reported as Supplementary material in Tables S1-S3.

The kinetic parameters at different reaction temperatures obtained from the differential equations Eqs. 2-(7) are presented in Table 3.

The comparison between the estimated and the experimental concentrations of the components is shown in Fig. 3 for the data set obtained at 60 °C. The comparison for 40 and 70 °C is provided in the Supplementary material Figure S2 and S3.

Table 3
Kinetic parameters obtained for the alkali transesterification of WCO at 40, 60, and 70 °C.

Kinetic parameter [L mol^{-1} min^{-1}]	40 °C	60 °C	70 °C
k_1	0.044	1.241	1.160
k_{-1}	0.085	3.008	3.421
k_2	0.249	0.694	1.061
k_{-2}	0.088	0.233	0.431
k_3	0.371	0.938	0.773
k_{-3}	0.006	0.022	0.044

The activation energy, as well as the pre-exponential factor, were obtained from Eq. 9. The values obtained for those variables, valid within the range of 40 – 70 °C are expressed in Table 4.

3.2.2. Kinetic study: comparison with the literature

The kinetic analysis of biodiesel production has been widely discussed in the literature and different reaction schemes were recently reviewed by Raheem et al. [40]. Despite different works considered a single reaction approach where a mole of TAG reacts with 3 moles of alcohol to produce 3 moles of FAME and one of glycerol [41–43], this approach was disregarded. Even if there is a clear advantage in terms of easier mathematical modeling and the necessity of less experimental data, the one-reaction model does not allow control of the biodiesel quality in terms of DAG and MAG maximum allowable content, as reported in the EN14214 [44]. This aspect has also an effect on the synthesis of the separation unit in case additional purification steps are required. Bambase et al. [45] followed the three consecutive equilibrium reactions approach as described in Section 2.6. The authors considered crude sunflower oil as feedstock and sodium hydroxide as the catalyst. The kinetic data obtained are comparable to those presented in this work and a comparative table is reported in the Supplementary material, Table S3.

3.2.3. RD design and optimization

The reactive distillation flowsheet simulated in the process simulator Aspen Plus is reported in Fig. 4.

In this configuration, the excess of methanol is separated as distillate and recycled while the glycerol is removed in the decanter in order to respect the biodiesel purity targets. A purge stream was introduced to

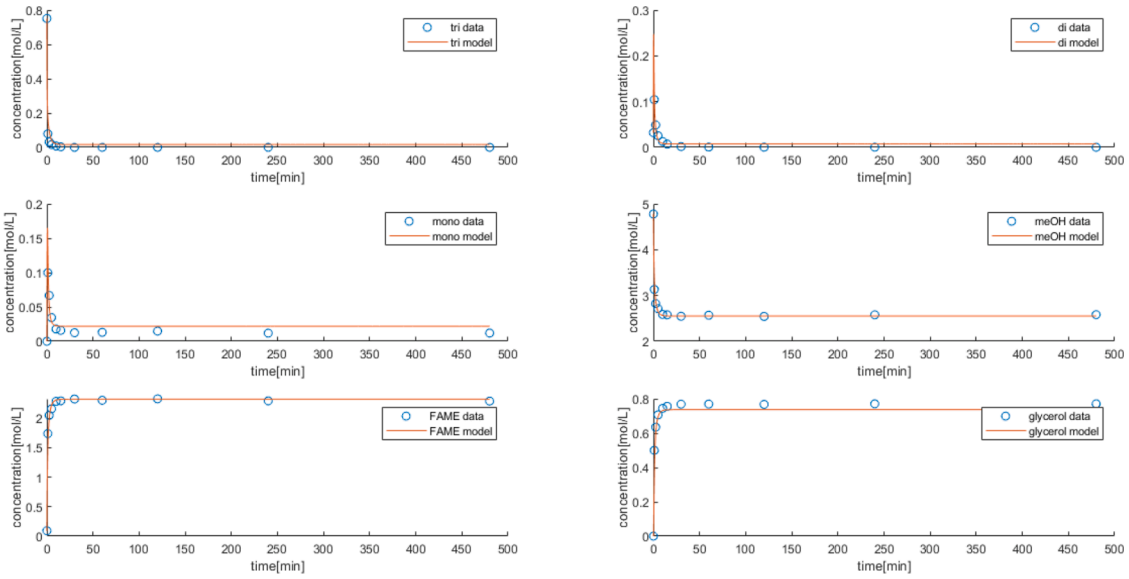

Fig. 3. Comparison between the estimated and the experimental concentrations for a reaction temperature of 60 °C.

Table 4
Activation energy and pre-exponential factor obtained for the alkali trans-esterification of pretreated WCO between 40 and 70 °C.

	E_a [kJ mol^{-1}]	A [L mol^{-1} min^{-1}]
k_1	105.339	$2.0309 \cdot 10^{16}$
k_{-1}	117.221	$3.7463 \cdot 10^{18}$
k_2	43.3471	$4.2640 \cdot 10^{6}$
k_{-2}	46.3823	$4.7006 \cdot 10^{6}$
k_3	24.8289	$5.6007 \cdot 10^{3}$
k_{-3}	57.5755	$2.4839 \cdot 10^{7}$

avoid the accumulation of water in the column. The feed composition was set according to the composition of the pretreated oil reported in Table 1. The content of triglycerides was equally divided between triolein and trilinolein. Diglycerides and FAME were defined accordingly. The amount of alcohol, including the recycled one, was set to respect the alcohol-oil molar ratio defined in the kinetic study.

As discussed by Errico et al. [46] for the purification of bioethanol through RD, its design and optimization require the analysis of different parameters. Here the most relevant ones are discussed. For RD the choice of the column pressure is of paramount importance since it has a direct impact on the temperature profile and therefore on the reaction rates and relative volatilities. In this study the column pressure was set to 1 atm according to the kinetic analysis. This choice allows the use of cooling water in the overhead condenser, and it is consistent with other works on RD for transesterification of triglycerides [27, 30, 31, 47, 48]. An important variable to set is the bottom stream flow rate. This can be theoretically estimated based on the reaction stoichiometry and the amount of TAG in the feed. However, this procedure would lead to a bottom temperature of about 340 °C that compromises the thermal stability of the FAME. Based on the results on biodiesel degradation reported by Li et al. [49], the maximum temperature allowed for the

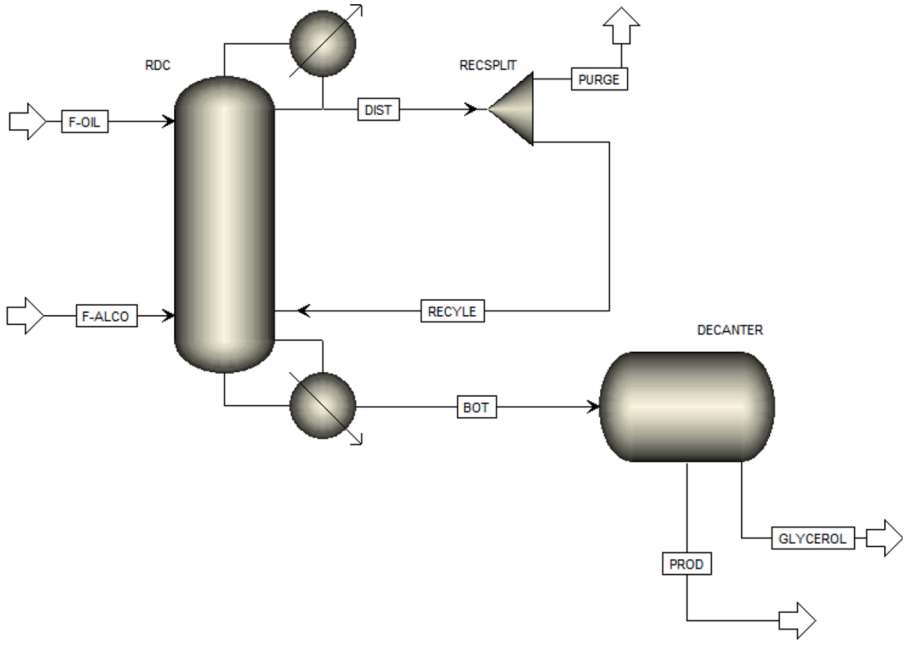

Fig. 4. Reactive distillation flowsheet.

bottom stream was 190 °C. The temperature constraint, together with the purity requirements of the EN14214 [44] in terms of organic components (namely, MG, DG and TG), were included in the *Optimization* function embedded in Aspen Plus. In the optimizer the minimization of the reboiler duty was set as objective function. The optimization was initialized using an initial design where the RD has 30 stages, the pretreated oil and the alcohol being fed at stages 3 and 12 respectively, and the reaction section included between stages 3 and 29.

The minimization of the reboiler duty was achieved by varying the bottom flow rate, reflux ratio, methanol feed rate, methanol split fraction, and stage liquid hold up. The initial values for all the manipulated variables were obtained by preliminary simulations and single variable sensitivity analysis. The variation range and the optimal value obtained for the manipulated variables are reported in Table 5.

The definition of the liquid hold-up is subordinated by the evaluation of the column diameter. In particular, Eq. 10 needs to be satisfied:

$$V \leq \frac{\pi D^2}{4} \cdot h \tag{10}$$

Where V is the liquid hold-up, D is the column diameter obtained after the optimization, and h is the weir height fixed to 12 cm [50]. The influence of the hold-up on the mass purity of the components and reboiler performances is given in the Supplementary material Figure S4 and S5 respectively.

As the last part of the optimization, the liquid phase composition profile of the RD, reported in Fig. 5, was considered for the evaluation of the optimal number of stages.

By the analysis of Fig. 5, it can be noticed that a large part of the stages has very little influence on improving the quality of the products. When the number of stages was reduced to 15 and the optimization was performed with the same boundary conditions, it was found that the reboiler duty increased by only 0.53 kW. The stages were further reduced until was still possible to reach the purity constraints. This limit corresponds to 11 stages with a correspondent reboiler duty of 309.11 kW. To identify the optimal design, an economic evaluation was performed including the capital and operating costs. The results are summarized in Table 6, where the total annualized cost (TAC) was also included.

Based on the TAC presented in Table 6, the final configuration resulted in the one with 15 stages. The product stream characterization for this design is reported in Table 7. The names of the streams were defined according to Fig. 4. The global mass fraction of FAME in exit from the decanter is 0.988.

In the final design the RD column's diameter resulted equal to 0.50 m.

4. Discussion

Considering the two-step process in its overall, the hydrated metal salt pretreatment has the advantage to produce an oil phase that can be directly processed in the transesterification step. This avoids the washing step required with a traditional acid esterification and the consequent generation of waste streams. Moreover, as highlighted by di Bitonto and Pastore [39], the methanolic phase containing the catalyst can be recycled after a treatment with drying agents to keep the residual acidity to a value lower than 1 mg_{KOH} g^{-1}. This has the impact in improving the global economy of the process limiting the consumption of catalyst.

The transesterification step performed in the reactive distillation had a specific heating requirement (SER) of 701.3 kJ per kg of biodiesel produced. To contextualize this value, in Table 8 are compared some relevant works for biodiesel production by RD.

It possible to notice that the transesterification step has an SER between 309 to 1669, even if it should be noted that a direct comparison it is not completely fair due to the differences in the feedstock, catalyst and kinetic model considered.

In particular, Gaurav et al. [29] considered a flowsheet similar to the one reported in Fig. 4. They considered a solid based catalyst of calcium oxide supported on Al_2O_3. Using Aspen Plus, they simulated the RD using pure triolein as feedstock while the kinetic parameters were based on commercial soybean oil and a single reaction scheme. Moreover, the kinetics parameters were obtained at about 20 atm while the RD was designed at 3 atm [51]. The impact of these assumptions on the simulation results were not quantified. The approach of using a model triglyceride to characterize crude soybean oil was also used by Boon-anuwat et al. [30] in the RD modeling for both cases of homogeneous and heterogeneous catalyst. Differently from the previous studies, Pérez-Cisneros et al. [31] considered a sequence of two RDs. The first RD performs the esterification of oleic acid using Amberlyst 15 as catalyst. The authors referred to the kinetic data obtained by Tessser et al. [52] for a pressure range of 2.8-5.3 barg, however, the RD was designed for a pressure of 1 bar. The second RD, used for the transesterification step, has 2 methanol feeds and MgO as solid catalyst. For this configuration the RD bottom temperature was reported to be 329.6 °C, that is above the biodiesel expected decomposition temperature. This arrangement reached the highest SER value among the studies considered.

Poddar et al. [48] compared the application of RD for the homogeneous and heterogenous transesterification reaction of triolein used as representative component of soybean oil. For the homogeneous case they used a 3-reaction scheme, however the distribution of the intermediates was not reported, and it was not possible to verify if the design respects the market purity requirements. The transesterification step was catalyzed by calcium oxide supported alumina with the same kinetic data used by Gaurav et al. [29]. Also in this case there is a difference in the RD operative pressure and the pressure used for the kinetic data.

Differently on what discussed above, the approach followed in this work was to characterize the RD feed in agreement with the chemical analysis performed on the treated oil and to obtain the kinetic parameters from pretreated oil samples and not model solutions.

The SER obtained in this work lies in the range of values reported in the literature with the possibility of further improvement if heat integration would be considered. Nevertheless, the use of heterogeneous catalysts, capable to promote the RD step, could be beneficial in the perspective of circular economy. Pure CaO, or new solid alkaline catalysts obtained by the deposition of CaO onto biochar obtained from avocado seeds [53], to be supported in the RD column, may perform the alkaline step of transesterification without consuming too much alkaline catalysts, which is a weakness point of the homogeneous catalysis.

It is important to note that the proposed process consists of a batch reactor followed by a continuous reactive distillation, which implies some important operative aspects that should be properly addressed. First, an accumulation tank is required for assuring a continuous feed to the reactive distillation column and reducing possible variations of column inlet compositions. Anyway, considering that the range of a single component in a feedstock is very broad, the operation of the pretreatment step involves some difficulties that can be addressed using optimal control, that means finding the time dependent profiles of the control variable to optimize a particular performance index. Then, the control of the reactive distillation column is required to effectively maintain the quality of the product at the designed targets. Considering that disturbances may seriously affect the transesterification steps,

Table 5
Manipulated variables range and optimal values for the reboiler duty minimization.

Variable	Lower bound	Upper bound	Optimal
Bottom flowrate [kg h^{-1}]	1600	1660	1650.75
Reflux ratio [kg kg^{-1}]	0.5	50	16.85
Methanol flow rate [kg h^{-1}]	160	180	167.81
Methanol recycle fraction	0.95	0.9999	0.95
Liquid hold-up [L]	10	23	23
Reboiler duty [kW]			290.24

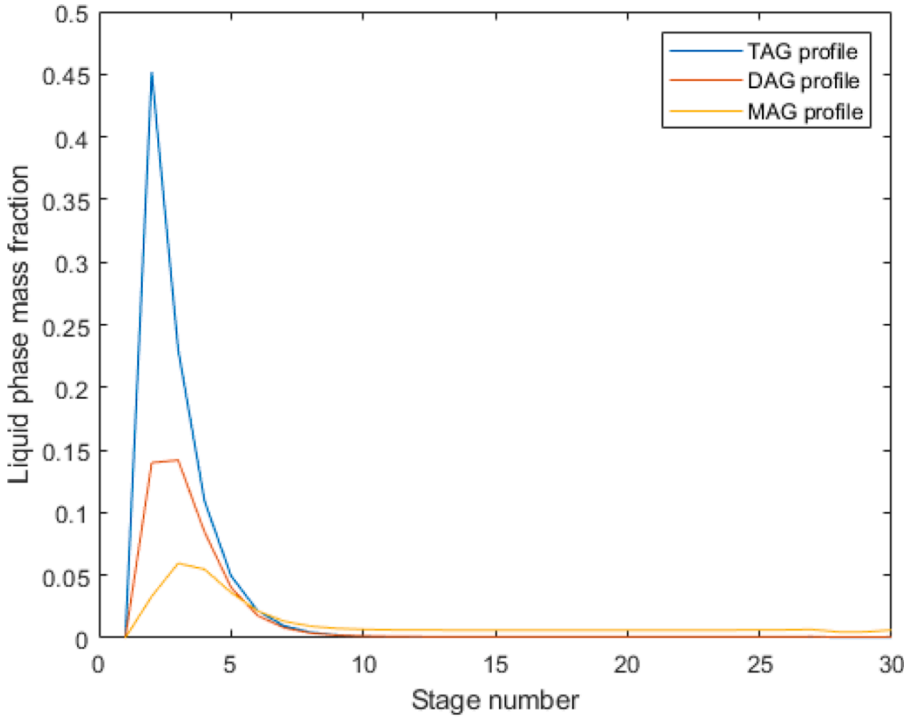

Fig. 5. Composition profile for the optimized design reported in Table 5.

Table 6
Energy consumption and economic evaluation for the RD stage optimization.

RD number of stages	11	15	30
Reboiler duty [kW]	309.11	290.77	290.24
Condenser duty [kW]	154.00	135.57	134.98
CC [$]	321000	344200	466500
OC [$ y^{-1}]	133545	125669	125236
TAC [$ y^{-1}]	165645	160089	171886

direct concentration control can be a valid solution, where state-estimation techniques can be used to estimate the controlled variables when their measurements are delayed or not available on-line.

5. Conclusions

A metal hydrated-salt based catalyst for direct esterification of waste cooking oil was considered as pretreatment for a 2-step process for biodiesel production. The esterified phase was directly used for the transesterification step through a reactive distillation column. Based on

Table 7
Stream characterization for the RD final design.

	F-oil	F-Alco	Dist	Purge	Bot	Prod	Glycerol
Flow rate [kg h^{-1}]	1484.02	168.22	32.89	1.64	1650.59	1492.55	158.04
Temperature [K]	293.15	293.15	339.52	339.52	447.00	293.15	293.15
Mass fractions							
Triolein	0.4659	0.00	0.00	0.00	0.0003	0.0005	0.00
Trilinolein	0.4659	0.00	0.00	0.00	0.0003	0.0006	0.00
1,2-diolein	0.019	0.00	0.00	0.00	0.0006	0.0007	0.00
1,2-dilinolein	0.019	0.00	0.00	0.00	0.0006	0.0007	0.00
Olein	0.00	0.00	0.00	0.00	0.0032	0.0035	0.00
Linolein	0.00	0.00	0.00	0.00	0.0032	0.0035	0.00
Methyl-oleate	0.015	0.00	0.00	0.00	0.4500	0.4942	0.00
Methyl-linoleate	0.015	0.00	0.00	0.00	0.4500	0.4942	0.00
Glycerol	0.00	0.00	0.00	0.00	0.0907	0.0000	0.9457
Methanol	0.00	1.00	0.890	0.9301	0.0070	0.0020	0.0542
Water	0.0002	0.00	0.110	0.0699	trace	0.0000	0.0003

Table 8
Literature specific heat requirement comparison.

Ref.	Feed	Reaction	Kinetic	Catalyst	Process	SER [kJ kg^{-1}]
[29]	Triolein	Transesterification	1 equilibrium reaction	Heterogeneous	RD	553
[30]	Trilinolein	Transesterification	3 equilibrium reactions	Homogeneous	RD + distillation	584
[30]	Trilinolein	Transesterification	1 equilibrium reaction	Heterogeneous	RD + distillation	309
[31]	Triolein	Transesterification	3 equilibrium reactions	Heterogeneous	RD	1669
[48]	Triolein	Transesterification	3 equilibrium reactions	Heterogeneous	RD	341
[48]	Triolein	Transesterification	3 equilibrium reactions	Homogeneous	RD + liquid-liquid extraction + distillation	475

real waste cooking oil samples, the esterified phase was characterized and used to obtain new kinetic parameters for the biodiesel production scheme. The reactive distillation scheme was modeled using experimental data and using a reaction scheme with the intermediate compounds. This approach overcomes the simplification of lumping the triacylglycerols as a single component to represent the oil, allowing a more reliable modeling of the transesterification step. The use of a three-reaction scheme in the reactive distillation allows the evaluation of biodiesel purity requirements making possible the comparison of the simulation results with the market requirements in terms of impurities. The reactive distillation was designed minimizing its reboiler duty taking into account the constraints imposed by the possible biodiesel degradation and the maximum amount of intermediates allowed in the product stream. The corresponding specific heat requirement for the transesterification step was evaluated in 701.3 kJ per kg of biodiesel produced.

Authors contribution

All the authors equally contributed to the work conceptualization, writing and editing. M.Grosmann, T. A. Andrade, and M. Errico performed the kinetic analysis and the process modelling. L di Bitonto and C. Pastore planned and performed the experimental campaign. M. Errico, C. Pastore and M. L. Corazza were responsible for the funding acquisition and project administration.

Declaration of Competing Interest

None.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2022.108980.

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