

## Full Length Article

## Two steps methanolysis and ethanolysis of olive pomace oil using olive-pomace-based heterogeneous acid catalyst

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## ABSTRACT

Olive pomace (OP) and olive pomace oil (OPO) are low-cost, non-edible, by-products of olive oil processing. Converting OPO into biodiesel by (trans-)esterification and olive pomace into a heterogeneous acid catalyst by sulfonation with sulfuric acid could promote waste-to-energy actions. OPO has a high fatty acid content of 126.39 mg<sub>KOH</sub>/g<sub>oil</sub>, which does not allow the use of base catalyst for biodiesel production. Homogeneous acid catalyst such as sulfuric acid could be used, however the wastewater should be neutralized and the catalyst could not be regenerated nor reused.

The objective of this paper is to use the OP to produce a heterogeneous acid catalyst, that will be used in the esterification reaction of OPO to produce biodiesel.

OP was pyrolyzed, activated with steam and sulfonated. Then OPO esterification was performed as at 60 °C and 65 °C for 5 h under agitation at 400 rpm using methanol and ethanol, respectively. The optimization of reaction was performed using a full factorial design by varying oil-to-methanol/ethanol molar ratio (1:3, 1:6, and 1:9) and catalyst loading (10 wt%, 15 wt%, and 20 wt%). The optimum esterification conditions were obtained at 1:9 oil-to-ethanol molar ratio and 20 wt% catalyst. Final products acidities reached 1.14 mg<sub>KOH</sub>/g<sub>oil</sub> and 3.89 mg<sub>KOH</sub>/g<sub>oil</sub> with methanol and ethanol, respectively.

Work was then focused on ethanolysis and a second step of homogeneous alkali-catalyzed transesterification was performed. FAEE yield registered 95.7% using the products of optimized first step. The physical and chemical properties of final product were measured and they respect EN14214 requirements except glycerides contents that were slightly higher than the norm. It registered a viscosity of 3.38 mm<sup>2</sup>/s, a flash point of 168 °C, and a Cold Filter Plugging Point of 14 °C. Its Copper Strip Corrosion class (1a) respects EN14214. Solid catalyst was regenerated and reused up to 6 cycles before being mechanically degraded.

## 1. Introduction

The increasing greenhouse gas emissions, air pollution, and climate change are some of the most serious issues that the world is urged to deal with. Global energy efficiency problems are worsening these issues. One of the largest sectors contributing to pollutant emissions is the transportation sector. In Europe, Transport represents almost a quarter of Europe's greenhouse gas emissions [1].

Biodiesel as a renewable alternative to diesel fuels has a good share of EU's future transportation fuels. Life-cycle analysis has shown that the

source-to-wheel CO<sub>2</sub> emissions savings from neat biodiesel combustion account for at least 60% with respect to petroleum diesel fuel, whereas for the most popular B20 blend it is of the order of 15–20% [2].

Moreover, the objective and reinforcement on legislative and regulatory pathways have encouraged the increasing use of biodiesel fuel. In EU itself, the consumption of biodiesel has experienced an impressive growth during the last years growing by 57% from 2007 to 2012 although it descends timidly since 2013 [3]. Nearly, 200 biodiesel plants are operational in Europe today, with a production capacity of over 8,5 million tons.

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Nonetheless, although the renewability of biodiesel is an extremely hopeful fact regarding GHG reduction of transportation sector, other issues should not be ignored, such as food prices and biodiversity. With the increase in global human population, more land may be needed to produce food for human consumption. The competition between food and fuel will be the main challenge, since edible oils still the main resource to produce biodiesel. Therefore, research on second-generation biodiesels from non-edible oils has been arisen.

Another peculiarities of biodiesel with respect to other biofuels is the fact that it can be produced from a variety of feedstock. Since each originating oil or fat is characterized by different fatty acid composition, it is not surprising that the final ester product will be different.

Therefore, biodiesel is a fuel produced from edible and non-edible vegetable oils including used cooking oils or animal fats like tallow and fish oil [4]. The production of biodiesel could be differed by two ways; esterification and *trans*-esterification. Esterification is performed to produce biodiesel from fatty acids, while *trans*-esterification is performed to produce biodiesel from triglycerides [5]. The transformation to biodiesel is being proposed as it is economically competitive and offers significant environmental benefits compared to conventional fuels especially toward the mitigation of greenhouse effects [6,7].

Olive pomace oil (OPO) as a non-edible by-product from olive oil production process has a low acquisition cost. Composition of OPO can be characterized by, lipid and free fatty acid (FFA) contents. There is a large variety of fatty acid types regarding the carbon chain length and its saturation level, but there are 3 types of fatty acids that are majorly present in OPO, namely the oleic acid (C 18:1), palmitic acid (C 16:0), and linoleic acid (C 18:2). More than 50% of fatty acid content in OPO is oleic acid. As reported by Alvarez Mateos et al. [8], the oleic acid content OPO ranges from 69.5% to 78.4% depending on the season [9]. Used OPO from Tunisia contains 54.68% FFA [10], while its content in Jordan, Turkey and Portugal are around 59.03–63.81% [11], 62.26%, and [12] 75%, respectively. This by-product is appropriate for producing biodiesel by converting its FFA to become methyl or ethyl esters [13].

In industrial scale, sodium hydroxide and potassium hydroxide are very popular catalysts used to produce biodiesel due to their cheap price and high reactivity [14,15].

However, alkali-catalysts are not suitable for OPO since it contains high amounts of FFA and water. Biodiesel production from high FFA

content using base catalyst forms soap instead of producing Alkyl-esters [16]. Thus, to produce biodiesel from low grade feedstock, a homogeneous acid such as sulfuric acid could be used to catalyze the esterification process [17,18]. But sulfuric acid can cause equipment corrosion and wastewater leaving the process requires neutralization before disposal.

Therefore, heterogeneous acid catalysts can be used to solve these problems. Heterogeneous catalyst and reactants exist in separate physical phases [19]. Thus, they can be easily separated and removed from the mixture using filtration and also they can be recycled in the process. Therefore, it can minimize the loss of the catalysts and achieve a high purity reaction products [20].

In literature, different kinds of heterogeneous catalysts were used. Table 1 shows a comparison between different studies that have dealt with the esterification of highly acid feedstock using different kinds of heterogeneous catalysts. In this table, the comparison takes in consideration feedstock, operating conditions, FFA conversion rate and reusability of catalyst. Among catalysts presented in this table, carbon based ones offer several advantages. Namely, low cost of production since they are made from biomass wastes, high specific surface areas [21] and high conversion rates reaching 98% under mild operating conditions. Furthermore, they can be reused several times while preserving a good activity. This lower deterioration rate after reuse can be mainly attributed to their hydrophobic nature that prevents water produced during reaction from leaching active sites [21].

To perform esterification and transesterification reactions, alcohol is also needed and the most popular alcohol used is methanol because of its cheap price and higher reactivity. However, ethanol could be derived from biomass, which is a sustainable resource [22]. Whereas, methanol is mostly produced from gas and coal [23]. Thus, it is more interesting to use ethanol as it is more environmentally friendly despite its higher price than the fuels from fossil feedstock. In addition, the rules stated from EU Renewable Energy Directive imply that greenhouse gas impact of biofuels in this case shall be taken to be zero. As for toxicology itself, Pohanka et al. [24] reported that accidental methanol poisoning could have much worse impacts than ethanol. Acute intoxication by methanol could happen due to ingestion, inhalation with high concentrations, and adsorption through the skin [25]. Meanwhile for ethanol, it has a low order of acute toxicity to humans from all routes of exposure [26]. Thus, the handling of ethanol would be safer and easier than methanol.

**Table 1**  
Heterogeneous acid catalyst comparisons.

No	Reference	Catalyst	Biodiesel reaction		FFA conversion rate	Reusability
			Feedstock	Reaction condition		
1	González et al., 2017	Oat hull, carbonized at 600 °C for 3 h; sulfonated with H <sub>2</sub> SO <sub>4</sub> at 140 °C for 30 min using microwave	waste cooking oil 3.21 mg	methanol to oil ratio (10:1), 140 °C, 30 min using microwave	75% in 15 min	33% after 6 cycles
2	Endut et al., 2017	Coconut shell, carbonized at 422 °C for 4 h, sulfonated with concentrated H <sub>2</sub> SO <sub>4</sub> at 100 °C for 15 h	Palm oil	methanol to oil ratio (30:1), 60 °C, 6 h	88.15%	n/a
3	Zhou, Niu, & Li, 2016	Bamboo, carbonized at 350 °C in 2 h, sulfonated at 105 °C in 2 h	Oleic acid	Ethanol to oil ratio (7:1)	98.4% after 2 h	93.66% after 5 cycles with re-sulfonation
4	Dias et al., 2012	HUSY zeolite (calcinated with ambient air at 550 °C for 8 h) and Ce/HUSY zeolites (stirred in a cerium nitrate solution at 80 °C and dried and calcinated like HUSY)	Oleic acid from refined soybean oil	Ethanol to oil ratio (30:1), transesterification at 200 °C in 24 h, residual methanol was removed in a rotary evaporator at 70 °C for 24 h	HUSY 99.7%, Ce/HUSY 99.8%	HUSY 96.4%, Ce/HUSY 99.5 after 3 cycles
5	Jiang, Lu, Sun, Ma, & Ding, 2013	Sulfonated cation exchange resin (SCER)	Oleic acid	Ethanol to oil ratio (9:1), 20 g catalyst, 82 °C, 8 h	93%	greater than 80% after 5 cycles
6	Yin et al., 2012	Organophosphonic acid-functionalized silica SG-T-P; Silica gel was activated with HNO <sub>3</sub> at 112 °C for 3 h and HCl at room temp for 6 h and calcined at 160 °C for 10 h; SG-T-P was synthesized	oleic acid	Ethanol to oil ratio (8.8:1), 14.5 wt% catalyst related to oleic acid, 112 °C, 10 h	77%	n/a
7	Oliveira et al., 2010	H3PW (12-tungstophosphoric acid) supported on ZrO <sub>2</sub> with 20% H3PW	Oleic Acid (98%)	Ethanol to oil ratio (6:1), 20 wt% of the catalyst related to oleic acid, 100 °C, 4 h	88%	70% after 2 cycles with calcination at 300 °C in 4 h

In this research, olive pomace oil (OPO) having high free fatty acids (FFA) content was used to produce biodiesel by esterification process using a solid acid catalyst. The use of ethanol as alcohol was investigated and compared to methanol, reputed to be more reactive but less attractive from environmental point of view.

## 2. Experimental procedure

### 2.1. Materials and methods

Olive pomace and unrefined olive pomace oil (OPO), with acidity of 126.39 mg<sub>KOH</sub>/g, were supplied by Abou Al-Walid group in Tunisia, sulfuric acid (17 M), Methanol and Ethanol (99% purity) were purchased from Sigma Aldrich.

### 2.2. Catalyst preparation

The olive pomace was pyrolysed and activated using superheated steam at 800 °C. Then, the obtained activated carbon is sulfonated with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to produce the solid acid catalyst. Activated carbon was sulfonized with 0.4 ml/g of H<sub>2</sub>SO<sub>4</sub> in a glass beaker and stirred for 15 min using an agitator. The activated carbon was dried in an oven for 18 h at 105 °C, after removing excess acid by filtration. After that, the sulfonated activated carbon was washed with distilled water until the pH of the rinsing water remains neutral after washing. Lastly the sulfonated activated carbon was dried in an oven again for 12 h at 105 °C.

### 2.3. Esterification procedure

#### 2.3.1. Esterification reaction

This part was realized to analyze the effect of alcohol type (methanol and ethanol), oil:alcohol ratio (1:9, 1:6, 1:3) and catalyst loading variation (10, 15, 20 wt%). The initial amount of 100 g of OPO was poured in a flat bottom round flask with the alcohol and catalyst regarding the desired condition. The mixture was then heated in a water bath at 60 °C and 65 °C, with methanol and ethanol, respectively, and stirred at 400 rpm for 5 h. A sample of approximately 5 ml was taken each hour to measure the acidity during the reaction (5 h = 5 samples). After 5 h esterification, the mixture was filtered to recover the catalyst. After that, a rotary evaporator was used to separate ethanol from oil. Lastly, final acidity was measured using the final product after the separation. Besides that, the glycerin content in the product including the monoglyceride, diglyceride, and triglyceride should also comply with the standard (EN 14105). The glycerin content was determined using gas chromatography (GC) explained in section 2.5.1.

#### 2.3.2. Acidity measurement

Acid values were measured at each hour of the esterification reaction. Since the esterification was performed for 5 h there will be 5 samples for each condition. For each sample 5 ml were taken from the reaction flask using a syringe and filtered. After that, the sample was washed using distilled water to eliminate alcohol in the solution. After removing the ethanol, 0.5–1 g of the sample was taken to be diluted with 15–20 ml of diethyl ether and ethanol solution. After that, titration using KOH solution is performed. The measured acid values were used to follow the evolution of the conversion rate of fatty acids during the reaction. This measurement is important as the final acid value will affect the transesterification reaction's yield. In addition, the fatty acid conversion rate would also determine the catalyst reusability to see whether the regenerated catalyst could still be used for another cycle.

### 2.4. Transesterification procedure

This process is performed for oil products from esterification reaction. The esterified oil was put in a round flask. For every 100 g of triglyceride in the oil, 40 g of ethanol or 20 g of methanol as the alcohol

and 1.5 g KOH as the catalyst were added. Alcohol and KOH were mixed first before adding them to the oil. The reaction was performed in a thermostatic bath for 5 h at 50 °C and agitated at 400 rpm. After 5 h of reaction, the product was poured in a separatory funnel overnight to separate the biodiesel and glycerine. Then a rotary evaporator was used to separate the alcohol and the biodiesel. Biodiesel yield of transesterification was calculated using Eq. 2:

$$\eta_{\text{Transesterification}}(\%) = \frac{\text{Mass of biodiesel obtained (g)}}{\text{Mass of esterification product (g)}} \times 100\%$$

### 2.5. Characterization

#### 2.5.1. Gas chromatography

Final product was then characterized using a gas chromatograph (GC) coupled to a flame ionizing detector (FID) in order to determine its mono, di and triglycerides content with ASTM method D 6584 and EN 14105. Free and bonded glycerin contents are also parameters of biodiesel quality. A high content of glycerin could be a problem during storage, or in fuel system due to the separation of glycerin. In addition, high total glycerin content could also damage injector, injection nozzles, pistons, and valves, when used in a diesel engine, as it can form deposits. The GC column used for glycerin characterization is an open tubular column with a 5% phenylpolydimethylsiloxane bonded and cross linked phase internal coating. The temperature of the flame ionization detector is 380 °C. The columns, either 10 or 15 m in length, 0.32 mm internal diameter, and 0.1 µm film thickness. The carrier gas is hydrogen with 3 ml/min air flow. Internal standards used for this characterization are 100 µm of butantriol and 100 µm tricaprane for 100 µm of sample. N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) is used for the derivatization. Free glycerin, mono glyceride, diglyceride, and triglyceride contents in compliance with EN 14105 standards could be calculated using the GC results. The standards for glycerin in biodiesel are listed in Table 2 below:

#### 2.5.2. Copper strip corrosion

This test method determines the corrosivity of biodiesel, diesel fuel or other hydrocarbons having a vapor pressure not exceeding 124 kPa at 37.8 °C on the copper strip. A copper strip is immersed in a volume of 30 ml of the test sample and placed in a stainless steel pressure vessel. Then, the container is heated in a water bath at temperature and time conditions specific to the class of the product to be tested (50 °C. maintained for 3 hrs 5 min for the Biodiesel). At the end of the heating period, the copper strip is removed, washed and the color and level of tarnish are assessed against the ASTM copper strip corrosion standard.

#### 2.5.3. Cold filter plugging point (CFPP):

Cold filter plugging point (CFPP) is the temperature below which diesel fuel clogs the fuel filter.

The CFPP of the samples was measured by an NTL 450 of the NORMALAB brand. This apparatus includes a double wall bath with insulation, a heat transfer fluid jacket, a test tube, an insulating ring and annular wedges, a 3-hole stopper, a pipette, a complete filtration set, 1 ASTM 5C thermometer and 2 thermometers 6C. It is cooled by a refrigeration unit.

The results obtained make it possible to evaluate the lowest temperature up to which the analyzed fuel will be able to flow freely. The

**Table 2**  
Glycerine standard.

Property	Unit	Upper limit
Free glycerine/glycerol	% wt	0.02
Monoglyceride content	% wt	0.7
Diglyceride content	% wt	0.2
Triglyceride content	% wt	0.2

lower the CFPP, the less risk there is of clogging the filter in extreme cold.

#### 2.5.4. Flash point

The flash point temperature corresponds to the lowest temperature at which a combustible body emits sufficient vapors to form, with the ambient air, a gas mixture which ignites under the effect of a source of ignition. This property varies inversely with the volatility of the liquid; it plays a very important role in evaluating the energy use of the pure state or as a source of synthesis. Indeed, a high value of the flash point is synonymous with safety during storage, handling and handling of the product. It was determined using a PENSKEY MARTENS NPM440 device with a precision of 1°C.

#### 2.5.5. Viscosity measurement

Dynamic viscosity was measured at 40 °C using an AND vibro viscometer. Density was measured using a pycnometer M50T (850–900 g/l) with a precision of 1 g/l. Then kinematic viscosity was obtained by dividing it by the density according to test method EN ISO 3104.

### 2.6. Catalyst regeneration

In this study, the solid acid catalyst was regenerated first before being reused because regeneration could result in a higher catalyst activity. The used catalyst was washed using heptane while being stirred for 2 days. Heptane was used because its capability to eliminate remaining oil in the catalyst and other impurities. After the regeneration, the heptane was removed by filtering and drying in an oven and remaining oil was recovered and added to esterified oil before undergoing transesterification.

## 3. Results and discussion

### 3.1. Acidity after esterification

The acid values were measured every hour of the reaction to follow the rate of the esterification reaction. Fig. 1 shows the acidity curves of homogeneous reaction which used  $H_2SO_4$  as the catalyst and heterogeneous reaction with two extreme conditions which were the highest and lowest amounts of alcohol and heterogeneous catalyst added. The general trend observed for different curves is the same, a constant reduction of acid value, with a decreasing reaction rate. This decreasing rate can be explained by the formation of water during reaction that slows down reaction via two mechanisms. The first one is by increasing the reverse reaction rate to reach a chemical equilibrium. The second effect is related to the miscibility of catalysts in the water which deactivates its catalytic effect.

The initial acidity of the OPO ( $t = 0$ ) is 126.39  $mg_{KOH}/g_{oil}$ . The acidity decreased by 91%–95% for ethanolysis and 72%–84% for

methanolysis during the first hour of reaction using highest amount of alcohol and catalyst.

#### 3.1.1. Comparison of homogeneous and heterogeneous reactions

When using methanol, homogeneous catalysis appears to be more efficient on the earlier phases of the reaction due to its miscibility with reagents. However, the reaction slows down earlier than heterogeneous case. And after 5 h of reaction, OPO reaches the same acid value obtained using heterogeneous catalyst with 1:6 oil to methanol molar ratio and 10 wt% catalyst load. This tendency can be explained by the hydrophobic nature of the activated carbon that repels formed water which allows to get better esterification conditions on the vicinity of the  $SO_3H$  catalytic sites.

Same trend was observed with ethanol. Since the reaction is faster with methanol (aspect that will be explained later in this paper), the reaction is already faster with heterogeneous catalyst after 1 h of reaction.

Heterogeneous reaction has shown the same performances of homogeneous one using 1:3 oil to ethanol molar ratio and 10 wt% catalyst loading.

#### 3.1.2. Comparison of alcohol effects on esterification process

Although the highest conversion rate obtained with ethanolysis during the first hour of reaction, the methanolysis continues with a steeper slope until reaching lower acid values after 5 h of reaction. The same aspect was observed with homogeneous and heterogeneous catalysis. This change in tendencies could be explained by two main characteristics of ethanol. The first one is its high miscibility with oil that has the tendency to increase reaction rate at the beginning of the reaction as compared to methanol, known to its poor miscibility with lipids. The second characteristic is the tendency of ethanol to form azeotropic mixture with water produced during reaction. This second aspect has a negative effect on the reaction, since it decreases the miscibility of alcohol with oil and it deactivates the catalytic effect of sulfuric acid or sulfonic sites. Furthermore, the hydrophobicity of activated carbon can repel the azeotropic mixture and reduces the adsorption of alcohol inside the pores where the reaction occurs.

Azeotropic effect on esterification using ethanol, was also observed by Lucena et al. who noticed also that it slows down the reaction [27]. Verma and Sharma [16] also compared ethanolysis and methanolysis using the same conditions and have observed same tendencies.

Now, knowing that homogeneous catalysis is faster than heterogeneous one at the earlier stages of reaction and slower at the advanced stages and knowing also that ethanolysis has a faster rate during the first hour of reaction and a faster rate at the late stages, we can understand why the methanolysis using highest catalyst and alcohol loadings (20% and 9:1), starts with a higher acid value during the first 2–3 h and then it reaches the lowest values after 3 h of reaction. In fact it has a bad miscibility at the beginning as compared to homogeneous catalysis and to heterogeneous ethanolysis which slowed it down, but later its lower sensibility to water allowed it to continue with a faster pace at the late stages, to reach their respective acid values after 2 to 3 h and to exceed them after that time.

#### 3.1.3. Effects of catalyst loading and alcohol:oil molar ratio

Figs. 2 and 3 show the contour plots of FFA conversion rates after 5 h of esterification reaction using ethanol and methanol respectively. As it can be noticed, FFA conversion rate increases with addition of alcohol and catalyst with the optimum condition is 1:9 oil to alcohol molar ratio and 20 wt% catalyst load. The lowest acid value was obtained with methanol and it reached 1.14  $mg_{KOH}/g$  which corresponds to a FFA conversion rate of 99%. Using ethanol under the same conditions gave an acid value of 3.9  $mg_{KOH}/g$  corresponding to a conversion rate of 97%. From these contour plots it can be concluded that molar ratio has higher influence on reaction than catalyst loading. This effect is supported by ANOVA that gave lower p-values for molar ratio than catalyst loading.

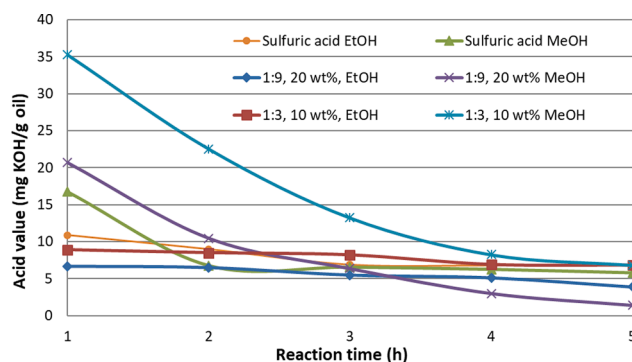


Fig. 1. Acidity curves of homogeneous and heterogeneous reaction using ethanol and methanol.



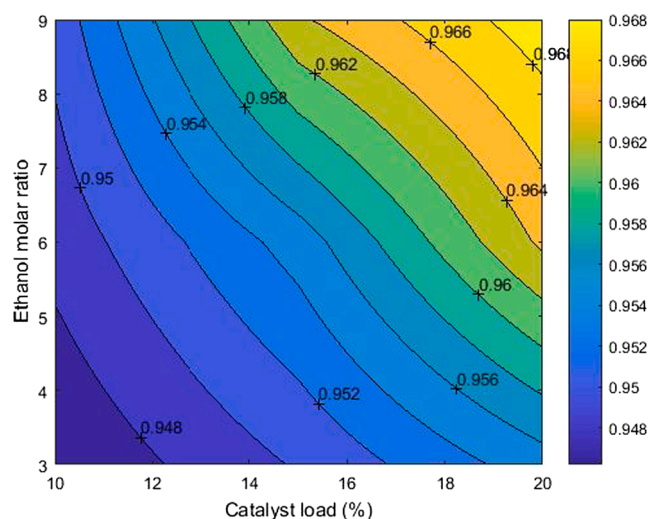


Fig. 2. FFA conversion rates plots after 5 h of ethanolysis.

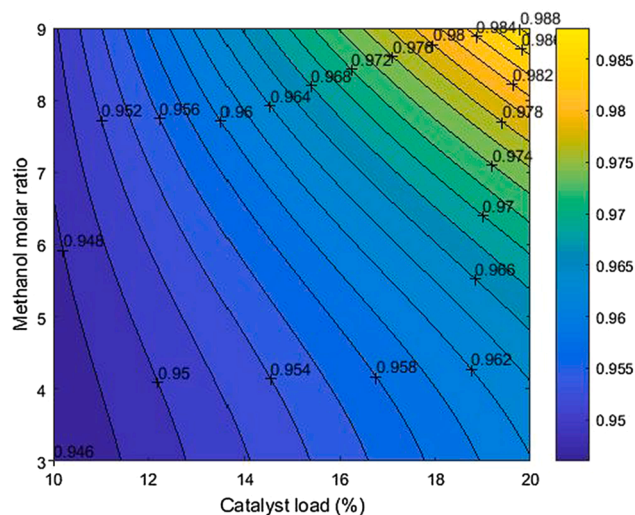


Fig. 3. FFA conversion rates plots after 5 h of methanolysis.

This predominance is more perceptible at low catalyst loads where iso-conversion value curves are more vertical.

The products of esterification were analyzed using GC-FID technique and their viscosities were also measured. Results are listed in Table 3.

It can be noticed that during reaction, glycerides were also degraded, which means that esterification and transesterification were occurring simultaneously during reaction. There is a significant gap between

results obtained with different alcohols under identical conditions. This effect can be attributed to the higher reactivity of methanol as compared to ethanol. Although the better miscibility of ethanol and its positive effects during early stages of reaction on the esterification process, the azeotropic effect coupled to its higher molecular size had decreased its overall reactivity leading to poorer performances as compared to methanol. That was translated in a higher glycerides content and higher viscosities. The reaction with methanol at optimum conditions yielded a product having characteristics very close to EN 14,214 requirements. Further optimization, like extending reaction time, increasing alcohol ratio or removing water during reaction could give a good quality biodiesel that fits European norm in only one step of reaction. However, due to the ecologic profile of ethanol and its good performances during reaction, the rest of the study will only focus on its use in a two-stepped esterification process.

### 3.2. Transesterification results

A transesterification was required after the esterification in order to convert remaining mono-, di- and tri-glyceride into ethyl-esters. As it is known, the FFA content affects negatively the transesterification. Thus, in order to investigate the effects of remaining FFA after esterification on the final yield of the two-stepped reaction, products of esterification having the lowest and highest FFA contents were transesterified.

In addition, the reaction was also performed for esterification product with the highest ethanol to oil molar ratio of 9:1 and the lowest catalyst load of 10 wt% considering the highest effect of molar ratio on esterification.

Besides acidity, the transesterification yield (Eq.4) is also important to see how much biodiesel could be produced from 100 g of OPO. The results of transesterification of the three studied conditions are shown in Table 4.

Since the acidities after esterification of all the samples are not to different, the transesterification yield of samples with the same ethanol molar ratio are almost the same.

From the result above, all of the diglyceride and triglyceride contents are above the standards. However, viscosities of products are compliant with the norm. Products from experiments 1:9, 20 wt% and 1:9, 10 wt% are very close to norm specifications and they could be transformed to good quality biodiesel by increasing reaction time or by a further purification for eliminating unreacted glycerides. The final transesterification product registered a viscosity of 3.38 mm<sup>2</sup>/s, a flash point of 168 °C, and a Cold Filter Plugging Point of −14 °C and it was of class 1a regarding copper strip corrosion. All of these characteristics comply with the EN14214 norm.

The purpose of transesterification part is mainly to prove the concept, i.e. solid acid catalyst from olive pomace activated carbon can bring highly acid feedstock to conditions allowing its transesterification. Since it is more logic to use a solid alkali-catalyst for the second phase, the homogeneous alkali-catalyzed transesterification was not optimized in this work.

### 3.3. Catalyst reusability

One of the benefits of using heterogeneous catalyst is that it can be reused for another reaction cycle. The combination of 1:9, 10% catalyst was used in order to study the effect of regeneration since it allowed to produce the same amount of FAEE as 1:9, 20%. Realized experiments have shown that the catalyst is still active even after 6 cycles. As it can be noticed in Fig. 4, the conversion rate of reaction after 5 h of reaction started to decrease from cycle to cycle until reaching 94% after the 6th use. While this conversion rate is still acceptable, the main limitation to the reuse of catalyst is its mechanical degradation. In fact, its grain size was decreasing over cycles until reaching a powdery aspect that makes its separation from oil very hard after the 6th cycle of regeneration. In fact, after each cycle the catalyst grains become thinner and thinner with

**Table 3**  
Glycerides contents of esterification products.

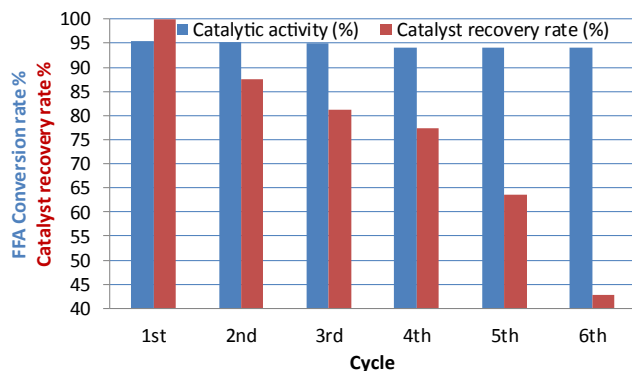
Sample	Monoglyceride	Diglyceride	Triglyceride	Viscosity (mm <sup>2</sup> /s)
1:9, 20 wt%, EtOH	0.2	7.3	0.8	11.8
1:9, 10 wt%, EtOH	2.1	2.6	6.3	18.9
1:3, 10 wt%, EtOH	5.7	8.3	21.4	21.9
1:9, 20 wt%, MeOH	0.4	0.8	0	3.02
1:9, 10 wt%, MeOH	3.8	16.2	0	4.93
1:3, 10 wt%, MeOH	0.25	3.8	12.4	14.4

**Table 4**

Reaction yields, GC-FID and viscosity analysis of transesterification products after FFA ethanolysis.

Sample	Monoglyceride	Diglyceride	Triglyceride	Acid value before TE (mgKOH/g)	Yield (%)	Viscosity before TE* (mm <sup>2</sup> /s)	Viscosity after TE (mm <sup>2</sup> /s)
1:9, 20 wt%.	0.8	2.3	0.07	3.89	95.7%	11.8	3.38
1:9, 10 wt%.	0.32	2.9	0.94	4.5	95.5%	18.9	3.53
1:3, 10 wt%.	5.7	8.3	1.4	6.83	80.1%	21.9	4.38

\* TE = transesterification

**Fig. 4.** Catalytic activity after regeneration.

a decreasing cycle-to-cycle recovery rate. At the second cycle, the recovery was 87% and it dropped to only 43% at the last cycle where only 15% of the original amount of catalyst was remaining. This grinding effect could be responsible of the constant conversion rate of FFA at the 3 last cycles, where the thinner size of catalyst grains enhances mass transfer between reagents and activated carbon and compensates the effect of sites deactivation.

The results of the present work are similar to those obtained by Zhou et al. [28] who used sulfonized carbonized bamboo that they succeeded to reuse up to 5 times after resulfonation with a FFA conversion rate higher than 93.66%. However, the procedure used in the present research is more eco-friendly because it does not require resulfonation. This could be explained by the higher porosity of AC as compared to carbonized biomass, that allows a better fixation of SO<sub>3</sub>H group. On the other hand, Gonzalez et al. [29] used sulfonized carbonized oat hull up to 6 cycles. However, they have observed a drastic decrease in FFA conversion capacity (from 75% to 33%). This drastic decrease could be explained by the accumulation of reaction products inside the pores of catalyst that blocks the access of reagent molecules to active sites. Thus, a regeneration using a solvent like heptane could moderate this drastic decrease.

### 3.4. Sulfuric acid usage balance

As stated in earlier section, the main benefit of heterogeneous catalyst is the reusability, thus the utilization of new catalyst can be reduced. The minimization of new catalyst used would result in reducing the amount of sulfuric acid used during the process, thus given the slight difference in yield and quality of FAEE obtained with 10 and 20 wt% of catalyst, the calculation will be based on a 10 wt% catalyst loading. In addition, the homogeneous reaction resulted in a higher final acid value than the heterogeneous reaction. The final acidity of homogeneous reaction after esterification is the same as the esterification using heterogeneous catalyst with 1:3 ethanol molar ratio and 10 wt% catalyst load. Assuming the transesterification with homogeneous reaction product gives the same result as the transesterification of 1:3 ethanol molar ratio with 10 wt% catalyst product, the biodiesel yield would be 80%. Based on these assumptions, a comparison between specific sulfuric acid use between homogeneous and heterogeneous catalysis was realized. Table 5 summarizes this comparison.

**Table 5**

Sulfuric acid balance for homogeneous and heterogeneous catalysts.

Reaction	H <sub>2</sub> SO <sub>4</sub> used for 6 cycles (ml)	FAEE produced (g)	H <sub>2</sub> SO <sub>4</sub> used (ml)/kg biodiesel
Homogeneous	12	480	25
Heterogeneous	4	570	7

For 1 cycle of homogeneous reaction 2 ml H<sub>2</sub>SO<sub>4</sub>/100 g<sub>oil</sub>, are needed thus for 6 cycles it needs 12 ml of H<sub>2</sub>SO<sub>4</sub> to produce 0.48 kg of biodiesel. Meanwhile for heterogeneous catalyst, it needs 0.4 ml H<sub>2</sub>SO<sub>4</sub> to sulfonize 1 g of activated carbon. Thus, for 10 g of activated carbon only 4 ml of H<sub>2</sub>SO<sub>4</sub> are needed to produce 0.57 kg of biodiesel. The amount of H<sub>2</sub>SO<sub>4</sub> used for heterogeneous reaction is lower than homogeneous reaction and it can be concluded that the amount of H<sub>2</sub>SO<sub>4</sub> used in heterogeneous reaction to produce biodiesel per liter is 72% lower than the homogeneous reaction.

## 4. Conclusions

Heterogeneous catalyst can be produced from olive pomace and it gives better performances than homogeneous one.

The acidity values decreased after esterification with ethanol and solid acid catalyst ranging from 92 to 95% starting from the first hour of reaction until the 5th hour at 65 °C.

The catalyst could be reused after regeneration up to 6 cycles with FFA conversion of 94% and it reduces specific H<sub>2</sub>SO<sub>4</sub> use by 72%. The catalyst regeneration was stopped after 6 cycles due to the decreasing size of the catalyst particles that resulted in a higher acidity and lower catalyst recovered for the next cycle.

Methanolysis has a lower final acidity and a higher yield (1.14 mg KOH/g and higher yield of 99%) than ethanolysis. The best operating condition after methanolysis was from the same condition as the best ethanolysis (1:9 oil-to-methanol 20 wt% catalyst) but resulted in a lower acidity of 1.41 mgKOH/g and higher yield of 96%. This result was because of an azeotropic condition formed due to the reaction of water and ethanol and caused a lower yield than methanolysis.

Despite of the differences, both ethanolysis and methanolysis were affected the most by the amount of alcohol added or the oil-to-alcohol ratio. The highest alcohol molar ratio of 9 resulted in the highest fatty acid conversion and reaction yield. Thus, transesterification was performed on the best ethanolysis conditions (1:9, 20 wt% and 1:9, 10 wt %), and product with the lowest operating condition (1:3, 10 wt%). In conclusion, methanol gave better results, but ethanol is more eco-friendly.

After an alkali-catalyzed step, FAEE yield was higher than 95% and its properties comply with EN14214. However, glycerides content was higher than standard's limits. Optimization of reaction by performing transesterification using methanol could decrease the viscosity to meet the standards.

## Declaration of Competing Interest

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

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