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Research Article

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Biodiesel production from unrefined and refined olive pomace oil: Comparative study

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ABSTRACT

The aim of this study was to determine the optimum conditions of the biodiesel production from refined and unrefined olive pomace oil. The refined olive pomace oil had an acid value of 2.34 mg KOH / g-oil. Therefore, transesterification reaction could be directly applicable due to the low free fatty acids content. To improve the yield of the transesterification reaction, some parameters were optimized: the catalyst and solvent concentration, the temperature and the reaction time. The biodiesel yield reached 100% with the following combination: 15: 100 ml (v/v) methanol to oil volume ratio, 1g of potassium hydroxide, at 50 °C during 60 min. The stirring rate was maintained constant (400 rpm). The unrefined olive pomace oil had an acid value of 44 mg KOH / g-oil. Due to its high free fatty acids content, a pretreatment step, an esterification reaction, was required to decrease the percentage of free fatty acids to the limit allowing the realization of the transesterification reaction. The optimum conditions of the pretreatment process which provided the lowest acid value were as follows, 65:100ml (v/v) methanol and 1.25 ml of sulfuric acid to oil volume ratio, at 50°C during 60 min and at a stirring rate of 400 rpm. Conditions already optimized with the refined olive pomace oil for the transesterification process were preserved for the pretreated one. The yield of the produced biodiesel in that case reached 99 %.

Key words: Biodiesel, free fatty acids, transesterification, esterification, refined and unrefined olive pomace oil.

INTRODUCTION

Tunisia is occupying the fourth ranking in the world olive oil producers [1]. Despite its economical benefits, Olive oil production is generating a huge amount of olive pomace which is containing a highly toxic compound. In Tunisia, the valorization of this waste into renewable energy constitutes new trends. The valorization has many environmental contributions in addition to the economical assets [2-5]. The virgin olive oil is extracted from the olive fruit whereas the residual oil which remains in the olive fruit pulp is well, the olive pomace oil. The olive pomace oil which is a by-product of the olive pomace is considered as a potential feedstock for the biodiesel production [5, 6]. The crude olive pomace oil is extracted directly by impregnation in an organic solvent, usually hexane; however the refined pomace oil is obtained by the refining of the crude one [7]. Due to its low organoleptic properties and the high concentrations of the polycyclic aromatic hydrocarbons (PAH), the crude olive pomace oil is not comestible; furthermore it can have a negative impact on the human health and on the environment too. There is a need for further valorization of this oil as a potential source for biodiesel production with high quality [8]. The interest of the agricultural investors in the conversion of agricultural residues in biodiesel is getting more and more important. It comes from the fact that they are their own suppliers of raw material. Biodiesel is a nontoxic and biodegradable fuel which can be produced from vegetable oils and animals fats containing essentially triglycerides. Biodiesel production could be summarized in two main steps, esterification and transesterification. On the one hand, the esterification reaction converts the free fatty acids into triglycerides in the presence of homogenous or heterogeneous acidic catalyst [9, 10, 11]. On the other hand, the transesterification reaction converts the triglycerides into biodiesel and glycerol in the presence of homogenous or heterogeneous base or acidic catalysts and alcohol [11-18]. The methanol has been commonly used, because it's cheaper than the other alcohols [19]. Also the potassium hydroxide and sodium hydroxide have been typically used, since they are less expensive and easy to manipulate in storage and transport [20, 21, 22]. Usually, the biodiesel is obtained from the refined vegetable oils by the transesterification reaction. This process is synthetically the most widely used in the industrial field. But, the production cost is higher than petroleum-based diesel [23-26]. To overcome that problem, acids oils with high content of free fatty acids, such as the unrefined olive pomace oil, could be used instead; they are much more cheaper. Due to its high free fatty acids, the pretreatment step of these oils was required to achieve the transesterification reaction and to avoid the soap formation [27, 28]. The pretreated unrefined olive pomace oil obtained by the esterification reaction in the presence of an acidic catalyst and methanol will be converted after the transesterification into biodiesel and glycerol.

In the current work we tried to optimize the transesterification reaction parameters: solvent volume ratio, basic catalyst mass, temperature and reaction time. Firstly, we intended to determine the optimum combination which gives the best biodiesel yield proceeding with the transesterification reaction of the refined olive pomace oil. Subsequently, this optimum combination will be applied for the pretreated unrefined olive pomace oil. We investigated the gain when using the unrefined olive pomace oil in comparison to the refined one. We studied the combination of sulfuric acid and methanol and their effect on the free fatty acids in the pretreated unrefined olive pomace oil at a fixed temperature, fixed reaction time and fixed stirring rate. Then, we determined the optimum free fatty acids conditions of the pretreated unrefined olive pomace oil which will be preserved in the transesterification reaction. In each optimum condition we evaluated the quality of biodiesel derived from refined and unrefined olive pomace oil.

EXPERIMENTAL SECTION

2.1 Materials

In the present study two kinds of oil have been used for the biodiesel production, the refined and the unrefined olive pomace oil. Both of them were provided by a Tunisian olive oil company. The potassium hydroxide, methanol and sulfuric acid were used in our processes. Experimentally, we used a round bottom flask (reactor), a hot plate with a magnetic stirrer and a rotary evaporator to remove the hexane excess which remains in the unrefined pomace oil.

2.2 Experimental procedure

The production of biodiesel was performed through two processes: the first one is direct, the tranesterification reaction of the refined olive pomace oil. In the second one, the case of unrefined olive pomace oil, we had to proceed firstly with a step of pretreatment (Esterification reaction) prior the transesterification reaction. Where the effect of various methanol and sulfuric acid concentrations on the acid value was studied, to determine the most effective combination which gave the lowest acid value at fixed reaction time, temperature and stirring rate. Characteristics of the oils are summarized in the table 1.

Table1. Characterization of the studied oils

	Unit	Refined olive pomace oil	Unrefined olive pomace oil
Acid value	mg KOH/g-oil	2.34	44
Viscosity at 40°C	mm^2/s	13.61	23.79
Density at 15°C	g/cm^3	0.91	0.92
Water content	ppm	500	500
Cost per liter	$	2.5	0.81

2.2.1 Biodiesel Production from refined olive pomace oil

The biodiesel production from refined olive pomace oil can be achieved directly by the transesterification reaction due to the low acid value. The production was conducted at various methanol volume ratios (10-20ml), various mass ratios of potassium hydroxide (0.25-1g), various temperatures (50-60°C) and various reaction times (20-60min) maintaining the same stirring rate (400rpm). All experiments were performed using100ml of the oil.

The effects of those parameters on the biodiesel yield were determined. In each experiment, 100ml of refined olive pomace oil was poured in the flask and heated before adding the liquid solution of methanol and potassium hydroxide with different ratios. Then the mixture was heated to temperatures within the range previously indicated. The mixture was kept to settle for two hours in the separating funnel. After separation the volume of the top layer containing methyl ester (Biodiesel) was measured. Then, the biodiesel was purified by successive rinses with hot distilled water and dried after that at 110°C for 20min to eliminate water traces. With the optimum combination, the yield of the biodiesel after the purification and drying was about 100%.

2.2.2 Biodiesel production from unrefined olive pomace oil

Due to the high free fatty acid content in the unrefined olive pomace oil, the pretreatment of this oil by the esterification reaction with different dosages of sulfuric acid in the presence of methanol was required to avoid the soap formation during the transesterification step. The aim of the pretreatment step is to reduce the free fatty (FFA) to the limit required to achieve the transesterification reaction, by its conversion into triglycerides.

Different dosages of sulfuric acids (0.5-1.25ml v/v) and different methanol to oil volume ratios were used, 40 ml, 45 ml, 50 ml, 55 ml, 60 ml, 65 ml and 70 ml (v/v), at 50°C, during 60 min and at 400 rpm as a stirring rate. This was to track the influence of these parameters on the acid value of the unrefined olive pomace oil and to determine the optimum combination which gave the maximum conversion percentage of FFA to FAME, accordingly to the maximum biodiesel yield.

We performed as follows; 100 ml of unrefined pomace oil was poured in the flask and heated at 50°C for 5 min. the preheated oil was mixed with different combination of sulfuric acid and methanol concentration. After one hour, the mixture obtained from the first step was kept to settle for two hours in separating funnel. When the settling is complete the excess of methanol in the top was removed. The acid value of the bottom phase was measured before the transesterification reaction. After that, the pretreated unrefined olive pomace oil with the optimum and non optimum FFA conditions were converted into biodiesel and glycerol by the transesterification process. The same optimum combination of the transesterification reaction of the refined olive pomace oil was preserved to be applied:(15: 100 ml (v/v) methanol to oil volume ratio, 1% w/v of potassium hydroxide, at 50 °C, during 60 min and using 400 rpm stirrer speed). When the reaction was complete, the solution was allowed to settle for two hours resulting in two distinct liquid phases: biodiesel phase at the top and the glycerol phase at the bottom. With this combination we got a maximum yield about 99% after purification and drying.

2.3 Physicochemical properties of biodiesel derived from refined and unrefined olive pomace oil:

The physicochemical properties of biodiesel derived from refined and unrefined olive pomace oil are compatible with the European norms of biodiesel. The physicochemical properties of biodiesel obtained from unrefined olive pomace oil in the optimum FFA conditions were close to those of biodiesel derived from refined oil. Table 2 summarized these properties in comparison with the standard properties of European norms biodiesel.

Table 2. Physicochemical properties of biodiesel derived from refined and unrefined olive pomace oil

Parameters	Units	Biodiesel from Refined olive pomace oil	Biodiesel from Unrefined olive pomace oil	Biodiesel (EN14214)	
				Min	Max
Acid value	mg KOH/g-oil	0.31	0.36	-	0.5
Viscosity at 40°C	mm^2/s	4.18	4.51	3.5	5
Density at 15°C	g/cm^3	0.87	0.88	0.86	0.9
Water content	ppm	410	450	-	500
Flash point	°C	128	163	110	-
Pour point	°C	13	17	-	-
Ester conversion	%	100	99	96.5	-

RESULTS AND DISCUSSION

3.1 Biodiesel production from refined olive pomace oil by transesterification process

Parameters affecting the biodiesel yield during the transesterification process of the refined olive pomace oil such as methanol to oil volume ratio, potassium hydroxide mass ratio, reaction temperature and reaction time were studied to determine the optimum combination which gave the maximum methyl ester (Biodiesel) yield.

3.1.1 Effect of reaction temperature on the yield of biodiesel

The results revealed that at 45°C, we obtained a relatively weak biodiesel yield (89%). For all combinations, biodiesel yield increased with an increasing temperature ranging from 45°C to 60 °C, despite a reduction of 2% of yield was noticed at 50-55°C. The highest temperature was 60°C because there was a risk that the methanol will be evaporated (the boiling point of methanol is 64°C). Also, to avoid the saponification reaction. The results indicated that 50°C was sufficient to accomplish the transesterification process, when the volume ratio of methanol to oil was 15:100ml (v/v), the mass ratio of potassium hydroxide (KOH) was 1g during 60min at stirring rate of 400rpm. The maximum biodiesel yield reached 100% ester content with 0.31 mg KOH/g-oil at 50°C and 0.78 mg KOH/g-oil at 60°C. But the properties of the biodiesel obtained at 60°C were not compatible with European norms biodiesel (max 0.5 mg KOH/g-oil). Moreover, at 50°C the separation between the glycerol and biodiesel was clearly observable. However, at 60°C the biodiesel color went dark. The biodiesel yield variation is shows in the fig.1.

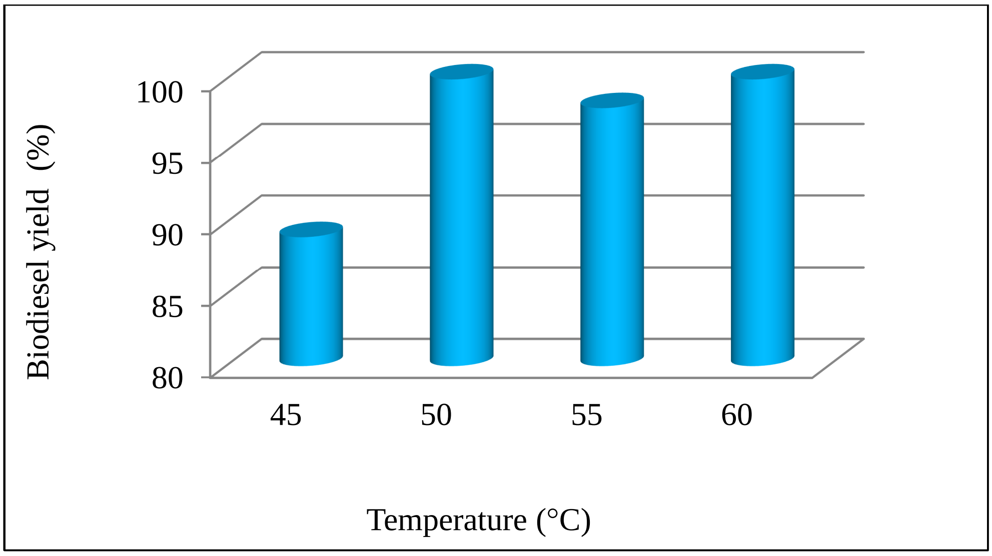

Fig.1. Effect of reaction temperature on the biodiesel yield using 15:100ml (v/v) methanol to oil volume ratio, 1g of potassium hydroxide in 60min

3.1.2 Effect of reaction time on the biodiesel yield

In this experiment the reaction time was varied from 20 to 60 min. The transesterification reaction was performed using 1g of KOH, 50 °C and 15:100ml (v/v) methanol to oil volume ratio at a constant stirring rate 400rpm. The results indicated that 20min was insufficient to achieve a perfect contact between the triglycerides of the refined olive pomace oil and the solution of methanol and potassium hydroxide. Fig.2. shows that when the reaction time increased from 20 to 60 min, the biodiesel yield increased from 81% to 100%. The results obtained from the present experiments with the refined olive pomace oil revealed that 60min was sufficient to make the transesterification reaction taking place till the end. The physicochemical properties of the biodiesel obtained after 60min were compatible with the European norms biodiesel (EN14214). However, within a range of 20-45min these properties are not. For example, the acid value of the biodiesel obtained after 20min was 0.93mg KOH/g-oil, after 30min was 0.73mg KOH/g-oil and after 45min was 0.67 mgKOH/g-oil, but within 60min, the acid value decreased to0.31 mg KOH/g-oil. In addition, the viscosities of biodiesels obtained in the same range of duration were higher than 5mm^2/s, the maximum allowed in the European norms biodiesel (EN14214). The viscosity of biodiesel obtained after 60min was 4.18 mm^2/s. Hence, the reaction time 60min was considered as the best duration for the normal and ideal progress of the transesterification reaction.

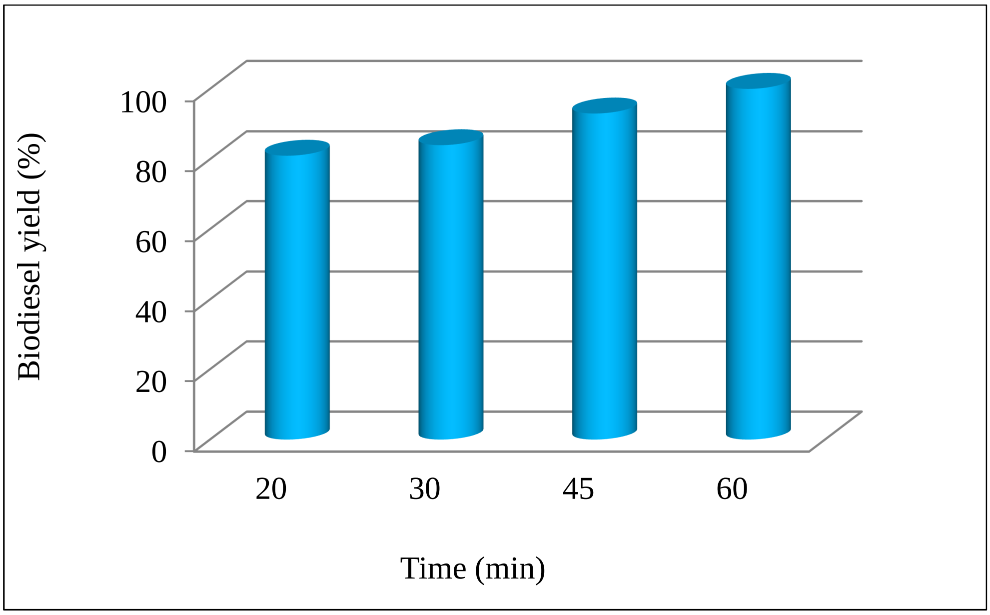

Fig.2.Effect of reaction time on the biodiesel yield (15:100ml v/v methanol to oil volume ratio, 1g of potassium hydroxide at 50°C and 400rpm)

3.1.3 Effect of methanol/oil volume ratio on the biodiesel yield

The amount of methanol to oil volume ratios used in the process was varied as follows; 10 ml, 12.5 ml, 15 ml and 20:100 ml (v/v) methanol-to-oil. The experiments were carried using the following combinations: In each potassium hydroxide mass ratio, reaction time of 60 min, at 50 °C and stirring rate of 400rpm. Results indicated that the biodiesel yield was affected by the combinations between the methanol volume and the potassium hydroxide mass.

With 10 ml of methanol and 0.25g of potassium hydroxide, the tranesterification reaction did not occur and there was not a clear separation between the biodiesel and glycerol phases. Furthermore, the viscosity of the final product was close to the viscosity of the pomace oil. It might be due to the deficiency of the methanol to ensure from the normal progress of the transesterification reaction. Fig.3. shows that as the methanol to oil volume ratio was increased from 10 to 20 ml, as the biodiesel yield increased from 83 to 89% at 0.25g; from 81 to 95% at 0.5g and from 85 to 96% at 0.75g of potassium hydroxide, but it was still lower than the biodiesel obtained when the potassium hydroxide mass was fixed at 1g. 1g of potassium hydroxide was sufficient to make biodiesel yield enhanced from 88% to 100% while the methanol to oil volume ratio was increased from 10 to 15:100ml (v/v). This yield decreased slightly when the methanol to oil volume ratio was above than 15:100 ml. It was concluded that the excess of methanol did not improve the methyl ester content. The experiments indicated that 15 ml of methanol was sufficient to reach 100 % of methyl ester. However, 10 ml of methanol with 0.25g of potassium hydroxide was insufficient for the accomplishment of the transesterification reaction.

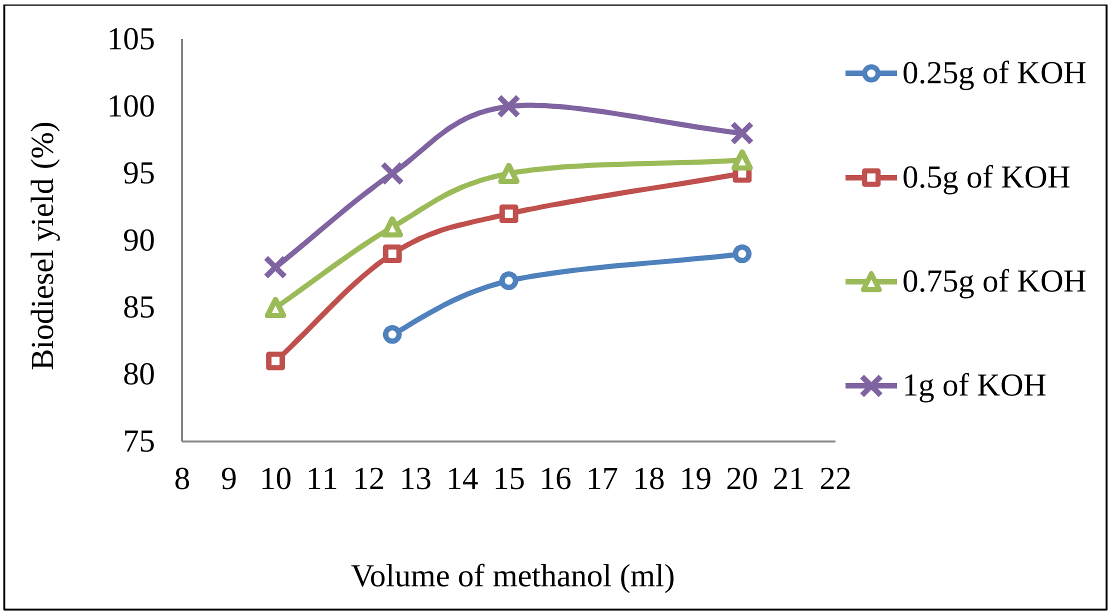

Fig.3. Effect of methanol/oil volume ratio on the biodiesel yield in the four hydroxide potassium mass ratio, reaction temperature 50°C, reaction time 60min and 400rpm

3.1.4 Effect of mass ratio of potassium hydroxide to oil on the biodiesel yield

Without catalyst the transesterification reaction did not take place. But, the amount of the catalyst should be optimized to avoid the soap formation, which causes mainly two problems: the reduction of the biodiesel yield and a problem of a separation between the two phases: the biodiesel and glycerol. The biodiesel production were realized with different mass ratios of potassium hydroxide (0.25-1g), at 50°C, during 60min a stirring rate of 400rpm and with the four volume ratios of methanol to oil (10, 12.5, 15 and 20ml (v/v). The effect of potassium hydroxide mass ratios to oil on the biodiesel yields is shown in fig.4.

The results indicated that, with each methanol to oil volume ratio the biodiesel yield increased with an increasing potassium hydroxide mass ratio. When increasing the potassium hydroxide mass ratio to oil from 0.25g to 1g, yields were increased from 81% to 88% at a fixed methanol to oil volume ratio, (10 ml). Samely for 15 ml biodiesel yields were increased from 87% to 100%. It was observed that, with 0.5, 0.75 and 1g of potassium hydroxide in 10 ml of methanol, the separation between biodiesel and glycerol was a bit difficult due to the phenomenon of emulsification. However, with 0.25g of potassium hydroxide there is no separation between biodiesel and glycerol phases, it may be due to the catalyst quantity insufficient to make the transesterification reaction progressing. Finally, we can confirm that the mass ratio of the base catalyst has a significant effect on the biodiesel yield.

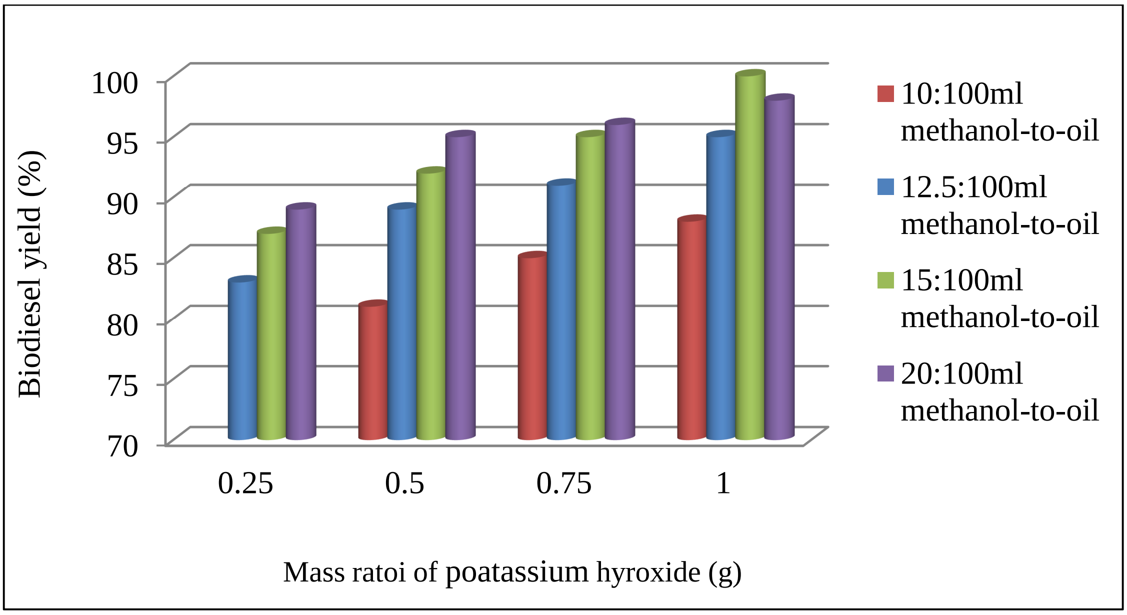

Fig.4. Effect of mass ratio of potassium hydroxide to oil on the yield of biodiesel in the fourth methanol volume ratio to oil, reaction temperature 50°C, reaction time 60min and 400rpm

3.2 Biodiesel production from unrefined olive pomace oil by two steps process

In order to reduce the content of free fatty acid in the unrefined olive pomace oil, the pretreatment with the esterification reaction using sulfuric acid was required prior the transesterification reaction. Different dosages of sulfuric acid and methanol to volume ratios were used in the esterification. A two-step process was realized to convert the high free fatty acids content in the unrefined olive pomace oil into biodiesel. The first step (esterification reaction) reduced the FFA content of this oil from 22% to 2%. The product obtained in the first step (pretreated oil) was converted by transesterification in the presence of an alkaline catalyst into biodiesel and glycerol in optimum conditions (15: 100 ml (v/v) methanol to oil volume ratio, 1% w/v of potassium hydroxide, at 50 °C, during 60 min and 400 rpm as a stirring rate). Results showed that the dosage of the sulfuric acid and the amount of methanol concentration had significant effects on the reduction of the acid value during the pretreatment step of the unrefined olive pomace oil. The optimum combination in the first step which gives 2% of FFA was as follows: 50°C, 60 min, 65 ml of methanol to oil volume ratio and 1.25 ml of sulfuric acid and 400 rpm.

3.2.1 Characterization of unrefined olive pomace oil

The determination of the components in the unrefined olive pomace oil was performed by gas chromatography coupled to mass spectrometry (GCMS). The table 3 shows the free fatty acid composition of unrefined olive pomace oil. The results revealed that the highest fatty acids were oleic, stearic, palmitic acid. Saturated fatty acids in the unrefined olive pomace oil represented 41.93 % while unsaturated fatty acids represented 58.06% of the mixture. The results depicted that the unrefined olive pomace oil could be considered as good raw materials for the biodiesel production due to the high level of the Oleic acid (54.68%). However, the high percentage of saturated free fatty acids in oil gives a high cetane number and the oil is less prone to the oxidation. Even, this type of FFA has a tendency to give a high cetane number and a better stability to the oxidation of the biodiesel. But, that can give a high cloud point and pour point of the biodiesel derived from this oil, which are considered as disadvantages [27, 28, 29].

Table 3. Fatty acids compositions of the unrefined olive pomace oil

Fatty acids	Formula	Common Acronym	Acid composition
Palmitic acid	$C_{16}H_{32}O_2$	C16:0	15,23%
Palmitoleic acid	$C_{16}H_{30}O_2$	C16:1	2,04%
Stearic acid	$C_{18}H_{36}O_2$	C18:0	26,42%
Oliec acid	$C_{18}H_{34}O_2$	C18:1	54,68%
Linoleic acid	$C_{18}H_{32}O_2$	C18:2	0,84%
Linolenic acid	$C_{18}H_{30}O_2$	C18:3	0,50%
Arachidic acid	$C_{20}H_{40}O_2$	C20:0	0,28%

3.2.2 Effect of sulfuric acid dosage

The hexane excess that remained in the unrefined olive pomace oil blocked the pretreatment step in the presence of sulfuric acid and methanol; it prevented the normal progress of the esterification reaction. This excess will be removed by distillation using a rotary evaporator. Once removed, the pretreatment of the unrefined olive pomace oil was studied by changing the catalyst concentration (sulfuric acid) over the range 0.5-1.25% at 50 °C, during 60 min and at different methanol to oil volume ratios namely, 40, 45, 50, 55, 60, 65 and 70:100 ml (v/v). The variation of the acid value during the esterification reaction at different catalyst concentrations is shown in Fig.5.

It was noticed that the acid value decreased with an increasing catalyst concentration, from 0.5 to 1.25 % in all methanol to oil volume ratios. The results displayed that from 0.5 to 0.75% of sulfuric acid in all methanol to oil volume ratios, the acid was unable to convert the FFA into triglyceride because its low concentration.

Indeed, the high free fatty acid deactivated the catalytic activity of the sulfuric acid. With 0.5 and 0.75% of sulfuric acid to oil volume ratio and all the volume ratios of methanol (40, 45, 50, 55, 60, 65, 70ml) the conversion percentages of the FFA to FAME were still low. It has been demonstrated that at low sulfuric acid concentrations, the percentage of FFA in the pretreated oil was higher than the limit of 2% required to achieve the transesterification reaction. Samely, when used 1% of sulfuric acid to oil volume ratio at low methanol to oil volume ratios (40, 45, 50 and 55ml). For example, at 55 ml of methanol, the conversion percentage of the FFA to FAME was 46%. However, with 1% of sulfuric acid to oil volume ratio at high amount of methanol the conversion percentage of FFA to FAME increased from 53% at 40 ml of methanol to oil volume ratio, to 80% at 65 ml of methanol to oil volume ratio. It was found that when using 1.25% of sulfuric acid to oil volume ratio, the acid value decreased from 44 mg KOH/g-oil to 4.16 mg KOH/g-oil with 65ml of methanol to oil volume ratio, giving the lowest percentage of FFA and the highest conversion percentage of FFA to free fatty acids methyl ester (FAME), 90.54%. The results showed that with 1.25% of sulfuric acid to oil volume ratio and all methanol volume ratios the conversion percentages of FFA to FAME increased compared to 0.5, 0.75 and 1% of sulfuric acid to oil volume ratio.

However, 1.25% v/v of sulfuric acid to oil volume ratio was sufficient for the pretreatment step only for a specific volume ratio of methanol. It has been observed that beyond 1.25% v/v of sulfuric acid to oil volume ratio, the color of the pretreated unrefined olive pomace oil turned dark. It may be due to the excessive addition of the sulfuric acid.

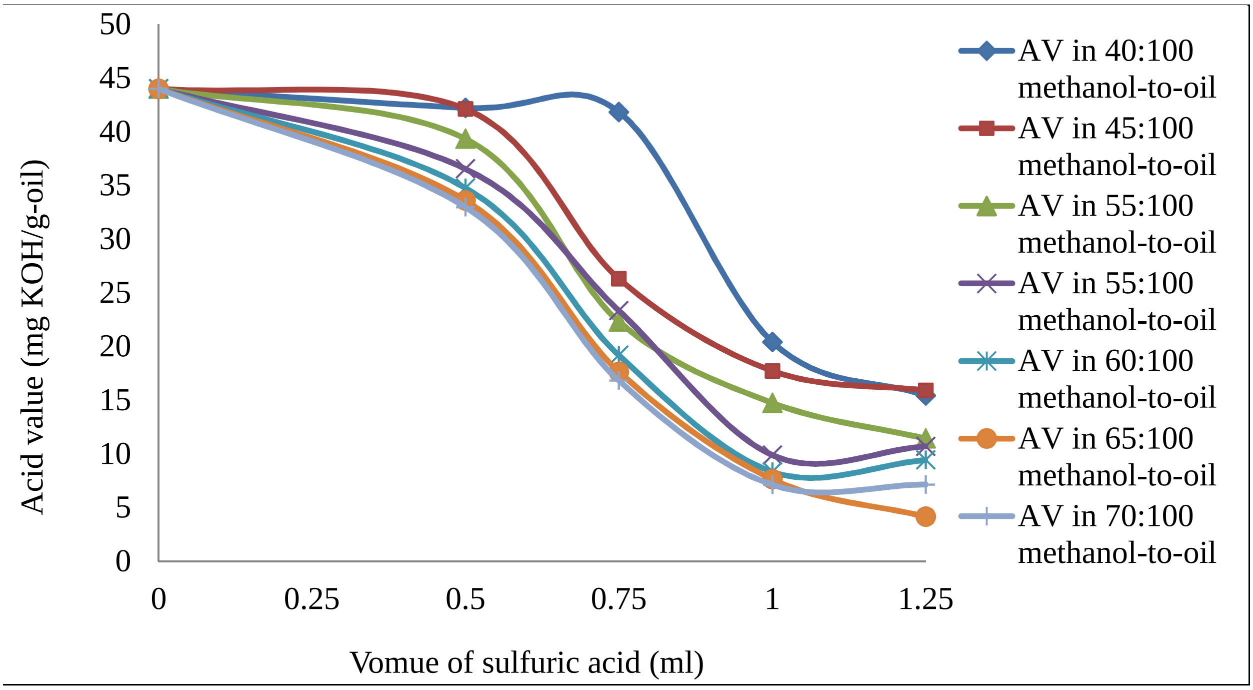

Fig.5. Effect of sulfuric acid dosage on the acid value (AV) in the all methanol to oil volume ratios 40, 45, 50, 55, 60, 65 and 70:100 ml

3.2.3 Effect of methanol to oil volume ratio

The methanol to oil volume ratio is one of the important factors that affect the conversion of FFA to triglycerides. The effect of methanol to oil volume ratio on the acid value during the pretreatment step is shown in the Fig 6. This effect was studied in order to determine the optimum volume ratio of methanol which gives the lowest acid value. During the first step, the methanol to oil volume ratio varied from 40 to 70 ml with 0.5, 0.75, 1 and 1.25% of sulfuric acid to oil volume ratios. The experiments were realized with the following combination: reaction time of 60 min, at 50 °C and stirring rate of 400 rpm. The results indicated that the residual content of free fatty acid in unrefined olive pomace oil was influenced by the amount of methanol. Fig.6 shows that in range 0.5-0.75% of sulfuric acid and in the all methanol to oil volume ratios the content of the FFA required to achieve the second step is always higher than 2%. For example, when using 0.5% of sulfuric acid at 70 ml of methanol the acid value was about 32.98mg KOH/g of oil, whereas, with 0.75% of sulfuric acid to oil volume ratio at the same volume of methanol, the acid value was 16.83 mg KOH/g of oil. Indeed, at low sulfuric acid concentration (0.5-0.75%) the enhancement of methanol to oil volume ratio had a little effect on the reduction of the acid value. However, with 1% and 1.25% of sulfuric acid, the increasing of methanol to oil volume ratios has more effect on the reduction of the acid value and the conversion of FFA to triglyceride. The lowest acid values were observed for a specific volume of methanol like 60, 65 and 70 ml.

It has been noticed that at 65 ml of methanol with 1.25% of sulfuric acid to oil volume ratio was sufficient to reduce the acid value from 44 to 4.16 mg KOH/g of oil, which gave the lowest percentage of FFA 2.08%, corresponding to the highest conversion percentage of FFA to FAME, 90.54%. A neglectable effect on the decrease of the acid value was observed with 70 ml of methanol to oil volume ratios when using 1 and 1.25% of sulfuric acid. This is, due to the excess of methanol concentration which may diluted the system and increased the occurrence of water molecules which prevents the normal progress of the esterification reaction.

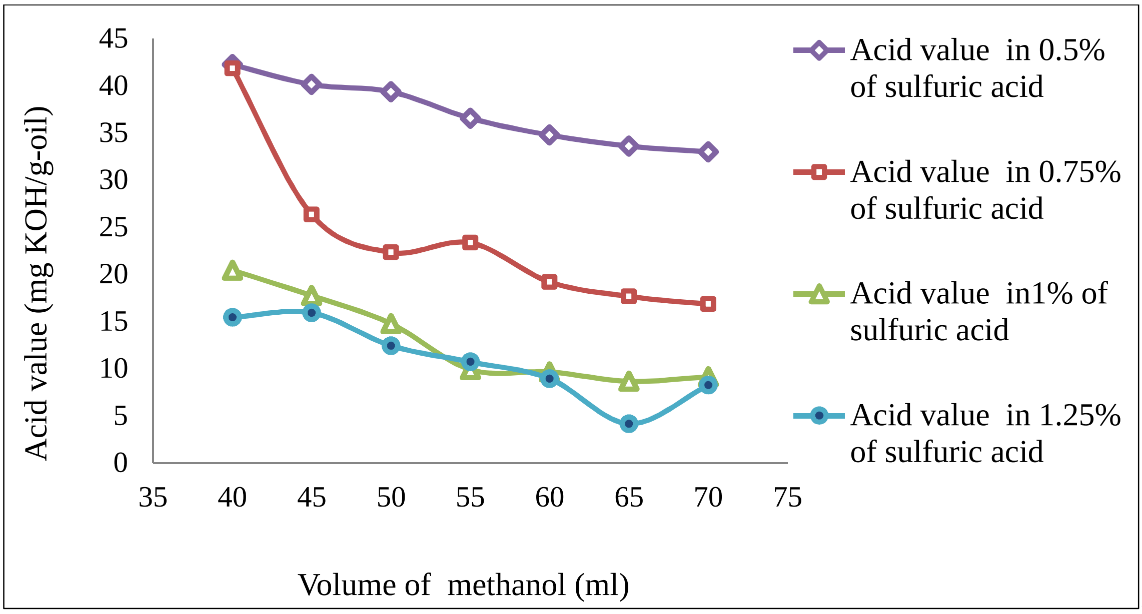

Fig.6. Effect of the methanol amount on the acid value during the esterification reaction using 0.5, 0.75, 1 and 1.25% of sulfuric acid to oil volume ratio

3.2.4 Effect of methanol and sulfuric acid combination on the biodiesel yield

The biodiesel yield derived from unrefined pomace oil was affected by the combination of methanol and sulfuric acid concentration. The pretreated oil with the optimum and non-optimum FFA conditions was carried to the second step transesterification reaction, they gave a different biodiesel yields. It has been observed that in the range 0.5-0.75% of sulfuric acid and the all volume ratios of methanol the transesterification reaction did not go on due to the high FFA content in the pretreated oil, which could cause the soap formation, after reacting with the base catalyst. In this range, even at high amount of methanol to oil volume ratio (70:100 ml) the conversion percentages of FFA to FAME were low, 21.88% in 0.5% of sulfuric acid and 61.75% in 0.75%. This happened because of the low resistance of the catalyst uncapable to provide enough catalytic activity during the pretreatment step.

The biodiesel yield improved with 1-1.25% of sulfuric acid only at high amount of methanol. On the other side, at lowest amount of methanol to oil volume ratio (40, 45, 50ml) the FFA percentages in the pretreated unrefined olive pomace oil were higher than the limit required to achieve the transesterification reaction. The results confirmed that the transesterification reaction could be applied only with 1 and 1.25% of sulfuric acid at high amount of methanol. The conversion percentages of FFA to FAME were higher than 70%. From these results we can conclude that the pretreated unrefined pomace olive pomace oil with the optimum and non optimum of FFA condition was converted into biodiesel only with 55, 60, 65 and 70ml of methanol. Besides, with 1 and 1.25% of sulfuric acid at high amount of methanol the biodiesel yields were not constant; they increased with an increasing methanol to oil volume ratios.

The biodiesel yield obtained with the optimum FFA condition (1.25% of sulfuric acid and 65 ml of methanol) reached the highest value 99%, with the lowest acid value 0.36 mg KOH/g-oil. Furthermore, the physicochemical properties of biodiesel obtained in this condition were compatible with the European norms biodiesel (EN14214). However, with the non-optimum FFA condition the biodiesel yields were lower than those obtained with the optimum FFA condition. Also, the acid value and the viscosity of the produced biodiesel were not compatible with the European norms biodiesel (EN14214). As an example, with the non-optimum FFA conditions the acid values of the biodiesel were always higher than 0.36 mg KOH/g-oil and 0.50 mg KOH/g-oil representing the maximum acid values allowed in the European norms biodiesel (EN14214). We can get that the best experimental configuration was obtained with 1.25% of sulfuric acid in 65 ml of methanol, giving a maximum yield with the best physicochemical properties. Table 4 shows the physicochemical properties of the biodiesel derived from unrefined olive pomace oil in the optimum and non-optimum FFA conditions.

Table 4. Physicochemical properties of the biodiesel derived from 100 ml of the unrefined olive pomace oil in the optimum and non-optimum FFA conditions

Pretreatment step		After pretreatment step		After transesterification reaction			
Volume of sulfuric acid (ml)	Volume of methanol (ml)	Acid value of the pretreated oil (mg KOH/g-oil)	Conversion percentages of FFA to FAME (%)	Density at 15°C g/cm^3	Viscosity at 40°C mm^2/s	Acid value of the biodiesel (mg KOH/g-oil)	Biodiesel yield (%)
1	40	20.43	53.56	-	-	-	-
1	45	17.74	59.68	-	-	-	-
1	50	14.76	66.45	-	-	-	-
1	55	9.89	77.52	0.90	5.94	0.71	83
1	60	9.64	78.09	0.90	5.98	0.64	82
1	65	8.65	80.34	0.89	5.81	0.61	85
1	70	9.13	79.25	0.90	5.89	0.67	84
1.25	40	15.43	64.93	-	-	-	-
1.25	45	15.91	63.84	-	-	-	-
1.25	50	12.43	71.75	-	-	-	-
1.25	55	10.71	75.65	0.90	5.84	0.68	79
1.25	60	8.93	79.70	0.90	5.86	0.63	84
1.25	65	4.16	90.54	0.88	4.51	0.36	99
1.25	70	8.24	81.27	0. 89	5.63	0.58	89

CONCLUSION

The refined olive pomace oil is an edible oil and despite of that it is used for the biofuel production**.** It was found that the unrefined olive pomace oil could be considered as potential and an economical source for the biodiesel production. The physicochemical properties of the biodiesel derived from the refined and unrefined olive pomace oil are similar and compatible to those indicated in the European norms biodiesel. The refined olive pomace oil with low acid value was firstly used to determine the optimum combination of methanol to oil volume ratio, potassium hydroxide mass ratio, reaction temperature and reaction time to accomplish the transesterification reaction. The effects of these parameters on the biodiesel yield were studied. The optimum condition which gave 100% of biodiesel yield was obtained with the following combination, 15:100 ml (v/v) methanol: oil, 1g of potassium hydroxide, at 50°C, during 60min and a stirring rate of 400 rpm. The same optimum combination was applied to the pretreated unrefined olive pomace oil (after esterification reaction). The transesterification reaction of the unrefined olive pomace oil did not occur that is due could be a result to the high content of free fatty acid. The pretreatment process of the unrefined olive pomace oil was required to reduce the acid value and to avoid the soap formation. We begun by studying, the effects of the dosage sulfuric acid and the methanol to oil volume ratio on the acid value. It has been observed that the free fatty acid content in the unrefined olive pomace oil was influenced by the sulfuric acid but for a specific volume of methanol. The pretreatment step reduced the percentage of FFA from 22% to 2.08% in 1.25% of sulfuric acid and 65 ml of methanol to oil volume ratio. It was observed that beyond 1.25% of sulfuric acid, the color of the pretreated oil turned dark. The transesterification reaction of the pretreated unrefined olive pomace oil with 2% of FFA gave 99% of methyl ester (biodiesel). The results revealed that, the two steps process improved the biodiesel yield produced from raw materials which is relatively cheap.

To sum up, valorization of the unrefined olive pomace oil as a source of renewable energy has two main advantages: one environmental connected to the pollution contest and human health, and the other one industrial, in relation with the cost of the production of the biodiesel which will be reduced.

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