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Waste Frying Oil with High Levels of Free Fatty Acids as one of the prominent sources of Biodiesel Production

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Abstract

The decrease of fossil fuel resources and the awareness of the impact of greenhouse gases emissions on the environment have created a need to find alternative energy sources to replace traditional ones. Thus, recent years have seen the development of several sectors of renewable energy production with the government incentives. The biodiesel production is an alternative of non-toxic, clean, renewable and biodegradable fuels production. The aim of this work was to develop a procedure for the biodiesel production from waste frying oil having an acid value of 32.82 mg KOH/g. The optimum conditions of the biodiesel production from waste frying oil in two-step catalyzed process were investigated. In the first step, the sulfuric acid was used as a catalyst for the esterification reaction to reduce the free fatty acids content in the oil under 2%, which was with different dosages. The next base catalyzed transesterification process converted the pretreated frying oil into biodiesel and glycerol in the optimum and non-optimum FFA conditions. In the optimum FFA condition the highest biodiesel yield was 98% with 0.214% of free fatty acid. The results depicted that the esterification reaction is an indispensable step as it leads to the production of an intermediary product with a low content of free fatty acid that can be directly used for the biodiesel production through the transesterification reaction.

Keywords: Biodiesel, tow-step catalyzed process, free fatty acid, waste frying oil, optimization

1. Introduction

Overall, there are four major categories of raw materials used as sources for the biodiesel production: edible and non-edible vegetable oil, animal fats and waste oils (waste frying oil) [1, 2, 3, 4]. The cost of biodiesel depends mainly on the feedstocks price which represents 75% of total production cost [1, 2]. Actually, edible oils are the main resources for the global biodiesel production (over than 95%) [2, 5]. However, there are main obstacles for not using these oils as feedstocks for biodiesel production. The high production cost, which is due to the demand for human consumption and the use of edible oils, competes with food supply in the long-term [1, 5]. Using other kinds of oils such as waste frying oil, non-edible oils and animal fats, constitute a new alternative to reduce the production costs [6, 7, 8]. Chemically, biodiesel is a mixture of methyl/ethyl esters with long chain fatty acids [8]. It can be produced directly by the transesterification reaction of raw materials with a low content of FFA (edible oils) [4, 9]. These raw materials will be converted into biodiesel and glycerol in the presence of alcohol and a base or acidic catalysts [10]. Methanol is the most commonly used alcohol due to its low cost [6]. Whereas the base catalysts are more preferable than acids catalysts due to their short reaction time, non corrosion property, low cost and high yield of biodiesel [11, 12]. However, the transesterification reaction of the oils with a high content of the free fatty acids can provoke saponification reaction, which consumes the catalyst and reduces its effectiveness resulting in a low ester conversion [12, 13, 14]. It has been claimed that, when the FFA level exceeds 5 %, the soap formation inhibits the separation between the biodiesel and glycerol, and decreases the yield of the final product [13, 14, 15]. Also, FFA can cause high losses of neutral oil due to saponification and emulsification during neutralization step [15, 16]. The cost of biodiesel production from refined lipid, as a feedstock is not economically profitable compared to the normal diesel. Oils with high content of free fatty acids (FFAs) like waste frying oil can be used for biodiesel production because they are less expensive than refined lipid [10, 14, 17, 18]. But the transesterification reaction of these raw materials into biodiesel will not proceed in the presence of base catalyst. A two step process is then proposed [10, 12, 19, 21, 22]. The first step is the pretreatment of these acids oils with acid homogenous catalyst or heterogeneous catalyst in the presence of methanol to form free fatty acid ester [23, 24, 25]. The second step is a transesterification process, in which the product of the first step reacts with the solvent and the base catalyst to form biodiesel and glycerol [22, 25, 26]. Many researches have been directed towards the heterogeneous catalysis (basic or acidic) for the biodiesel production from vegetable oils (refined, unrefined). Despite its advantages, they are not profitable in the industrial field, because of the very high activation energy of this type of catalysis and the reaction temperature which is higher than needed in homogeneous catalysis, as well as the pressure. Therefore these extreme conditions of temperature and pressure, the slow reaction rate and the cost made from the homogeneous catalysis more industrially useful compared to heterogeneous one [25-31]. Biodiesel production using the homogeneous catalysis process is favoured due to its low cost, the high rate of the reaction under mild conditions of temperature and pressure [25-31]. Esterifying of FFA in the presence of a homogeneous acidic catalyst (sulfuric acid) gives the possibility of improving the use of the oils with high FFA for biodiesel production [10, 23, 27]. The test of the biodiesel obtained from waste frying oil on commercial diesel engines provides better performances and gives less gases emissions apart from NO_x [32].

The aim of this study was to investigate the effect of various methanol quantities and sulfuric acid concentration on the reduction of free fatty acid content in waste frying oil. Methanol and sulfuric acid concentrations during the pre-treatment step were optimized to determine the optimum conditions in the pretreatment step which gave the lowest acid value, furthermore, to carry out the best experimental configuration to reach a maximum biodiesel yield.

2. Materials and methods

2.1. Materials

The waste frying oil used in this study was collected from Tunisian restaurants. The potassium hydroxide, methanol and sulfuric acid, ethanol, toluene and phenolphthalein were used as chemicals, a round bottom flask was used as a reactor and a hot plate with a magnetic stirrer was used for heating the mixture in the flask. While stirring, temperature was maintained at 60°C.

2.2. Experimental procedure

In this study, a two-step catalyzed process was performed for the biodiesel production from waste frying oil of Gourna. The esterification, as a first step, was to reduce the FFA contents will be followed by the second alkali transesterification step. The experiments revealed the effects of various methanol and sulfuric acid concentrations on the acid value of the oil during the esterification reaction and gave the most effective combination which allows reaching the lowest acid value at a fixed reaction time, fixed temperature and fixed stirring rate. The esterified oil was subjected to transesterification process to obtain the methyl ester.

2.2.1. Determination of the compounds of waste frying oil:

The physicochemical properties of used waste frying oils vary from those of refined and crude oils. During frying, the chemical composition of the vegetable oils change, as well as the physical and organoleptic properties [25]. This is due to degradation of free fatty acids (monounsaturated and polyunsaturated). At high temperatures the free fatty acids are very sensitive; they undergo chemical transformations such as: oxidation reaction, polymerization and hydrolysis [25, 32, 33]. Heat and water accelerate the hydrolysis of triglycerides and enhance the content of FFA in the oil [32, 34]. In addition, the viscosity of the oil increases due to the formation of dimeric and polymeric acids and glycerides in used frying oils [25, 32, 35]. The determination of the components present in the waste frying oil was performed by gas chromatography coupled to mass spectrometry (GCMS). The table 1 shows the free fatty acid composition of the waste frying oil used in this study.

2.2.2. Method for determination of the acid value:

The acid value is the number of milligrams of KOH required to neutralize all acid in one g of sample. The acid value is determined by titration of the sample (oil or Biodiesel) dissolved in the mixture of ethanol-toluene with a standardized titration solution of KOH in ethanol.

In this method, a weighed amount of the sample (oil or Biodiesel) was added into a flask and it was dissolved in an ethanol-toluene mixture; phenolphthalein was added as an indicator. KOH was used as titrant solution. The titration process was stopped when the solution turned into pink color. The acid value (AV) was calculated using the next equation:

$$\mathrm{AV(mg\ KOH/g)} = \frac{56.1 \times \mathrm{C_{KOH}} \times \mathrm{V_{KOH}}}{\mathrm{m}}$$

Where: 56.1 is the molecular weight of the solution employed for titration (g/mol).

-V_{KOH} is the consumption during titration (ml).

-C_{KOH} (mol/1) is the concentration of the titration KOH solution.
- m is the weight (g) of the analyzed sample.

-Remember that the percentage of FFA in the sample is approximately equal to half the acid value: $\%FFA \approx \frac{AV}{2}$

Table1: Average fatty acid composition in waste frying oil.

Fatty acid (trivial name/rational name)	Methyl ester (trivial name / rational name)	Formula	Common acronym	Acid Composition
Palmitic acid/ Hexadecanoic acid	Methyl Palmitate/Methyl Hexadecanoate	$C_{16}H_{32}O_2$	C16:0	15,86%
Stearic acid / Octadecanoic acid	Methyl Stearate/Methyl Octadecanoate	$C_{18}H_{36}O_2$	C18:0	4,87%
Oleic acid / 9(E)-Octadecenoic acid	Methyl Oleate/ Methyl 9(E) Octadecenoate	$C_{18}H_{34}O_2$	C18:1 (E)	29,83%
Linoleic acid / 9(Z),12(Z) Octadecadienoic acid	Methyl Linoleate /Methyl 9(Z),12(Z) Octadecadienoate	$C_{18}H_{32}O_2$	C18:2 (Z,Z)	28,85%
Linolenic acid/ 9(Z),12(Z),15(Z)-Octadecatrienoic acid	Methyl Linoleate /Methyl 9(Z),12(Z),15(Z)-Octadecadienoate	$C_{18}H_{30}O_2$	C18:3 (Z,Z,Z)	2,49%

2.2.3. Pretreatment of waste frying oil by esterification reaction using sulfuric acid

In this step, 100ml of waste frying oil was poured into the reactor, and heated at 60°C. The acid catalyst was added to the preheated waste frying oil at different dosages (0.5-1.25% v/v) in the presence of methanol. To investigate their influence on the acid value, different methanol to oil volume ratios were used, namely 40ml, 45ml,50ml, 55ml, 60ml, 65ml and 70ml (v/v), at 60°C, during 60min with 800 rpm as stirring rate. The mixture was kept to settle for 2 hours resulting in two distinct liquid phases. The methanol-water fraction at the top was removed using separating funnel. The acid value of the bottom phase containing the pretreated waste frying oil (triglycerides) was measured before reacting with potassium hydroxide in the second step (transesterification).

2.2.4. Alkaline catalyzed transesterification reaction

The pretreated waste frying oil under optimum and non optimum conditions of the FFA were used in the second step to produce biodiesel using potassium hydroxide as a base catalyst. Firstly the pretreated oil was heated up to 60°C. The 1%w/v of potassium hydroxide was dissolved in 20% of methanol to oil volume ratio under vigorous stirring, and then added to the pretreated waste frying oil. The mixture was again heated to 60°C and stirred at 800 rpm for 30 minutes. After that, the solution was kept to settle 2 hours in a separating funnel. The bottom glycerol layer and the top methyl ester layer were then separated. The physicochemical properties of biodiesel derived from waste frying oil in the optimum condition are compatible with the European norms biodiesel. Results are shown in the table 2.

Table 2: Physicochemical properties of biodiesel derived from waste frying oil in the optimum condition.

Parameter	Unit	Waste frying oil	Pretreated waste frying oil	Biodiesel	Biodiesel (EN14214)	
					Min	*Max*
Viscosity @40°C	mm^2/s	23.12	8.43	3.8	3.5	5
Density @15°C	g/cm^3	0.91	0.89	0.87	0.86	0.9
Sulfur	ppm	-	-	1,23	-	10
Acid value	mg KOH/g	32.83	2.24	0.428	-	0,5
Flash point	°C	-	-	173	101	-
Pour point	°C	-	-	11	-	-
Water content	ppm	1765	-	345	-	500
Ester conversion	%	-	-	98	96.5	-

3. Results and Discussion

3.1. Acid catalyzed esterification process for biodiesel production

The main factors affecting the biodiesel production from waste frying oil are: free fatty acid, water content, methanol and catalyst type, Alcohol to oil ratio, catalyst concentration, reaction temperature, reaction time and stirring rate [36]. In our study we tried to carry out the effects of various alcohol and catalyst concentrations on the acid value during the esterification process as well as their effects on the biodiesel yield after the transesterification reaction. According to the experiment, the optimum combination for the esterification reaction was as follows: 60°C as reaction temperature, one hour as reaction time and with 1% v/v of sulfuric acid to oil volume ratio at 55ml of methanol. This, induced an acid value lower than 2mgKOH/g-oil, which is equivalent to an FFA equals to 1%.

3.1.1. Effect of sulfuric acid dosage

Due to the high free fatty acids content in waste frying oil (16.415%), the transesterification reaction of this oil can risk the soap formation in the presence of potassium hydroxide. To avoid the saponification reaction, the pretreatment of this oil by the esterification reaction with sulfuric acid in the presence of methanol was required to reduce the free fatty acids (FFA) to the limit necessary to achieve the transesterification reaction.
The amount of sulfuric acid during the pretreatment step was varied within the range of 0.5–1.25 % (v/v).
Figure 1 shows the effect of sulfuric acid amounts on the acid value of waste frying oil. The results indicated that the dosages of sulfuric acid during the esterification process affected the free fatty acids content in the oil, consequently the conversion percentages of FFA to FAME. It was found that in all methanol to oil volume ratios a low amount of sulfuric acid (0.5% or 0.75%) was insufficient to reduce the acid value to the limit necessary to give a requested conversion of the pretreated oil (triglycerides) into biodiesel. As an example, in the range (0.5-0.75% v/v) of sulfuric acid to oil volume ratio in all methanol to oil volume ratios the acid values were always higher than 5mg KOH/g-oil. In addition, the conversion percentages of the FFA to FAME were relativity low; they did not exceed 84%. This might be due to a low resistance of the catalyst and its inability to provide enough catalytic activity during the esterification reaction to convert the free fatty acids into triglycerides. However, in the range (1-1.25% v/v) of sulfuric acid to oil volume ratio with a high amounts of methanol (55, 60, 65, 70ml) the acid values were always lower than 4mg KOH/g-oil. It has been demonstrated that the acid value reached an optimal value with 1% of sulfuric acid to oil volume ratio and increased slightly with 1.25%. With 1% of sulfuric acid to oil volume ratio, the acid value decreased from 8.33 mg KOH/g-oil at 40ml of methanol to 2.19 mg KOH/g-oil at 55ml of methanol, which represents the lowest acid value that can be reached. Therefore, 1% of sulfuric acid to oil volume ratio at 55ml of methanol gave the lowest percentage of FFA which is 1.095% and 93.32%, conversion percentage of FFA to FAME. But with 1.25% of sulfuric acid to oil volume ratio, we noticed that the acid value increased progressively compared to 1%. The results indicated that an excessive amount of sulfuric acid did not show any reduction of the acid value of the pretreated waste frying oil. As a result, increasing the volume of sulfuric acid has no effect on the enhancement of the conversion percentage of FFA to FAME. The study showed that the lowest acid value in all experiments was obtained with this combination: 1% of sulfuric acid to oil volume ratio and 55ml of methanol gave an acid value of 2.24 mg KOH/g-oil. Whereas the highest acid value (10.34 mg KOH/g-oil) was obtained with a combination of 0.5%v/v sulfuric acid to oil volume ratio at 40ml of methanol corresponding to 68.5% as a conversion percentage of FFA to FAME.

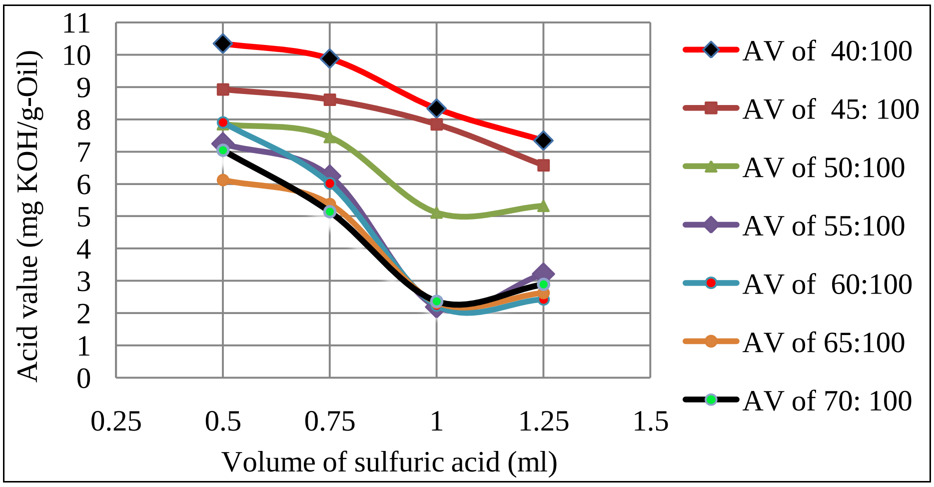

Figure 1: Influence of sulfuric acid amount on acid value during esterification process by using 40, 45, 50, 55, 60, 65 and 70:100, methanol-to-oil volume ratio.

3.1.2.Effect of methanol volume ratio

The effect of the methanol amounts on the acid value and the FFA content in the waste frying oil after an hour of esterification process by using 0.5, 0.75, 1 and 1.25%v/v of sulfuric acid to oil volume ratios is shown in the figures (2- 5). The results indicated that with each amount of sulfuric acid the FFA content in the oil was influenced by the quantity of methanol. They revealed that with 0.5, 0.75, 1 and 1.25% of sulfuric acid at low amounts of methanol there was no significant effect on the reduction of the acid value.

Figures (2-5) depicted that with 40, 45 and 50ml of methanol the acid values of the pretreated waste frying oil were always higher than 5mg KOH/g-oil, which led to the lowest conversion percentage of FFA to FAME. Moreover, a very high amount of methanol was required to reduce the acid value of the pretreated oil below 2 mg KOH/g. Figures 4 and 5 shows that with 60, 65 and 70ml of methanol the acid values were lower than 3mg KOH/g-oil. Whereas, the lowest acid value was obtained with 55ml of methanol and 1% of sulfuric acid to oil volume ratio corresponding to the highest conversion percentage of FFA to FAME (93.32%). This condition was designated as the optimum for the reduction of the acid value of the waste frying oil. Indeed, figures (2-5) shows that the acid values and FFA decreased gradually with an increasing amount of methanol (from 40 to 55ml), then slightly increased when the methanol volume ratios increased. For example, figure 4 shows that with 1% of sulfuric acid to oil volume ratio the acid value decreased from 8.33 mg KOH/g-oil at 40ml of methanol, to 2.19 mg KOH/g-oil at 55ml. Then it increased from 2.24 to 2.37 mg KOH/g-oil with an increasing amount of methanol from 60 to 70ml to-oil volume ratio. Samely, figure 5 depicted that with 1.25% of sulfuric acid to oil volume ratio, as the methanol amount increased from 60 to 70ml to-oil volume ratio the acid value increased from 2.43 to 2.89 mg KOH/g-oil. Increasing the methanol amount beyond 55ml has no significant effect on the reduction of acid value. This could be due to the fact that higher amount of methanol could dilute the system, resulted in a reduction of the sulfuric acid efficiency. Also, because to the fact that water produced during the pretreatment step can inhibit the activity of sulfuric acid which retards the rate of reaction.

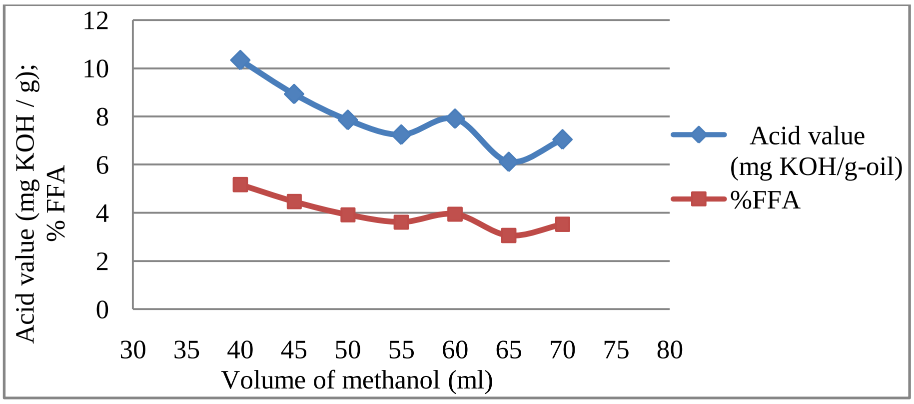

Figure 2: Influence of methanol amount on acid value and FFA during acid esterification process by using 0.5% of sulfuric acid-to-oil volume ratio.

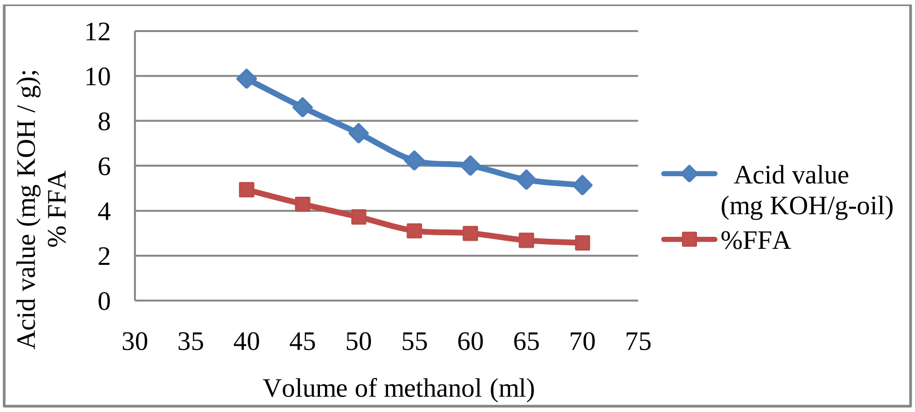

Figure3: Influence of methanol amount on acid value and FFA during acid esterification process by using 0.75% of sulfuric acid-to-oil volume ratio.

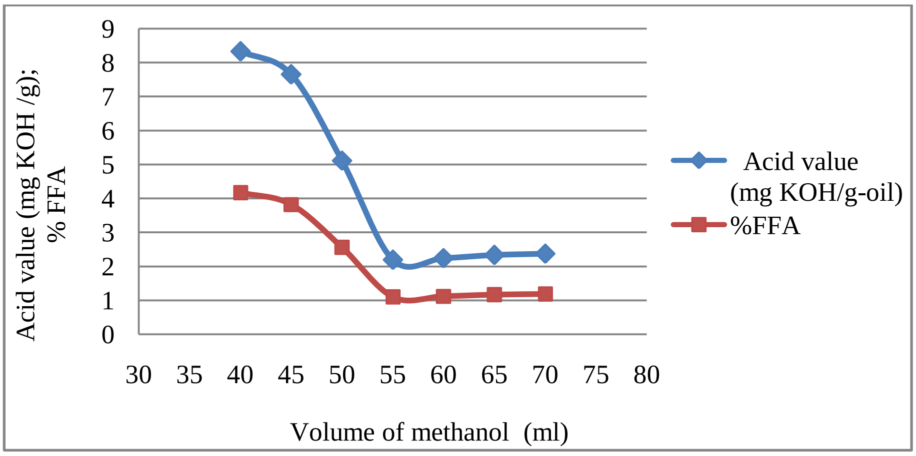

Figure 4: Influence of methanol amount on acid value and FFA during acid esterification process by using 1% of sulfuric acid-to-oil volume ratio.

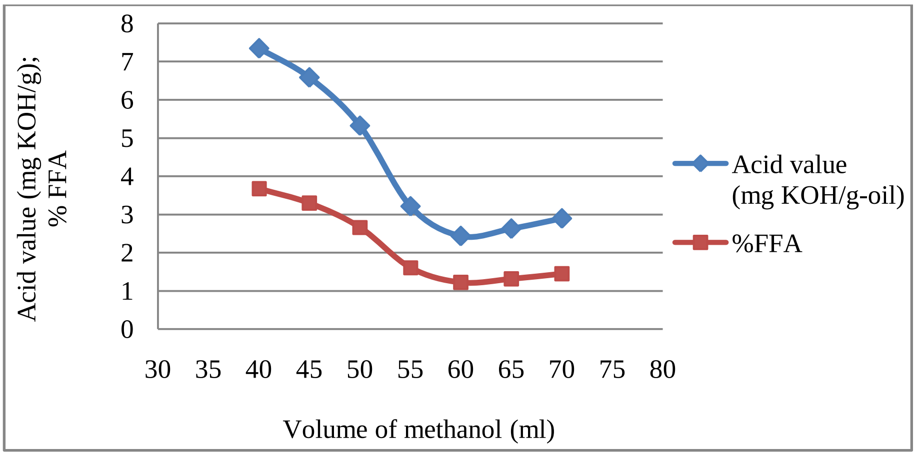

Figure 5: Influence of methanol amount on acid value and FFA during acid esterification process by using 1.25% of sulfuric acid-to-oil volume ratio.

3.1.3. Effect of methanol and sulfuric acid on biodiesel yield

The results depicted that the biodiesel yield was affected by the dosage of sulfuric acid and the amount of methanol. At low catalyst concentration, biodiesel yield was low even at a higher amount of methanol.

Table 3 shows that with 0.5 and 0.75% of sulfuric acid to oil volume ratio and in all volumes of methanol (40, 45, 50, 55, 60, 65, 70ml) the ester conversion percentages were relativity low; about 80% (they did not exceed 82%). Also, the acid values of the biodiesel obtained in this range were not compatible with the European norms biodiesel. European biodiesel standard (EN14214) recommends that the acid value should not exceed 0.5mgKOH/g. As an example, when using 0.5% of sulfuric acid to oil volume ratio at 70 ml of methanol, the acid value was 1.13 mg KOH/g, however with 0.75% of sulfuric acid to oil volume ratio at the same volume of methanol, the acid value was 0.83 mg KOH/g. Experimentally, it has been observed that in the range 0.5-0.75% in all methanol to oil volume ratios, the glycerol yields remained high, also the separation between the biodiesel and the glycerol was a bit difficult because of the soap formation.

In the range 1-1.25% of sulfuric acid to oil volume ratio the results showed a significant increase of the esters conversion percentages. The experiment indicated that as the sulfuric acid concentration increased, the biodiesel yield increased, with an increasing methanol to oil volume ratios. With 1 and 1.25% of sulfuric acid to oil volume ratio at 55, 60, 65and 70ml of methanol the esters conversion percentages were always higher than 92%. The highest biodiesel yield was obtained with the optimum condition (1% of sulfuric acid to oil volume ratio and 55ml of methanol) giving the lowest acid value 0.428 mg KOH/g. It was found that the acid values of the biodiesel obtained in the non-optimum FFA conditions were always higher than 0.50 mg KOH/g. With 1.25%

of sulfuric acid and in all methanol to oil volume ratios, the esters conversion percentages were close to those obtained with 1% of sulfuric acid. But with this volume, the acid values of the biodiesel were higher than the maximum standard value (0.50 mg KOH/g). The results confirmed that the best experimental configuration was with1% of sulfuric acid to oil volume ratio in 55 ml of methanol letting a maximum biodiesel yield with the best physicochemical properties. Results are summarized in the table 3:

Table 3: Biodiesel yield with different combinations of methanol and sulfuric acid by using 100ml of waste frying oil.

Volume of sulfuric acid (ml)	Volume of methanol (ml)	Acid value of the pretreated oil (mg KOH/g-oil)	Conversion of FFA to FAME (%)	Acid value of the biodiesel after washing and heating (mg KOH/g)	Ester Conversion after washing and heating (%)
0.5	40	10.34	68.50	1.34	73
0.5	45	8.93	72.79	1.29	75
0.5	50	7.85	76.08	1.17	78
0.5	55	7.24	77.94	1.11	78
0.5	60	7.91	75.90	1.23	76
0.5	65	6.12	81.35	1.05	80
0.5	70	7.04	78.55	1.13	78
0.75	40	9.88	69.90	1.31	72
0.75	45	8.61	73.77	1.27	74
0.75	50	7.45	77.30	1.24	76
0.75	55	6.24	80.99	1.06	79
0.75	60	6.01	81.69	1.03	79
0.75	65	5.38	83.61	0.89	80
0.75	70	5.14	84.34	0.83	82
1	40	8.33	74.62	1.21	79
1	45	7.65	76.69	1.15	81
1	50	5.11	84.43	0.81	85
1	55	2.19	93.32	0.42	98
1	60	2.24	93.17	0.58	95
1	65	2.33	92.90	0.62	91
1	70	2.37	92.78	0.63	90
1.25	40	7.34	77.64	0.97	79
1.25	45	6.58	79.95	0.93	78
1.25	50	5.32	83.79	0.84	80
1.25	55	3.21	90.22	0.73	92
1.25	60	2.43	92.59	0.64	92
1.25	65	2.62	92.01	0.65	91
1.25	70	2.89	91.19	0.68	90

Conclusion

The effect of free fatty acids (FFAs) on the biodiesel production process was treated. The FFAs can prevent the production process by deactivation of the catalyst, soap formation (the reason is that the alkaline catalysts react with the free fatty acids to form soap during the transesterification reaction) and also the separation between the glycerol and biodiesel. A two-step process is developed to convert the high FFAs content in the acids oils into esters. Therefore, a pretreatment step of waste frying oil is necessary to remove free fatty acids before proceeding with the alkali transesterification step. The effects of alcohol to oil volume ratio and catalyst amount on the FFA were investigated in the first step (Esterification reaction). It was found that there were significant effects of sulfuric acid dosages on the reduction of the acid value subsequently on the conversion of FFA to FAME and finally on the biodiesel yield. The first step (acid catalyzed) reduced the FFA content of the waste frying oil to less than 2%. After that, transesterification process was realized to produce the methyl esters and glycerol. The optimum conditions for the pretreatment step were found to be as follows: methanol to waste frying oil volume ratio 55:100 ml, 1% v/v of sulfuric acid to-oil volume, at 60 °C, during 30 min and 800 rpm as a stirring speed. The highest methyl ester (biodiesel) yield with this optimized combination was 98%. The results confirmed that waste frying oil could be considered as an economical alternative for biodiesel production with the development of a pretreatment step using the sulfuric acid as a catalyst and the methanol as a solvent.

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