ORIGINAL RESEARCH PAPER

Esterification of Waste Cooking Oil Followed by Transesterification by CaO Nanoparticles: Application of Taguchi Methodology

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ABSTRACT
In order to produce biodiesel from waste cooking oil and optimize its yield, a two-stage process of esterification/ transesterification has been used in this study. First, we used the acidic catalysts H_2SO_4 in order to diminish the content of free fatty acid (FFA) in oil that caused reducing the oil acidity from 6.1% to 0.57% through esterification. Then, the biodiesel was produced by transesterification of resulted oil using heterogeneous CaO nanoparticles as catalyst. At each stage, the best possible conditions have been determined by applying Taguchi methodology for each major variable, including time, temperature, alcohol/oil molar ratio, and the amount of catalyst. The optimum conditions for esterification are achieved at 80°C temperature, 120 minutes time, 6:1 molar ratio of alcohol/oil, and H_2SO_4 content of 1% (w/w oil). The optimum condition for transesterification were found in 100 °C temperature, 90 minutes time, 8:1 molar ratio of alcohol/oil, and 3% (w/w oil) of CaO nanoparticles as catalyst. After applying full optimization of these two stages, the yield of the produced biodiesel has achieved 96.4%.

Keywords: *Biodiesel, Waste cooking oil, Transesterification, CaO nanoparticles, Taguchi methodology*

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INTRODUCTION

In the recent years, biodiesel has been known as one of the most important renewable resources for replacing fossil fuels. They are usually produced from non-food waste such as vegetable oils, animal fats and waste edible oil [1-5].

From among the most important ways to produce biodiesel, transesterification (alcoholysis), which is the reaction of fat with alcohol to produce ester and glycerol, is the famous one. The free fatty acid (FFA) content in the oil needs to be very low (lower than 1%) to prevent the soap creation that stops continuing process, resulting major reduce in the yield. Hassani et al. [6] Used waste cooking oil with high FFA (9.85%) toward esterification in the presence of the sulfuric acid catalyst. Based on their work, the acidity of oil reached to the less than 1.5%. They reported high yield of biodiesel (96.66%) following transesterification process.

During esterification with acidic catalysts,

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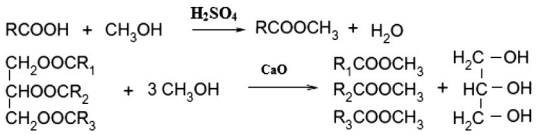
the FFA content could be reduced,which is necessary for transesterification process [7]. H_2SO_4 has widely been used as a catalyst in esterification of vegetable oils or animal fats because of its rational low price and excellent catalytic property [1, 8]. For example, in a study conducted by Ong et al. [1], various vegetable oils have been subjected to reduce FFA during esterification by H_2SO_4 acid catalyst. In a study conducted by Alptekin and Canakci [8], H_2SO_4 catalyst indicated better results than hydrochloric acid (HCl) and sulfamic acid (H_3NSO_3) catalysts.

At transesterification stage, the basic catalysts are preferred than acidic catalysts because they have higher yield, lower cost, lower reaction temperatures and pressures [9, 10]. However, the basic catalysts react with FFA during transesterification resulting soap formation that prevents the progress of reaction [2]. Vicente et al. [11] suggested the use of basic methoxide catalysts instead of KOH. Soriano et al. [12] reported that using acidic catalysts are more appropriate for waste cooking oils having high FFA content, although the reaction is much slower and requires greater use of alcohol.

The advantage of solid heterogeneous basic catalysts rather than homogeneous catalysts includes their easier separation and recovery, and higher yield of biodiesel [13]. For this reason, solid heterogeneous catalysts have been widely considered in recent years. Liu et al. [14] used solid basic catalyst CaO to produce biodiesel from soybean oil. In another study, Wang et al. [15] used solid basic catalyst $Ca_{12}Al_{14}O_{33}$ and CaO for transesterification of vegetable oil on canola family. In another study, Kawashima et al. [16] investigated transesterification of soybean oil in the presence of CaO and $CaCO_3$. In another study, the catalytic activity of the crystalline catalyst of CaO-Fe_3O_4 was investigated [17].

In this study, we used H_2SO_4 and CaO nanoparticles as catalysts for esterification and transesterification of waste cooking oil, respectively, by taking into account Taguchi optimization methodology approach [18].

To the best of our knowledge, there is no report focusing on application of the Taguchi optimization methodology approached for both esterification and transesterification processes of waste cooking oil by using above-mentioned catalysts. The effects of different variables, including temperature, time, methanol/oil molar ratio and the amount of catalyst (H_2SO_4 and CaO nanoparticles) have been investigated to determine the optimal reaction conditions.



Scheme. 1. The reaction of esterification and transesterification.

MATERIAL AND METHODS

Materials and Equipment

All the main chemical substances used in the biodiesel production process include: waste cooking oil (obtained from the restaurant of Qaemshahr University), Methanol (99.8%, Merck), sulfuric acid (99.0%, Merck), Ca(NO3)2.6H2O (Merck), and potassium hydroxide (Merck). To remove any adsorbed species including H_2O and CO_2 from the surface of the catalyst, calcination of CaO nanoparticles catalyst has been done using furnace (Behpajoh 901, Iran). To prevent catalyst deactivation, it is necessary to fast using of calcinated CaO nanoparticles.

Preparation of CaO nanoparticles

The protocol described by Wang et al.[19] was used for preparation of CaO nanoparticles; 1gr of Ca(NO3).6H2O was dissolved in water and heated to 40˚C. Whereas the solution was being mixed speedily, 20 mL of KOH 0.1N was added to the solution. The reaction was lasted for 30 min then, purification as well as the washing was carried out at pH=7, resulting Ca (OH)2 salt which was left for 24 h at 60˚C to be dried. Then, it was calcinated at 600˚C for 7 h and CaO nanoparticles was formed. The morphology of CaO nanoparticles was checked using Field Emission Scanning Electron Microscope (SEM, LEO-1530VP). The crystalline structure of CaO nanoparticles was confirmed by X-ray diffraction (XRD, PHILIPS, X'pert-MPD system, l=1.54 A˚).

Conditions of esterification

The esterification process has been repeated for diverse methanol/oil molar ratios, H_2SO_4 catalyst concentrations, temperatures, and reaction times.

All these experiments have been performed at laboratory scale equipment. In each case, 50 gram of waste cooking oil was added into the reaction flask equipped with reflux condenser, magnetic stirrer and thermometer. After esterification reaction, the mixture was settled overnight (T=23 ˚C, P=1 atm). The main mixture was used for purification to remove any water and unreacted methanol. To remove any acidic catalyst content, the esterificated oil was eluted by distilled water four times and then the system were left to be settled and the water phase was removed. After elution, the pH of finally resulted oil reached to 6.5 from its initial value (5.0), which is a confirmation for elimination of acidic catalyst content. The FFA content of each oil was determined using the method reported by Barthet et al. [20].

Conditions of transesterification

Each typical reaction was carried out in a 250 mL round-bottom flask containing 50 grams of esterificated oil equipped with a thermometer and mechanical stirring. Molar ratios of methanol/oil were adjusted at different amounts to find the optimum situation. At preferred temperature, desired amount of methanol as well as catalyst (CaO nanoparticles) was added whilst stirring at 1000 rpm in order to remain the system homogeneous in temperature and suspension. The mixture was left overnight for settlement. Two phases were appeared ,including methyl ester and glycerin. The earlier phase was decanted and centrifuged to participation of catalysts. The mixture then heated to 100˚C for 30 min to remove any remaining alcohol and water.

Taguchi method and design of experiment

Minitab 17 software was used to apply Taguchi algorithm. Based on Tables 1 and 2, we considered 4 factors of time (min), temperature (˚C), molar ratio of alcohol/ oil and the amount of catalyst (as percent of the oil) at 4 different levels. In this method, the average impacts of each variable on the acidity (at esterification) and on the yield of biodiesel (at transesterification) were investigated. Based on the number of variables, Taguchi algorithm suggests 16 optimal tests for esterification as well as transesterification processes (see Table 1 and 2).

Table 1.The variables for each level of esterification

parameters	Level 1	Level 2	Level 3	Level 4
H_2SO_4 (gr)	0.2	0.5	1	1.5
Methanol/Oil	3:1	6:1	9:1	12:1
Temperature (°C)	80	90	100	110
Time (min)	30	60	90	120

Table 2. The variables for each level of transesterification

parameters	Level 1	Level 2	Level 3	Level 4
CaO nanoparti-cles(gr)	0.5	1	1.5	2
Methanol/Oil	6:1	8:1	10:1	12:1
Temperature (°C)	60	80	100	120
Time (min)	30	60	90	120

RESULT AND DISCUSSION

The SEM picture of the synthesized CaO nanoparticles is shown in Fig.1 (up). Scrutinizing on the morphology feature of the particles reveals that the synthesized CaO nanoparticles have lower dimensions than 100 nm that implies that the produced catalysts are in nano-dimension. The XRD pattern of resulted CaO nanoparticles is also depicted in Fig 1 (down). XRD result discovered that the samples are monophasic cubic nanoparticles with lattice constant a=4.801Å having nano-sized particles. The representative peaks were higher in intensity and thinner in spectral width, confirming that the samples are of good crystallinity. No peaks agreeing to impurities were noticed, confirming that the sample has high quality.

Esterification

The initial FFA for raw oil was measured 6.1%, which means we could not directly use this raw oil toward transesterification. To reduce the FFA content of oil to less than 1%, a pre-treatment step (esterification) was carried out [6, 21].

In each of the 16 experiments of esterification suggested by the Taguchi method, the specified amounts as shown in Table 1 are provided for each reaction. In Table 3, the values of 16 parameters of Taguchi method along with the results of %FFA for each experiment are listed.

Table 3. The results of esterifications in situations suggested by Tagochi method

No.	Factor	Quantity	Level	%FFA	No.	Factor	Quantity	Level	%FFA
1	H_2SO_4	0.2	1	%1.34	9	H_2SO_4	1	3	%1.57
	CH_3OH/Oil	3:1	1			CH_3OH/Oil	3:1	1	
	Time	30	1			Time	120	4	
	Temperature	80	1			Temperature	100	3	
2	H_2SO_4	0.2	1	%1.01	10	H_2SO_4	1	3	%1.06
	CH_3OH/Oil	6:1	2			CH_3OH/Oil	6:1	2	
	Time	60	2			Time	90	3	
	Temperature	90	2			Temperature	110	4	
3	H_2SO_4	0.2	1	%0.89	11	H_2SO_4	1	3	%0.62
	CH_3OH/Oil	9:1	3			CH_3OH/Oil	9:1	3	
	Time	90	3			Time	60	2	
	Temperature	100	3			Temperature	80	1	
4	H_2SO_4	0.2	1	%1.10	12	H_2SO_4	1	3	%1.23
	CH_3OH/Oil	12:1	4			CH_3OH/Oil	12:1	4	
	Time	120	4			Time	30	1	
	Temperature	110	4			Temperature	90	2	
5	H_2SO_4	0.5	2	%1.23	13	H_2SO_4	1.5	4	%1.57
	CH_3OH/Oil	3:1	1			CH_3OH/Oil	3:1	1	
	Time	90	3			Time	60	2	
	Temperature	90	2			Temperature	110	4	
6	H_2SO_4	0.5	2	%0.57	14	H_2SO_4	1.5	4	%0.95
	CH_3OH/Oil	6:1	2			CH_3OH/Oil	6:1	2	
	Time	120	4			Time	30	1	
	Temperature	80	1			Temperature	100	3	
7	H_2SO_4	0.5	2	%1.34	15	H_2SO_4	1.5	4	%1.10
	CH_3OH/Oil	9:1	3			CH_3OH/Oil	9:1	3	
	Time	30	1			Time	120	4	
	Temperature	110	4			Temperature	90	2	
8	H_2SO_4	0.5	2	%1.10	16	H_2SO_4	1.5	4	%1.12
	CH_3OH/Oil	12:1	4			CH_3OH/Oil	12:1	4	
	Time	60	2			Time	90	3	
	Temperature	100	3			Temperature	80	1	

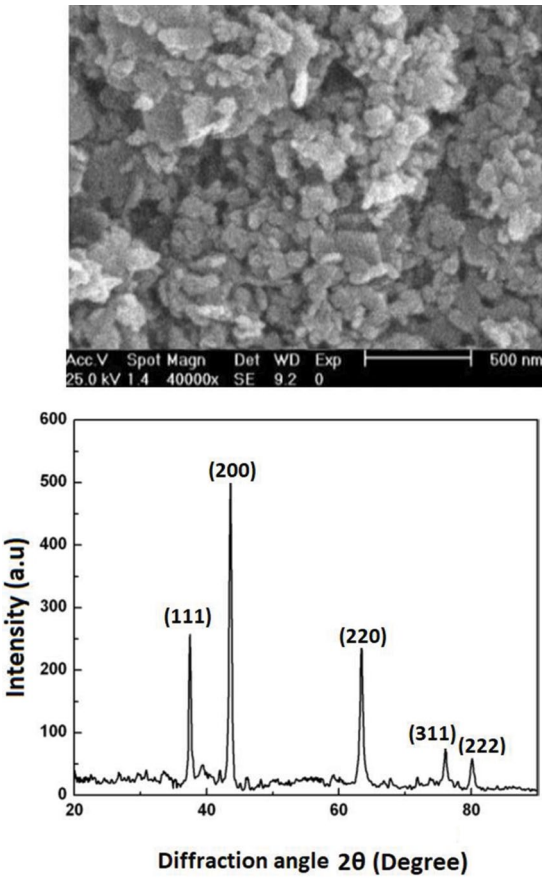


Fig. 1. The SEM picture (up) and the XRD pattern (down) of synthesized CaO nanoparticles.

Then, the obtained FFA values in all experiments entered into the Taguchi algorithm and the mean effect of each variables on the amount of %FFA is achieved. The average impact of H_2SO_4 amount (Figure 2), Methanol/oil molar ratio (Figure 3), reaction time (Figure 4), and temperature (Figure 5) on the amount of %FFA are shown. The best level was determined as the minimum value of resulted FFA. In each graph, the horizontal axis indicates the variable levels. As can be seen in Figure 2, considering the average effects of acid concentration, we can conclude that the amount of 0.5 gr catalyst (1% w/w oil) for esterification gives the lowest % FFA. At a higher acid concentration, the FFA content is increased; most likely, because of reveres reaction that can be catalyzed to produce FFA, however at lower concentration of acid, it seems that the amount of catalyst is not sufficient for esterification reaction. Figure 3 shows the average effects of methanol/oil ratio in esterification process. As can be seen in this figure, applying the ratio of 6:1 for methanol/oil during esterification reaction gives the lowest %FFA, indicating that at higher and lower ratios, the efficiency of esterification reaction is low. Figure 4 represents the average effects of reaction time on the %FFA of resulted oil. It is obvious that the time of 30 min is insufficient for completing the esterification reaction so the %FFA value is relatively high. However, by increasing the times over 60 min, the change is insignificant that implies the reaction is completed. The average effects of temperature on the %FFA of resulted oil are depicted in Figure 5. Apparently increasing the temperature from 80°C diminishes the efficiency esterification reaction (higher value of FFA). This can be attributed to this matter of fact that higher temperature facilities side reactions so that the %FFA of resulted oil can be affected.

According to the minimum Figures 2-5, optimal values of the variables for esterification of waste cooking oil are achieved in the amount of the H_2SO_4 as 0.5 g, ratio of methanol/oil as (6:1), reaction time of 120 minutes and temperature of 80°C. The amount of FFA reduced from 6.1 to about 0.57 by applying above-mentioned situations.

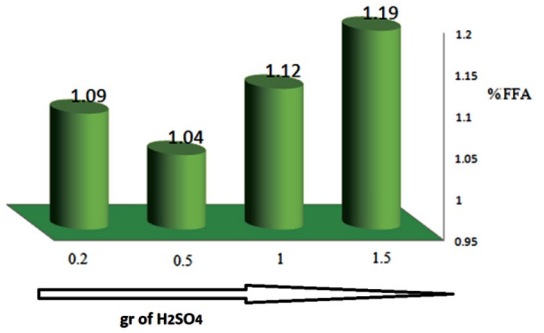


Fig.2. Average effects of H_2SO_4 concentrarion (left to right : 02, 0.5, 1, and 1.5 gr) on %FFA.

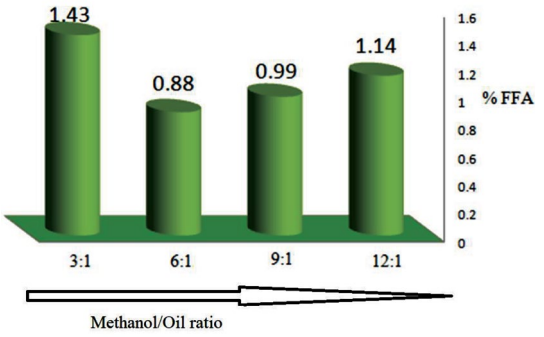


Fig. 3. Average effects of Methanol/Oil ratio in esterification (left to right 3:1, 6:1, 9:1, and 12:1) on % FFA.

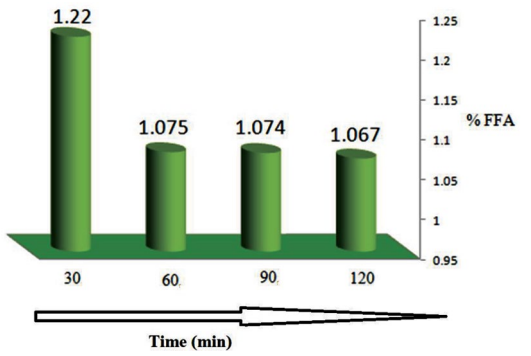


Fig.4. Average effects of time (left to right 30, 60, 90, and 120 min) on % FFA.

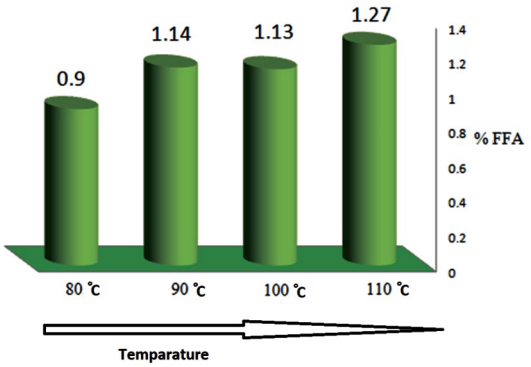


Fig. 5. Average effects of temperature (left to right 80, 90, 100, and 110°C) on %FFA.

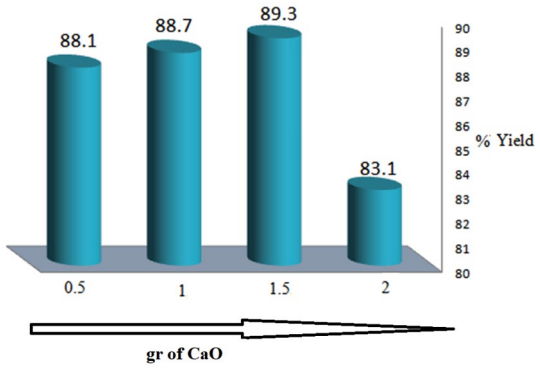
Transestrification

To produce biodiesel (methyl ester), the esterificated oil (reduced FFA) was used for transesterification. To optimizition the process of transesterification, we used Taguchi method by taking into account the parameters and levels listed in Table 2. The yield of biodiesel is calculated from the weight ratio of methyl ester/ oil [22]. All yield are entered into the Taguchi algoritm, then the mean effect of each variable and their optimum results were achieved.

In each experiment, parameters including amounts of CaO nanoparticlrs as catalyst, molar ratios of methanol/oil, temperature, and reaction times have been used to investigate their effect towards biodiesel production.

Taguchi method suggest 16 experiments for transesterification process. the specified amounts as shown in Table 2 are provided for each exprement. In Table 4, the values of these parameters along with the results of yield for each experiment are listed.

In the following, the average effects of CaO nanoparticles catalyst (see Figure 6), methanol/oil ratio (see Figure 7), reaction times (see Figure 8) and temperatures (see Figure 9) on biodiesel yield have been depicted. The maximum amount each impact in the each figure is considered as the best level. In each of the following graphs, the horizontal axis indicates the level of variables.



Figu.6. Average effects of the amounts of CaO nanoparticles catayst (left to right: 0.5, 1, 1.5, and 2 gram) on % yield.

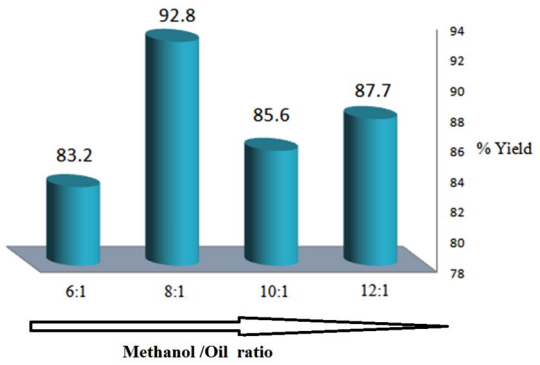


Fig. 7. Average effects of Methanol /Oil ratio in transesterification (left to right: 6:1, 8:1, 10:1, and 12:1) on % yield.

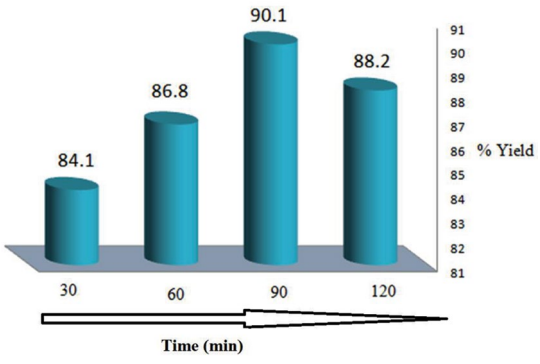


Fig. 8. Average effects of different reaction times of (left to right: 30, 60, 90, and 120 min) on % yield.

Table 4. The results of transesterifications in situations suggested by Tagochi method

No.	Factor	Quantity	Level	%Yield	No.	Factor	Quantity	Level	%Yield
1	CaO	0.5	1	%76.28	9	CaO	1.5	3	%87.02
	CH_3OH/Oil	6:1	1			CH_3OH/Oil	6:1	1	
	Time	30	1			Time	90	3	
	Temperature	60	1			Temperature	120	4	
2	CaO	0.5	1	%93.98	10	CaO	1.5	3	%96.50
	CH_3OH/Oil	8:1	2			CH_3OH/Oil	8:1	2	
	Time	60	2			Time	120	4	
	Temperature	80	2			Temperature	100	3	
3	CaO	0.5	1	%93.74	11	CaO	1.5	3	%85.34
	CH_3OH/Oil	10:1	3			CH_3OH/Oil	10:1	3	
	Time	90	3			Time	30	1	
	Temperature	100	3			Temperature	80	2	
4	CaO	0.5	1	%88.48	12	CaO	1.5	3	%88.32
	CH_3OH/Oil	12:1	4			CH_3OH/Oil	12:1	4	
	Time	120	4			Time	60	2	
	Temperature	120	4			Temperature	60	1	
5	CaO	1	2	%86.08	13	CaO	2	4	%83.44
	CH_3OH/Oil	6:1	1			CH_3OH/Oil	6:1	1	
	Time	60	2			Time	120	4	
	Temperature	100	3			Temperature	80	2	
6	CaO	1	2	%92.60	14	CaO	2	4	%87.93
	CH_3OH/Oil	8:1	2			CH_3OH/Oil	8:1	2	
	Time	30	1			Time	90	3	
	Temperature	120	4			Temperature	60	1	
7	CaO	1	2	%84.20	15	CaO	2	4	%79.01
	CH_3OH/Oil	10:1	3			CH_3OH/Oil	10:1	3	
	Time	120	4			Time	60	2	
	Temperature	60	1			Temperature	120	4	
8	CaO	1	2	%91.72	16	CaO	2	4	%82.15
	CH_3OH/Oil	12:1	4			CH_3OH/Oil	12:1	4	
	Time	90	2			Time	30	1	
	Temperature	80	3			Temperature	100	3	

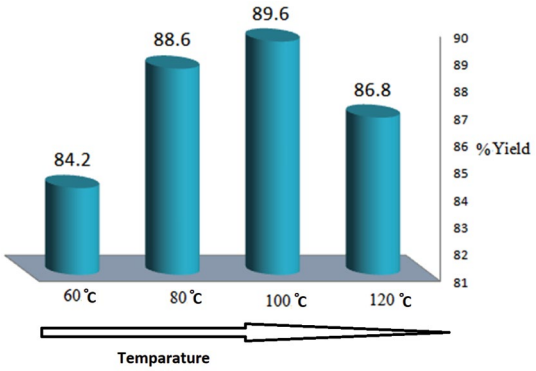


Fig. 9. Average effects of different temperature of reaction mixture (left to right: 60, 80, 100, 120˚C) on % yield.

The optimal values of the variables are achieved at 8:1 molar ratio of methanol/oil, 3% w/w of catalyst (1.5 gr CaO nanoparticles), reaction time of 90 minutes, and reaction temperature of 100˚C. Applying the best situations of all parameters results 96.4% yield for biodiesel production. The amount of the catalyst is one of the factors, which have the highest effects on the yield of methyl ester. The concentration of the catalyst in this study has been optimized because the high and low amounts of catalyst reduce the effectiveness of biodiesel production through reinforcing secondary reactions such as: hydrolysis and saponification, especially when a strong acid such as sulfuric acid is used [23]. In a literature review, the critical values for the catalytic concentration has been changing between 0.25 to 3% oil weight (%Wt) and it is often reported to be about 1% weight [24-26]. In this study, the optimal values of the catalyst concentration in the esterification and transesterification stages have been reported to be 0.5% and 1.5 %wt.

The molar ratio of methanol/oil is also another important effective factor on the yield of biodiesel. Based on the literature review, the optimal yield of biodiesel in molar ratios of alcohol to oil has obtained from (6:1) to (9:1). A right amount of alcohol to oil molar ratio is required in order to break the chains of glycerol, fatty acids, but its amount should not exceed a certain limit. In addition, in the presence of much excess of methanol, the purification process becomes more difficult and expensive [27]. In this study, the optimal values of the molar ratio of alcohol to oil in the esterification and transesterification stages was found at (6:1) and (8:1), respectively.

The effects of reaction time on the yield of biodiesel at different time intervals have been studied. Productivity increases at the start of the experiment and before reducing slowly, it reaches a maximum amount [23]. In this study, the optimal reaction times at esterification and transesterification stages have been achieved 90 and 120 minutes, respectively.

The temperature factor plays major role in any catalytic system that causes the development of the phase transitions, also if it becomes too high, it can be harmful through reinforcing the secondary reactions (hydrolysis and saponification which cause the breaking of ester chains) [23]. The time for the optimum yield is different according to the different circumstances of each system and it is usually in the range of 20˚C to 80˚C [24, 28]. In this study, the optimal values of the reaction temperature in the esterification and transesterification have been found as 80˚C and 100˚C, respectively.

CONCLUSION

In the present study, we aimed to produce biodiesel from waste cooking oil using a two-stage process (esterification and transesterification) along with the optimization of conditions through the Taguchi optimization methodology. At optimum situations for esterification, the FFA content reduced to less than 1% (0.57%) which is ideal for transesterification process. By applying a Taguchi methodology for transesterification stage we found that maximum yield of biodiesel catalyzed by using CaO nanoparticles catalyst (3% w/w), with methanol/oil molar ratio of (8:1) and 100˚C temperature, and reaction time of 90 minutes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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