Optimization of biodiesel production process from household waste oil, rapeseed, and microalgae oils as a suitable alternative for jet-fuel

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Abstract

In this study, to investigate the possibility of replacing non-renewable jet engines with biodiesel produced from household waste oils, rapeseed, and *Neochloris oleobundance* microalgae, biodiesel was first produced by two-stage transesterification using methanol, alkaline and acidic catalysts of potassium hydroxide and sulfuric acid, and then were compared to jet fuel quantitatively and qualitatively. To optimize the biodiesel production, first, the effect of 4 parameters of oil-to-methanol molar ratio, catalyst weight percentage, temperature, and process time at three levels for household waste and rapeseed oils was investigated by Taguchi method. Then, under the obtained optimal conditions, the effect of catalyst weight percentage and process time as the most impressive parameters were examined at three levels on microalgae oil transesterification by response surface method. The biodiesel production efficiency under optimal conditions of all three samples of waste oils was 85.83%, rapeseed 72.7%, and microalgae 86.25%, which is one of the highest values reported. Analysis of all samples by GC-Mass and evaluation of the final results of the transesterification reaction efficiency was over 96%. Combustion analyzes of calorimeter bombs and qualitative specifications analyses such as flash point, cloud point, pour point, freezing point, viscosity, density, and specific gravity were performed on the produced biodiesels to investigate the effects of biodiesel on engine performance. Results Analysis showed that all three biodiesel samples have the same performance as Jp-4 jet fuel and can use it as jet fuel without any sediment. In addition, the biodiesel produced from microalgae oil had the best performance and efficiency.

1. Introduction

It is predicted that the number of passengers in the aviation industry will increase from 2.4 billion in 2010 to 16 billion in 2050 [IATA 2011]. Although the aviation industry's quota of CO_2 emissions is much lower than other sectors of the aviation industry (contributing only 2% of total GHG emissions) [1], this quota is increasing most likely 2 to 3% per year [2], because the industry is growing to fulfill the demand for transportation [3]. Therefore, the International Aviation Association [IATA], to handle this problem, allocates a challenging goal that is to reduce 50% of the aviation industry's net CO_2 production by 2050 in comparison with 2005 levels [4]. A promising approach to achieve this goal is to use alternative jet fuels derived from renewable sources [5]. On the other hand, airlines face significant challenges with rising jet fuel prices (based on crude oil), dependence on crude oil imports, and environmental degradation due to GHG emissions. Renewable aircraft fuels, known as biofuels, are the most desirable alternative. The use of these fuels, while reducing fossil fuel consumption, is less dependent on petroleum-based fuels and cleaner than them, also have a low volume per unit of energy (Gallon per Btu) and reduce GHG emissions by up to 60% compared to petroleum-based jet fuels. Renewable aviation fuels can be produced domestically (by any country) from different sources, thus providing a reliable source of liquid fuel for the aviation industry [6].

For biodiesel production, fast growth structures and high-fat content are preferred. Different countries use various biological sources such as corn, soybean, canola, jatropha, palm, and microalgae [7]. Due to the exclusive features of microalgae such as non-competition with the food industry, environmental compatibility and easy decomposition in nature, rapid growth, the possibility of growing in non-agricultural areas, the ability to use wastewater for growth, reducing the salinity of water and to fertile soil, no negative impact on water sources, without wastewater, the possibility of genetic manipulation, non-toxic, 10times of CO_2 consumption and decreased 78% CO_2, reduced emissions of harmful chemicals and pollutants, lack of sulfur, high production capacity, ease of transport, high-fat content in cell structure, having vitamins and valuable substances for animal and aquatic feed after oil extraction, it seems that in comparison with other oil sources, microalgae have a higher ability to produce biofuels on a commercial scale [8, 9].

One of the most substantial steps in economizing the biodiesel production operation is choosing the correct method to convert oil into biodiesel. According to the processing techniques and properties of biodiesel, biodiesel production procedures can be divided into direct mixed physical methods, microemulsion, and chemical methods pyrolysis and transesterification [10]. Among the various ways of converting oil to biodiesel, the best affordable method to overcome the high-viscosity problem is the transesterification or alkalization method, which according to Fig. 1, is a reversible three-step reaction [11].

The transesterification reaction is the most common process for the conversion of triglycerides to their equivalent methyl esters. The first step is acidic esterification, in which the oil at the right temperature and time at first reacted with methanol along with the acid catalyst. In the second step, the resulting solution is combined again with methanol and alkaline catalyst, against the previous step, at the appropriate temperature and time. Finally, the desired substance is poured into the Separatory funnel to separate the biodiesel from glycerol. Eventually, the biodiesel produced by this method can purify in ways like distillation, adsorption, ion exchange resin, or washing with water. Purification of the final product has particular importance for achieving international biodiesel standards. Untreated biodiesel contains various impurities such as glycerol, soap, metal ions, methanol, catalysts, water, and glycerides. Engine performance can reduce with high levels of impurities [13]. The rinsing method with water is widely used to remove any residues of potassium salts and soap as byproducts of free fatty acids, glycerin, and methanol [14].

In 2017 Aljabarin et al. after algae drying and oil extraction from it, produced biodiesel and concluded that the biodiesel properties are similar to diesel oil, except that it reduces CO2 emissions and doesn't emit any SO_2 sulfur [15]. Ge et al. reported the production of biodiesel from rapeseed oil in 2017, and after examining some of its physical and chemical properties concluded that biodiesel produced from this oil can be used in the engine and reduces emissions, as well as in combination with fossil fuels can improve fuel properties [10]. In 2018, Cercado et al. reported the transesterification process by ultrasonic with mineral catalysts and concluded that the use of mineral catalysts is more cost-effective and achieves a biodiesel production efficiency of more than 85% [16]. In 2019, Jesus et al. purified algae biodiesel by using green solvents and studied its physical, chemical properties, and chemical composition, and found that the purification of biodiesel with green solvents has the same results as purified by hexane. They also concluded that green solvents have great potential to replace hexane in the biodiesel treatment process and that the price of these solvents is the only factor that limits their large-scale use [13].

Despite many studies on cost reduction and optimization of the biodiesel production process, due to the diversity of primary production sources, optimize the biodiesel production from primary sources in each region and then compare their performance with fossil fuels to find a suitable quality biodiesel replacement for this fuel is essential. Therefore, in this study, biodiesel production from household waste oils and rapeseed and microalgae *Neochloris Oleoabundance* as a high-fat strain was optimized. This biodiesel was produced in the presence of acid catalyst sulfuric acid and alkaline catalyst potassium hydroxide by the two-step transesterification method. Then by design experiments method, impressive parameters in production for each kind of oil were inquired also can be selected optimal conditions for biodiesel production. Finally, the quality of biodiesel from three types of oils was investigated and compared with jet fuel.

2. Materials And Methods

2.1 Production of biodiesel from oil

2.1.1 Oil preparation

In this process, household waste oil, rapeseed oil, and *Neochloris Oleoabundance* (Oil Fox Company) microalgae, which is in the group of high-fat microalgae, were used. Household and rapeseed oils were filtered through Whatman 1 filter paper before use to separate impurities and prevent them from affecting the process. Then the characteristics of all three oil samples containing acidity, acid number, soap index, molecular mass, and moisture content were determined.

The amount of free fatty acids of the used oils were measured using titration by 0.1 N KOH solution. After the resulting solution turned purple for 5–10 seconds, the volume of KOH solution used was recorded. Then the percentage of free fatty acids in each oil was calculated according to Eq. 1. Finally, the pH of the final solution was measured.

%FFA= $\frac{0.5 \times A \times N \times W_{cat}}{W}$ [17](1)

A: Volume of used base solution (mL) N: Normality of base solution (0.1)

W_{cat}: Catalyst molar mass (56.1) W: Used oil mass (g)

The acid number is 1.99 times the acidity that follows Eq. 2. The procedure of calculating the acid number is the same as the method of calculating the free fatty acids of oil.

AV = $\frac{A \times N \times W_{cat}}{W}$ (2)

A: Volume of used base solution (mL) N: Normality of base solution (0.1)

W_{cat}: Catalyst molar mass (56.1) W: Used oil mass (g)

To measure the index of saponification, 50 ml of KOH solution and alcohol were poured into a 250cc flask containing 4–5 g of oil and a flask without oil (as blank). The flasks were heated at 80–85°C in a water bath for 30 min and cooled to a range of 30–40°C liquid state, then titrated with 0.5N HCl standard solution. Eq. 3 shows the soap index.

Soap index (mgKOH/g) = $\frac{N \times 56.1 \times (A - B)}{W}$ [13](3)

N: Normality of acid A: Volume of acid used for control titration (mL)

W: Weight of oil (g) B: Volume of acid used for sample titration (mL)

In the transesterification process, to obtain the most suitable amount of catalyst and methanol, as well as to evaluate the performance and efficiency of the oils in the process, it is necessary to calculate the molecular mass of the oils. According to Eq. 4, to calculate the molecular weight of oils, it is necessary to know the values of compounds and fatty acids in the oil. These amounts obtain by chromatography.

MW_{oil} = 3 × $\sum_i(MW\square \times \%m\square) + 38$ (4)

MW_i: Molecular mass of fatty acid i

m_i: Percentage of fatty acid i in the raw material

Another effective feature of the oil is its moisture content. It was measured by a scale of 0.001g (Sartorius TE124S) and oven (Behdad model) with a temperature of 80°C for 2 minutes. Finally, the moisture content of the oil was calculated from Eq. 5.

W= $\frac{\mathrm{m}\square - \mathrm{m}\square}{\mathrm{m}\square - \mathrm{m}\square}$ × 100 (5)

m_1: mass of container and sample before heating (g)

m_2: mass of container and sample after heating (g)

m_0: mass of container (g)

2.1.2 Transesterification process

According to the results, all three samples of oils with free fatty acids were over the limit, so the two-step transesterification process had to be used to convert the free fatty acids to methyl esters first and then, other fatty acids involved to react. In the acid esterification of the first step, the oil temperature was increased to 60°C and added sulfuric acid 1 (w/v) % (98% - Merck) into the available oil. Then, it was stirred for one hour at 60°C and 600 rpm by a magnetic stirrer (Heidolph). The molar ratio of oil to methanol (Merck) was 1:6. By doing this step, the free fatty acids in the oil were converted to methyl ester. The consumed methanol amount was determined by Eq. 6. In the second step, the temperature of the resulting solution was brought to the optimum, and then methoxide containing the optimal weight percentages of potassium hydroxide (Merck) and methanol, with the appropriate molar ratio was added to the oil solution. The resulting solution was stirred for a while at 600 rpm by a heater stirrer to convert the remaining fatty acids to methyl esters. Finally, the produced solution was poured into the separatory funnel to separate the biodiesel from glycerol.

$$\text{Molar ratio of oil to methanol} = \frac{Oil\ mass / _{Molecular\ mass\ of\ oil}}{Methanol\ mass / _{Molecular\ mass\ of\ Methanol}} \qquad (6)$$

2.1.3 Biodiesel purification

The by-products produced during the biodiesel production process must be separated from the biodiesel so that there is no change in the final quality and performance. Glycerol is one of the produced byproducts which was separated by precipitation. Also, due to the alkalinity of the catalyst used, soap materials must be separated from the resulting biodiesel during the water washing process. For water washing of biodiesel, 50% by weight of hot water was added to the biodiesel and placed on the stirrer for a few minutes. The final product was then poured into a decanter to be two-phased and the soapy material to precipitate and separate. This process was continued until no soap remains in the biodiesel and finally clear water is precipitated. In the final stage of purification, a rotary evaporator (Heidolph) was used for 2 hours at 70°C to remove water and methanol remaining in biodiesel.

2.1.4 Optimization of effective parameters in the transesterification process

To maximize the amount of biodiesel, the effect of four impressive parameters in the oil transesterification process, including catalyst concentration, the molar ratio of oil to methanol, temperature, and process time, was investigated at three levels on the conversion of waste oil and rapeseed to biodiesel (Table 1). Using Taguchi experimental design to perform the transesterification process with two-time replications in 9 experiments. Finally, the biodiesel production efficiency is calculated based on Eq. 7. Table 3 shows the test conditions and the average of the results, also the Statistical analysis of these experiments performed by Qualitek-4 software.

Biodiesel production efficiency = $(m_{biodiesel} / m_{oil}) \times 100$ [18](7)

m_{oil}: mass of primary oil (g)

$m_{biodiesel}$: The mass of the final biodiesel obtained (g)

According to the analysis of transesterification processes of rapeseed oils and waste oil results, catalyst concentration and reaction time had the highest effects on biodiesel production efficiency. So, to recognize optimal conditions for transesterification of microalgae oil, according to Table 2 these two factors were examined in three levels during 13 experiments with two-time replications by the response surface method (RSM). The purpose of using the response surface method was to identify and analyze the efficient variables on outputs with the least number of experiments. Table 4 shows the experiments conditions and the average of the results, also statistical analysis of these experiments done by Design Expert-11 software.

Table 1
Factors and levels to optimize the effective parameters in the process of transesterification of rapeseed oil and waste oil based on Taguchi statistical design

Factors Levels	Catalyst percentage (%)	Molar ratio of oil to methanol	Temperature (°C)	Time (Minute)
1	0.8	1:4	55	40
2	1	1:6	60	60
3	1.2	1:8	65	80

Table 2
Factors and levels for optimizing the transesterification process of microalgae by the response surface method

Factors	symbol	module	Levels of factors		
			+1	0	-1
Catalyst percentage	c	%	1.3	1.1	0.9
Time	t	Minute	70	60	50

2.2 Qualitative and quantitative analysis of biodiesel production

If biodiesel does not have enough quality for operating well in a jet engine, its production cannot expand commercially. Biodiesel is composed of a mixture of fatty acid monoesters that the percentage of each monoester can affect biodiesel thermophysical properties such as viscosity, density, cetane number, thermal value, flash point, and cloud point. Also, directly affect the combustion process and engine performance. The thermophysical properties of produced biodiesel such as density, viscosity, thermal value, cloud point, pour point, freezing point, and flash point temperature were measured. In addition, the weight percentage of methyl ester of fatty acids in biodiesel was measured by gas chromatography in combination with mass spectroscopy using GC-Mass (Agilent USA).

Due to the importance of fuel viscosity on engine performance, in this study, the viscosity of the samples was measured at 40°C by Anton Paar SVM 3000 viscometer, which is a Stubinger viscometer with very high measurement accuracy according to ASTM D7042 standard.

The density of 3 kinds of produced biodiesel (waste, rapeseed, and microalgae) was measured by Anton Paar SVM 3000 Densitometer at 15°C (based on ASTM D4052).

The specific gravity of biodiesel samples in this study was calculated based on their biodiesel density and water density at 15°C according to Eq. 8.

Specific weight of biodiesel at 15°C =Biodiesel Density (15°C)/water Density (15°C) (8)

The flashpoint is measured in both open and closed systems. The more volatile the compounds in the sample, the flashpoint is lower. Therefore, the flashpoint should be measured in a closed system [19]. According to the characteristics of the samples in this study, the flashpoint was measured in a closed system by Pensky-Martens according to the ASTM D93 standard.

In this study, the thermal value of biodiesel produced from three types of waste oils, rapeseed and microalgae were measured by a calorimeter bomb device (adiabatic model C4000) under 30bar pressure O_2 according to ASTM D4809 standard.

The clouding temperature was measured according to the ASTM D97 standard by PT-1210 cloud point detector. After recording the cloud temperature, the temperature of the material diminishes so that it freezes completely and does not move anymore. As a result, this temperature will be the same as the freezing point temperature. After measuring the temperature of cloudiness and freezing, the material was heated until the first drop of liquid gains from the material. This temperature is the drop point temperature.

3. Results And Discussion

3.1 Results of oil profile analysis

The percentage of free fatty acids was measured based on the oleic acid in the oil. The presence of free fatty acids should be less than 0.5% because if there is not, it causes corrosion and thus reduce the resistance to oxidation [18]. Therefore, the percentage of free fatty acids in each oil also each oil's density were calculated. The percentage of free fatty acids in household waste oil, rapeseed oil, microalgae were 1.09%, 0.68%, oil 2.19%, and the oils densities were 1.15, 1.23, and 0.96, respectively.

Acidity is a measure of the amount of free organic acids in fats and is calculated in terms of the acid that is most common in the sample. The acid number is the milligram of potassium hydroxide required to neutralize the free acids of one gram of sample [20]. Therefore, the acid number for waste oil is 2.18, for rapeseed oil is 1.36 and for microalgae oil is 4.38. Acidity is a criterion to measure the free organic acids amount of fats. It is calculated according to the acid that is more in the sample. The acid number of mg of potassium hydroxide required to neutralize the free acids is one gram of sample. It means the acid number is the milligram of potassium hydroxide required to neutralize the free acids of one gram of sample [20]. The calculated acid numbers for waste oil, rapeseed, and microalgae oils used in this study were 2.18, 1.36, and 4.38, respectively.

By definition, the saponification number indicates the relative molecular weight of the oil glycerides. The lower the molecular weight of the fatty acids in the fat (short-chain fatty acids), the higher the number of glyceride molecules per gram of fat. Since each molecule of glyceride requires three molecules of potassium hydroxide to be saponified, glycerides that have a lower molecular weight have more soaps. Therefore, the saponification number with the average molecular weight of oil glycerides [21] has an inverse ratio, which was 74.36, 93, and 132.26 for waste oil, rapeseed, and microalgae oils, respectively. According to these values, microalgae oil glycerides had less molecular weight than other samples of this research, and the highest molecular weight was related to the waste oils glyceride.

One of the significant and influential features in biodiesel production is the molecular mass of the primary oil. The high molecular weight of vegetable oils and their relatively high viscosity limit the use of these oils as fuel. There are various methods and processes to reduce the viscosity of vegetable oil, including dilution, thermoforming, and esterification processes [22]. Among the mentioned methods, esterification is more common than other methods. The measured molecular mass was 915.42 for waste oil, 879.999 for rapeseed oil, and 820 for microalgae oil. As expected, waste oil had a higher molecular weight and viscosity than other samples, so the transesterification process for waste oils has more limitations than rapeseed and microalgae oils. Also, microalgae oil had the lowest molecular weight and viscosity compared to the other two samples. This showed that biodiesel production from microalgae oil would be much better than others.

The presence of water has a more negative effect on the ester exchange reaction than the presence of free fatty acids, so the feed should be without water (less than 0.1). Also, the presence of water and free fatty acids causes the formation of soap and the consumption of catalysts. As a result of reduced catalyst efficiency, a decrease in alkyl ester efficiency occurs even a low amount of water in the feed or water produced by the free fatty acid esterification reaction reduces the conversion of fatty acid methyl ester, as well as the formation of soap instead. Therefore, the moisture content measured for waste oil was 0.02%, 0% rapeseed, and 0.01% microalgae oil. The moisture content of the oils was very low and negligible and was within the allowable range that shows all three samples can have esterification reaction well.

3.2 Optimization of transesterification of waste oils and rapeseed oil

The purpose of optimizing the transesterification process of waste and rapeseed oils is to maximize the amount of methyl ester produced. Taguchi's statistical design method was used to optimize the significant conditions and parameters in the transesterification reaction of waste and rapeseed oils. There are many factors in the production of biofuels, but some of them have a high impact and are considered operational factors. The parameters investigated in the optimization in this study were the molar ratio of oil to methanol, catalyst concentration, temperature, and reaction time.

The conditions of each experiment with the percentage of oil to biodiesel conversion are depicted in Table 3. By performing the experiments according to the circumstances designed in this study, the highest conversion efficiency of waste oil to biodiesel was 62.45% (Experiment 8), and rapeseed oil was 65.15% (Experiment 9). Analysis of variance with software suggested other points where all parameters are in the third level as optimal points (Table 4).

Waste oil transesterification was performed under optimal conditions: 1.2 (w/v)% catalyst, 1:8 molar ratio of oil to methanol, 65°C, and 80 min reaction time. The production efficiency was 85.83%, which was much better than the efficiency of the eighth experiment (as the best run). Waste oils have a lot of impurities because they have been used several times before and have changed the structure of the oil. As regards the negative effect of those changes and impurities on efficiency, thus for having the complete reaction requires more temperature, time, and amounts of material. Therefore, when all parameters were at their highest quantity, the best conditions for transesterification of waste oil get. The predicted value was confirmed after operating experiments two times under mentioned condition.

Table 3

Conditions for performing experiments to optimize various factors on the performance of the transesterification process of waste oils and rapeseed oil by Taguchi method with a percentage of oil conversion to biodiesel

Factors **Run Number**	**Catalyst percentage (%)**	**Molar ratio of oil to methanol**	**Temperature (°C)**	**Time** **(Minute)**	**Rapeseed oil conversion percentage (%)**	**Waste oil conversion percentage (%)**
1	0.8	1:4	55	40	35.9 ± 0.5	failed
2	0.8	1:6	60	60	21.7 ± 0.5	failed
3	0.8	1:8	65	80	57.12 ± 0.5	61 ± 0.5
4	1	1:4	60	80	45.75 ± 0.5	41.17 ± 0.5
5	1	1:6	65	40	53.17 ± 0.5	21.45 ± 0.5
6	1	1:8	55	60	57.5 ± 0.5	45.8 ± 0.5
7	1.2	1:4	65	60	34.45 ± 0.5	54.5 ± 0.5
8	1.2	1:6	55	80	46.3 ± 0.5	62.45 ± 0.5
9	1.2	1:8	60	40	65.15 ± 0.5	56.1 ± 0.5

Based on the analysis of variance data in Table 4, the optimum point for biodiesel production from rapeseed oil was 1% (wt%), the molar ratio of oil to methanol 1: 8, reaction temperature 65°C in 40 minutes with a yield of 72.7% compared to the efficiency of the ninth experiment and the average efficiency of the nine experiments performed, that is 46.33%, is much better and shows better performance under optimal conditions. The efficiency achieved was desirable in comparing the efficiency obtained in this research with the software efficiency. Once again, the rapeseed oil transesterification process has performed under optimal software conditions; as expected, the yield was 72.7% and higher than the yield of the ninth experiment conditions. According to the circumstance of the ninth experiment in Table 3, the efficiency was the highest at 60℃ with 1.2% of catalyst. According to the analysis of results variance (in Table 4), efficiency can be increased from 65.15 to 72.7% by 5℃ increasing the temperature (brought to 65℃) likewise decreasing the catalyst to 1%.

Based on the data from the analysis of variance of the results in Table 5, a maximum effect on the production efficiency of biodiesel from waste oil is the catalyst concentration with approximately 46% impact as well as rapeseed biodiesel, the molar ratio of oil to methanol is about 55.7% impact. Small changes in this amount cause significant variations in the production efficiency of rapeseed biodiesel. Also, the temperature has a minimum effect on the production process of biodiesel from waste and rapeseed. As a result, the temperature changes have little influence on efficiency. However, the time has more impression on the production of waste biodiesel than the molar ratio of oil to methanol. The percentage of catalyst and time in the reaction of rapeseed biodiesel production is almost equal and affects the process to the same extent.

Table 4
Optimal conditions for biodiesel production from waste oil and rapeseed oil

parameters	**Optimal values**		**level**		**Contribution**	
	waste	**rapeseed**	**waste**	**rapeseed**	**waste**	**rapeseed**
Catalyst concentration (w/v) %	1.2	1	3	2	17.2	5.80
Molar ratio of oil to methanol	1:8	1:8	3	3	10.9	13.58
Temperature (℃)	65	65	3	3	5.2	1.90
Time (Minute)	80	40	3	1	14.48	5.06
Current Grand Average of Performance of waste oil 38.05						
Expected Result at Optimum Condition of rapeseed 85.83						
Current Grand Average of Performance of rapeseed oil 46.33						
Expected Result at Optimum Condition of rapeseed 72.70						

3.3 The effect of various factors on the conversion efficiency of waste and rapeseed oils to biodiesel

3.3.1 Temperature effect

According to Table 5, the temperature parameter had a minimum effect on the rate of waste oil conversion. According to Fig 2 and Fig. 3, the influence of temperature on the production of biodiesel from rapeseed oil and waste oil has been diminishing initially, then has an increasing rate with escalating temperature. The ester exchange reaction is endothermic that causes a positive effect on the conversion percentage by the enhancement in temperature. According to the reducing part of the graph, especially for waste oil, it is predicted that in this temperature range, the process is not complete. These changes, especially for rapeseed oil, are very insignificant and can be ignored; So, the temperature will not have much efficacy on the conversion percentage of rapeseed, as shown in the analysis of the variance table. Likewise, increasing the temperature raises the miscibility of the reactants and reduces the reaction time.

Table 5
Statistical parameters obtained from analysis of variance of waste oils and rapeseed

Factors **Features**	**Time**		**Temperature**		**Molar ratio of oil to methanol**		**Catalyst concentration**		**Total**	
DOF (f)	rapeseed	waste	rapeseed	waste	rapeseed	waste	rapeseed	waste	rapeseed	waste
	2	2	2	2	2	2	2	2	8	8
Sum of Sqrs. (S)	326	1795	25	264	835	1000.7	314	2611	1499	5671.4
Variance (V)	163	897	12.4	132	417	500	157	1306		
Pure Sum (S’)	326	1795	25	264	835	1001	314	2611		
Percent P(%)	21.74	31.65	1.65	4.66	55.7	17.64	20.9	46.04	100	100

Aladetuyi et al. (2014) used residual oil of spent bleaching earth at 100°C for 120 minutes to produce 81.2% biodiesel [23]. Also, Klabsong et al. (2017) were able to produce 77.64% biodiesel from residual oil from POME (Palm Oil Mill Effluent) at 230°C for 300 minutes [24].

3.3.2 Time effect

The time effect ascending procedure on the conversion rate of waste oil indicates a direct relationship between time and conversion percentage. Therefore, by elevating it, the reactants have more time to react, thus increasing the yield of the process. According to Fig. 3, after 60 minutes for waste oil, reaction progress speed was more than other times and augmented with more slope, so the best time for the transesterification reaction for waste oil is 80 minutes.

The time parameter is more important than the temperature parameter and has a 21.74% effect on the biodiesel production efficiency of rapeseed oil. According to Fig. 2, the yield of rapeseed oil reaction abates with passing the time. Although the experiments performed at times longer than 60 minutes had a pleasant efficiency, the maximum efficiency observed at 40 minutes. The presence of catalyst caused to raise the reaction speed accordingly the highest efficiency can be achieved in the shortest time (40 minutes). Likely at longer times, the catalyst participates in the reaction as a reactant that it can have two consequences. First, it reduces the methyl ester production efficiency for having a reactant role in the process. Second, because the catalyst has more contact with the reactants, the production of impurities increases afterward, fewer fatty acids have converted to methyl esters. As a result, 40 minutes was selected as the optimum time for rapeseed biodiesel production.

Hindryawati et al. (2017) used residual oil from palm decanter cake for 300 minutes to produce biodiesel, which achieved a yield of 70.2%. [25]. Ricca et al. (2013) also used sludge oil in producing biodiesel in 24 hours then reached 62.3% efficiency [26]. According to the experiments performed in this study, the production of waste oil biodiesel and rapeseed biodiesel is faster than production in other studies.

3.3.3 Effect of catalyst concentration

Catalyst percentage with 46.04% is the most efficient factor in converting waste oil to biodiesel when it increases, the process efficiency augments too, but the growth range is limited. The excessive increase of catalyst percentage will cause process disruption and raise costs. As can be seen from Fig. 3, the amount of catalyst and the percentage of waste oil conversion is almost directly related, so the highest percentage (1.2%) as the optimal state of this parameter is selected for waste oil. According to Fig. 2, in rapeseed oil transesterification, by increasing the percentage of catalyst, the efficiency of the process first increases and then decreases. Increasing the catalyst amount from the optimum value is likely to cause the catalyst to react with the fatty acids. In other words, the catalyst acts as a reactant, and fewer fatty acids are converted to methyl esters and production efficiency reduced, but its slope is not high. The optimum catalyst concentration for rapeseed oil is 1% and does not need to be more increased.

Tang et al. (2016) by a concentration of 5% HCL as an acid catalyst reached a 10% yield of biodiesel production from Nannochloropsis Gaditana [27], which predicted that an excessive amount of catalyst caused the catalyst to act as a reactant and react with other reactants, and reduce the production efficiency. Also, Franseschi et al. (2016) investigated biodiesel production from African palm oil by the two-step transesterification method, which had 90% biodiesel efficiency with 2.5% NaOH as an alkaline catalyst in 150 minutes [18]. Since the goal is to produce biodiesel at the lowest costs, thus increasing the number of raw materials such as catalysts will augment the final price of biodiesel. Therefore, this study aims to achieve the highest production with the least raw materials. In this research, with 1.2% of catalyst, 85.83% obtained for waste oil biodiesel efficiency, which compared with other investigations, by the minimum catalyst, gain a suitable yield.

3.3.4 Effect of oil to methanol molar ratio

According to Fig. 2 and Fig. 3, the effect of the molar ratio of oil to methanol in both samples is the same and has the same descending trend. Accordingly, with escalating the molar ratio of oil to methanol, the production efficiency of both of them diminishes and represents that the increase of more than 1:6 of this ratio did not have much efficiency on the production process. Enhancing the amount of methanol in the reaction mixture leads to more dissolution of glycerin and alcohol and significantly affects its purity. If this ratio grows more than a limit, the purity of biodiesel produced will reduce. Growing this ratio more than the permissible limit will disrupt biodiesel production, and the segregation of glycerin from biodiesel becomes difficult. Therefore, the lowest molar ratio (1:8) is selected as the optimum amount of this parameter for every two samples of waste and rapeseed. Reviewing the studies of Prafulla et al. (2009) in converting Karanja oil to methyl ester with a molar ratio of 1: 6, they achieved an efficiency of 80% and concluded that by reducing this amount to a molar ratio of 1:9, they could achieve higher efficiency [28]. Also, Zeng et al. (2009), by a 1:101 molar ratio, could achieve a 97% biodiesel yield of sunflower oil, which is a very high amount of methanol consumed, which leads to more impurities and consequently more expensive purification process and thus increase production costs [29]. Comparing the results obtained in this study with others can conclude that both types of oils convert to methyl ester with a lower amount of methanol, and desirable production efficiency is obtained.

3.4 Optimization the efficiency of converting microalgae oil to biodiesel

The purpose of the previous analysis on waste and rapeseed oils was to realize the main factors finally select more notable parameters. Eventually, catalyst concentration and reaction time were selected as the most significant parameters. These two parameters were optimized by the response surface statistical method with CCD (Central Composite Design) algorithm also their efficacy on yield was investigated. This optimization included 13 experiments whose average results are (repeated twice) in Table 6. Experiment conditions 9 with the conversion efficiency of 86.25% have the highest biodiesel production yield.

Table 6

Conditions and response (percentage conversion to biodiesel) Optimization experiments of effective parameters in the process of transesterification of microalgae oil based on the statistical method of response surface

Factors No.	**Catalyst concentration (%)**	**Time (minute)**	**Microalgae oil percentage conversion to biodiesel (%)**
1	1.1	70	54.6
2	0.9	60	39
3	1.3	60	66.75
4	1.1	60	57.4
5	0.9	70	23.05
6	1.1	60	51.15
7	1.1	50	50.15
8	1.1	60	70.7
9	1.3	70	86.25
10	1.3	50	53.75
11	0.9	50	36.25
12	1.1	60	70.75
13	1.1	60	60.85

The influence of selected factors on the transesterification yield was found by analyzing the variance of the experimental results by Design expert-11 software. Also, the conditions and optimal production efficiency were predicted. Furthermore, a mathematical model was obtained according to the regression coefficients. The P-values show the relationship between the response variable (biodiesel conversion percentage) and independent variables. Also, P-value is used to evaluate the significance of each regression coefficient. Factors with a P-value of less than 0.05 are effective parameters. Based on the obtained coefficients and values, the P-value of the catalyst was less than 0.05 (0.0006) and had a positive effect on process efficiency. The standard error (SE) less than 10% indicates a suitable model, so if the standard error is less than 5% represents an admirable result and a high-quality model. In this project, the standard error for both parameters is 3.03% and for the interaction of two parameters is 3.71%, which as a result, the efficiency is desirable, and the designed model has been successful.

Equation 9 is the model obtained on this basis. In this model, “Y” represents the conversion percentage, “C” and “t” represent the percentage of catalyst and time, respectively. The negative sign of the coefficients in the model means that the target parameter has a negative efficiency on the conversion percentage and the positive sign illustrates a positive influence on the conversion percentage. Accordingly, in the present model, both parameters have a positive effect on the conversion percentage, therefore the efficient parameters have been selected correctly. In other words, by increasing these parameters, the conversion percentage elevates.

$$Y = -102.96789 + 79.75862 \times C + 1.95864 \times t + 5.71250 \times C \times t - 150.96983 \times C^2 - 0.065388 \times t^2 \quad (9)$$

Table 7 shows the results of the analysis of variance calculated by the software to confirm the model. Lack of fit measures the inability of the model to represent laboratory data that are not regressed. The P-value for the lack of fit quality was 0.74, which is not significant and shows that the selection of parameters and the removal of insignificant parameters were done correctly and demonstrates the pleasant fit of the model. The values of R^2 and R^2_{Adj}. of this model are 0.8837 and 0.8006, respectively. Their high and close proximity to each other indicates the adequacy of the model. R^2_{Adj} demonstrates more accurate results than R^2; because in R^2_{Adj} the mean squares are used besides the degree of freedom, the inverse of R^2 that uses the sum of squares. Also, the $R^2_{predicted}$ value in this design is 0.665, which means that is the farther away from one, the more experiments will have to be repeated. $R^2_{predicted}$ and R^2_{Adj} differences should be less than 0.2, which according to the values obtained in this project, the difference between these two values is 0.1841 and is in the appropriate range. It shows that the results obtained are desirable and the model achieved is successful. Optimization of the esterification conditions of waste oil and rapeseed oil and its consequences can have significant efficacy on the esterification performance of microalgae oil.

Table 7
Analysis of variance calculated for the response surface method by the software

Source	Sum of squares	df	Mean squares	F-value	P-value
Model	2929.51	5	585.90	10.64	0.0036
c	1960.23	1	1960.23	35.58	0.0006
t	94.01	1	94.01	1.71	0.2327
c×t	522.12	1	522.12	9.48	0.0179
c^2	100.72	1	100.72	1.83	0.2184
t^2	118.09	1	118.09	2.14	0.1866
Pure error	292.31	4	73.08		
Cor total	3315.14	12			
Residual	385.62	7	55.09		
Lack of fit	93.31	3	31.10	0.4256	0.7456

Figure 4 shows the comparison of the obtained values with the predicted values for the biodiesel production efficiency by the model. In this diagram, the predicted value for each actual response has been determined by the actual and predicted equation. The higher the value of R^2 and close to one, the less the data scatter around the 45° line. In addition, if the data is above the line, it has a positive error, and if it is below the line, it has a negative error. If the selected model is suitable, it will have both positive and negative errors. A positive error means that the software has predicted a value higher than the actual value. According to this graph, the data have a proper normal distribution. Likewise, the predicted and actual values are in good agreement as the value of R^2 is obtained close to one. It means that the model fits well with the data. The adaption of the predicted responses of the model with the actual values is higher if the variance of the data around the line be more.

Figure 5 shows the contour or two-dimensional diagram of the interaction of the parameters. According to Fig. 5, the time parameter does not affect the yield much. As shown in the analysis of the variance table (Table 8), the P-value for the time parameter was higher than 0.05. As a result, in this project, by increasing the amount of catalyst, the efficiency of the process enhances. Also, this amount has a greater efficacy on the yield than time. According to the contour diagram, the highest efficiency, which is above 80%, is obtained in the highest amount of catalyst (1.3%) and the highest time (70 minutes).

A 3D graph can be used to find the optimal point, the point with the highest efficiency. As shown in Fig. 6, the catalyst percentage with the highest value was more efficient; however, time had little effect. In addition, it displays that the selected parameters are impressive well as the chosen range for each of the parameters is the suitable selection. Figure 6 indicates catalyst is more effective than time, and as the concentration of catalyst increases, the efficiency of the process also elevates. According to Fig. 6, a point with a catalyst value of 1.3% in time 70 minutes has the highest efficiency at 86.25% is known as the optimum point.

Salam et al. (2016) examined methyl ester production of transesterification of oil of two algae types of C. Vulgaris and N. Occulata by different catalysts. Their highest methyl ester production respectively was 57.5% and 53.8% in the molar ratio of 8.5:1, process time of 24 h, and temperature of 60°C [30]. Sidra et al. (2016) also investigated biodiesel production from non-edible oils such as jatropha oil by transesterification process using CaO-Al_2O_3 nanocatalyst. They examined the effect of molar ratios of oil to methanol on transesterification efficiency in two values 1:3 and 1:5. The maximum biodiesel production efficiency of the transesterification process of Jatropha oil by particle nanocatalyst CaO-Al2O3 was 82.3% that obtained in the molar ratio of oil to methanol 1:5 [31]. The optimal conditions selected in the present study led to the biodiesel production efficiency of 86.25%, which is higher than the values obtained in other studies. In comparison to other sources of biodiesel production, microalgae oil has higher efficiency. Based on the results obtained, it can be concluded that the microalgae Neochloris oleoabundans have produced more than other microalgae in research conducted by others.

3.5 Results of qualitative analysis of produced biodiesels

3.5.1 Viscosity

Kinematic viscosity is one of the most critical properties of engine fuel. It plays a significant role in fuel injection, mixing, and combustion properties. Within the fueling system, fuel viscosity is effective in softening the system. If the fuel has a low viscosity, it cannot provide effective softening properties for the fuel injection system. Hence, corrosion and dropping increased into the fuel system. If the fuel used has a high viscosity, the fuel injection system will need more energy to spray the fuel. It is caused the fuel to be poorly distributed, energy production reduced and increased particulate matter and exhaust fumes. Fuel viscosity affects the spray pressure, the diameter of the sprayed particles, their penetration into the combustion chamber, and lubrication of engine parts. The viscosity of the primary crude oil is of great importance in the viscosity of the final biodiesel produced. The viscosity of the final biodiesel also has a large effect on the fuel performance of the engine, especially in cold weather. High viscosity values cause problems in fuel pumping and filter closure. In addition, viscosity is related to the size of the spray droplets produced by the burner nozzles [32, 33, 34].

In this study, the viscosity of biodiesels measured at 40°C for waste oil, rapeseed, and microalgae biodiesel was 7.2, 4.85, and 4.2 mm^2/s, respectively. However, the viscosity of standard biodiesel is in the range of 1.9-6 mm^2/s, which by comparing the obtained values, the waste biodiesel has a lower quality than the other two types, which is predicted due to the low quality of the primary oil.This amount also causes poor fuel distribution, reduced energy production, and increased particulate matter and exhaust fumes. The quality of rapeseed and microalgae biodiesel is close to each other, but due to their quantity, as expected, the quality of microalgae is higher than other oils, is more suitable for use in the engine, and causes more proper combustion in the engine.

3.5.2 Thermal value

The thermal value of the fuel is a substantial factor in evaluating its quality and efficiency. Biodiesel fuel has low hydrogen to carbon ratio because of the presence of oxygen in its molecular structure. Therefore, it has a low thermal value, but diesel fuel lacks oxygen. Also, biodiesel contains esters of unsaturated fatty acids with different levels of unsaturation, which is another reason for its low energy level compared to diesel. Research shows that the use of biodiesel (in pure form), due to its low thermal value, reduces heat production. One of the most significant tests in the measurement of flammable materials is to determine the thermal value [35].

The measured thermal values for waste biodiesel, rapeseed, and microalgae were 39.566, 39.932, and 40.2 (Mj/Kg), respectively, which were evaluated in the presence of oxygen. Also, the thermal value range of diesel fuel is 40–45 (Mj/Kg) it resulting in the obtained biodiesel that replaces diesel fuel without making changes in the engine. Likewise, by comparing the thermal value of biodiesel produced and fuels used in the aviation industry, the obtained values are close to the thermal value of JP-4 fuel (42.8 Mj/Kg), especially biodiesel obtained from microalgae oil compared to the two types. Its features will be close to Jp-4 fuel's properties, which can be applied in jet and aircraft engines without modification.

3.5.3 Acidity

Total acid number (acidity) is the amount of KOH used to neutralize fuel acids per gram of fuel. In this study, the acid number of biodiesel produced from waste oil, rapeseed, and microalgae was equal to 0.38, 0.45, and 0.41 (mgKOH/g oil), respectively. The acid number of all three types of biodiesel was the desired value in comparison to standard diesel (0.7-1) and standard biodiesel (> 0.5). The presence of free fatty acids in the fuel causes corrosion and reduction of oxidation resistance. By comparing the acid number of produced biodiesel with standard conditions, waste biodiesel and rapeseed, especially microalgae, have proper oxidation resistance will not cause corrosion problems for engine parts, and are acceptable.

3.5.4 Flash point

The flashpoint is the lowest temperature in which the fuel is sufficiently converted to steam and then combined with air to make the mixture flammable. When the flame passes over it, the mixture ignites for a moment and then goes out. Flashpoint plays a vital role in fuel safety, so the flashpoint must be considered in fuel transportation and storage time. The flashpoint depends on the volatility of the fuel, which is an important fuel feature for starting and warming up the engine. Also, a fuel with a high flashpoint creates carbon residue in the combustion chamber, so the flashpoint of the engine fuel should not be too high.

The flashpoint of fuel depends entirely on the components mixed with the low flashpoint. Only at high contents of the mixture component with the higher flashpoint increases fuel flashpoint significantly. The amount of biodiesel flashpoint is affected by the amount of methanol in it. If the methanol amount in biodiesel increases by 0.5%, the biodiesel flashpoint decreases by about 50% [36, 37]. According to ASTM, this value is 130°C for standard biodiesel, more than 130°C for microalgae biodiesel, and higher than 62°C for standard diesel. In this study, the flashpoint for waste biodiesel was 162°C, rapeseed biodiesel 174°C, and microalgae biodiesel 188°C. According to the chromatogram of each biodiesel, microalgae biodiesel has more mixture components and, as expected, has flashpoints higher than other samples. All three specimens are within the standard range and consumable. Microalgae biodiesel has a flashpoint higher than the other specimens that it is more suitable for safety in storage time and transportation.

3.5.5 Cloud point

Cloud point depends on the temperature that affects the biodiesel in different climatic and geographical conditions. The technical characteristics of biodiesel include the cloud point and its higher lubrication property. In addition, the cloud point and the pour point indicate the fuel fluidity properties at low temperatures. The fuel cloud point determines the temperature limit on fuel usage. In this study, the cloud point of biodiesel from waste oil, rapeseed oil, and microalgae oil was + 6°C, 2°C, and − 3°C, respectively. These values are the first temperature at which each sample has seen milky. These temperature values are also effective in fuel fluidity and engine lubrication. This feature for standard biodiesel is in the range of -3°C to 12°C. Therefore, the microalgae biodiesel cloud point is in the acceptable range. According to the obtained results, unlike the other two samples, microalgae biodiesel can have a good performance at much lower temperatures and in cold climates. It shows the superiority of microalgae biodiesel over waste biodiesel and rapeseed biodiesel.

3.5.6 Freezing point

As the fuel cools to the appearance of hydrocarbon crystals, followed by heating the sample, the temperature at which the last crystal disappears; is defined as the freezing point of aviation fuel. This explanation differs from the physical definition of a freezing point, which is the temperature of the phase transition between a liquid and a solid. The freezing point is effective in pumping fuels at low temperatures. Material with a higher viscosity value has a higher freezing point. These two properties can describe the fluidity of jet fuel [35].

The latest hydrocarbon crystals appeared for waste oil biodiesel at -5°C, rapeseed biodiesel at -11℃, and microalgae biodiesel at -17℃, which is known as the freezing point. These values indicate that the microalgae biodiesel has a more suitable fluidity and can be pumped well at a lower temperature than the other two samples. Also, due to the relationship between viscosity and freezing point, as expected, waste biodiesel with higher viscosity has a higher freezing point, against microalgae biodiesel with the lowest viscosity has a lower freezing point. According to ASTM standards, the freezing point of jet A and Jet A-1 are − 40℃ and − 47℃, respectively, which are used as commercial and primary jet fuel in the United States and Europe.

3.5.7 Pour point

Another fuel property is the pour point. The pour point of the biodiesel produced does not depend on the type of catalyst and the reaction conditions but the amount of saturated fatty acids in the oil. The pour point is the lowest temperature at which fuel can flow. The fuel is solidified after this temperature and cannot be used. This point is significant for moving fuel at cold temperatures. The pour point measured in this study for waste oil, rapeseed, and microalgae biodiesels was zero, -6°C and − 12°C, respectively. According to ASTM, the standard biodiesel pour point is -11.6°C. The presence of impurities in the primary oil has a high effect on the pour point of biodiesel. Waste oil had more impurities than rapeseed oil and microalgae as well as rapeseed oil is more impure than microalgae oil. As a result, as expected, the residual biodiesel will not perform well at sub-zero temperatures like the rapeseed biodiesel. In contrast, the pour point of microalgae biodiesel is close to the standard, so microalgae biodiesel has a high resistance at low temperatures and works well at temperatures below standard.

3.5.8 Density and specific gravity

Density and compressibility have a substantial influence on the engine fuel injection system. The amount of fuel injected, injection timing, and injection process are directly affected by this parameter. Density also impresses the emission of exhaust gases, and typically high density will increase the emission of nitrogen particles and oxides. Fuel density is considerable for the quantity of aircraft weight because fuel is a volumetric quantity. It also affects the amount of fuel injected, its timing and the injection process. The density of waste biodiesel and rapeseed biodiesel was 0.88 (g/mL), microalgae biodiesel was 0.85 (g/mL) at room temperature. Also, the density of waste biodiesel at 15°C was 0.901 (g/mL), rapeseed biodiesel at 15°C was 0.883 (g/mL), and microalgae biodiesel at 15°C was 0.882 (g/mL). By comparing the values obtained and the existing standards for biodiesel at a temperature of 15℃ (0.82 to 0.9 g/mL), the density of produced biodiesel in this study is in the standard range. Microalgae biodiesel has a lower density than two other kinds of biodiesel, which will reduce the emission of nitrogen particles and oxides compared to waste and rapeseed biodiesel. In addition, the standards at room temperature have reported for biodiesel 0.88 (g/mL) and microalgae biodiesel 0.85 (g/mL). By comparing standards with the density of produced biodiesels in this study, three kinds of produced biodiesels have a proper density. So, they will have positive influences on the injection system. Likewise, at room temperature, the density of microalgae biodiesel is lower than other types of biodiesel, which indicates the superiority of microalgae biodiesel over other types of biodiesel. Due to the very low density of water at 15℃ (0.992 g/mL), the specific gravity of the obtained samples is equal to the density.

3.5.9 Percentage of biodiesel humidity

The presence of water and moisture in biodiesel is undesirable and needs to be measured. The amount of water content is not in the specifications of air turbine fuels. However, the existence of water in the fuel is undesirable because its presence can cause microbial growth and accelerate corrosion. The presence of a small amount of water can even cause the filter to close at high altitudes so that low temperatures cause water to freeze. If the moisture content is more than 0.5% (wt.% of oil), it disrupts the biodiesel production process and causes the generation of soap. Making soap is a sign of low conversion efficiency. In the present study, the moisture content of produced biodiesel from waste oil, rapeseed oil, and microalgae oil is equal to 0.3%, 0.1%, and 0.01%, respectively. These values are within acceptable limits also, are negligible as well as it does not create a problem in the principal process.

3.6 GC-Mass results of produced biodiesels

After sample preparation and injection into GC-Mass chromatography, based on the concentration of compounds in the sample, responses were issued by the detector. Calculations were performed based on the observed chromatograms from detector responses. The chromatogram consists of peaks corresponding to the concentrations of the compounds in the injected sample, including solvents, methylated fatty acids, and standard internals. Figure 7, Fig. 8, and Fig. 9 indicate the chromatograms of biodiesel of waste, rapeseed, and microalgae oils, respectively. Biodiesel fuel is composed of a mixture of some fatty acid monoesters. The presence of the weight percentage of each of them in biodiesel fuel affects its thermophysical properties. In other words, the biodiesel fuel properties are dependent on the monoester of its constituent fatty acids. The most important of which in the biodiesel monoester are octadecanoic and palmitic, hexadecanoic, stearic, eicosnoic and decoscanic fatty acids. Research on biodiesel fuels derived from different vegetable oils shows that the weight percentage of each of these fatty acid monoesters in biodiesel fuel has limitations. The amounts of fatty acids in the biodiesel fuel impose unique properties on the fuel that directly affect the combustion process and engine performance. In other words, the purpose of GC-Mass analysis in this study was to determine the final biodiesel components and check the accuracy and completeness of the transesterification process of waste, rapeseed, and microalgae oils. Examining the components of Table 8 for biodiesel from waste oil and observing the methyl esters in the sample, concluded that the reaction was performed correctly, and the fatty acids of the waste oil were converted to methyl esters.

Another goal of this analysis was to obtain the conversion efficiency of fatty acids to their methyl esters. Examining the chromatogram obtained from waste biodiesel (Fig. 7) and its components in Table 8 concluded that on average over 96% of fatty acids in waste oil are converted to methyl ester. Also, examining Fig. 8 shows that the fatty acids of rapeseed oil converted to methyl ester and the transesterification process of rapeseed oil performed well so that for this oil, the yield was approximately 92%. As expected, most fatty acids with 99% efficiency are converted to methyl ester and its derivatives. Many of the primary fatty acids in the oil were the same, therefore the methyl esters of these oils also were similar.

Table 8

Results of GC-Mass chromatography for waste biodiesel

RT (min)	Area (Ab*s)	Area%	Name	Quality	Molecular Formula
31.853	31781929	0.3	Methyl myristate	98	$C_{15}H_{30}O_2$
35.59	20384483	0.2	9-Hexadecenoic acid, methyl ester, (Z)-	99	$C_{17}H_{32}O_2$
36.136	1301547967	14.1	Methyl palmitate	99	$C_{17}H_{34}O_2$
37.495	9641727	0.1	Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester	83	$C_{18}H_{34}O_2$
37.948	9447521	0.1	Heptadecanoic acid, methyl ester	98	$C_{18}H_{36}O_2$
39.657	7100486351	76.7	11-Octadecenoic acid, methyl ester	99	$C_{19}H_{36}O_2$
39.914	346049208	3.7	Methyl stearate	99	$C_{19}H_{38}O_2$
40.913	12880101	0.1	Methyl linoleate	93	$C_{19}H_{34}O_2$
42.57	8165498	0.1	1-(4'-pentenyl)-1,2-epoxycyclopentane	89	$C_{10}H_{16}O$
42.838	129711893	1.4	11-Eicosenoic acid, methyl ester	99	$C_{21}H_{40}O_2$
43.26	85746195	0.9	Eicosanoic acid, methyl ester	99	$C_{21}H_{42}O_2$
46.081	43506289	0.5	13-Docosenoic acid, methyl ester, (Z)-	93	$C_{23}H_{44}O_2$
46.462	56901716	0.6	Docosanoic acid, methyl ester	99	$C_{23}H_{46}O_2$
49.097	13951570	0.2	15-Tetracosenoic acid, methyl ester	99	$C_{25}H_{48}O_2$
49.437	29590537	0.3	Methyl lignocerate	99	$C_{25}H_{50}O_2$

In addition to determining the components of the biodiesel sample, by analyzing the GC-Mass chromatogram, information about the concentration of each component is obtained according to the level below each peak and the departure time of each component. The area below the curve of each peak corresponds to its concentration in the sample. Figure 7 shows that the octadecanoic acid methyl ester has the highest surface area below the biodiesel diagram, resulting in the highest concentration of 76.7% for this component. Chromatogram analysis of rapeseed biodiesel also shows that octadecanoic acid methyl ester with the highest peak of 87.9% of the total surface area is taken and consequently has the highest concentration in rapeseed biodiesel (Fig. 8).

Sample components exited from the device column based on their stability time. In other words, the component that comes out at the beginning is less stable than the other components, and the part that comes out at the end is the most stable component of the mixture. Table 8 indicates the retention time of each component. The first component exit from the waste biodiesel in 31.85 min belonged to methyl myristate, which concluded that this component was less stable than the other components. The most stable component of this mixture was methyl lignoceric, which remained in the device column for 49.43 minutes.

The basis of separation in GC-Mass is adsorption and desorption of the components of the mixture in the stationary phase. According to Table 9 and the relevant chromatogram, in the investigation of the retention time of each component, methyl hexadecanoic acid was the first output after 35.48 minutes, and then methyl palmitate was detected by the detector in 36.06 minutes. The difference in their exit time means that the components such as methyl hexadecanoic acid that initially leave the column have a linear motion. While according to the exit time of the methyl palmitate, the molecules of this component move towards the wall and leave the column with the help of the wall. The components that leave the column later than the others also have a vortex motion.

Table 9

Results of GC-Mass chromatography for rapeseed biodiesel

RT (min)	Area (Ab*s)	Area%	Name	Quality	Molecular Formula
35.487	8468423	0.1	7,10,13-Hexadecatrienoic acid, methyl ester	98	$C_{17}H_{28}O_2$
35.59	22060336	0.2	9-Hexadecenoic acid, methyl ester, (Z)-	99	$C_{17}H_{28}O_2$
36.064	524543547	4.6	Methyl palmitate	99	$C_{17}H_{34}O_2$
37.495	13377419	0.1	11-Hexadecenoic acid, 15-methyl-, methyl ester	93	$C_{18}H_{34}O_2$
39.78	10037493225	87.9	9-Octadecenoic acid, methyl ester, (E)-	99	$C_{19}H_{36}O_2$
39.945	261837622	2.3	Methyl stearate	99	$C_{19}H_{38}O_2$
41.695	10080155	0.1	2-Methyl-4-nitroresorcinol	43	$C_7H_7NO_4$
42.859	216508365	1.9	11-Eicosenoic acid, methyl ester	99	$C_{21}H_{40}O_2$
43.27	106958494	0.9	Methyl arachate	99	$C_{21}H_{42}O_2$
46.081	81945286	0.7	Methyl erucate	94	$C_{23}H_{44}O_2$
46.472	51165595	0.4	Docosanoic acid, methyl ester	99	$C_{23}H_{46}O_2$
49.097	31720372	0.3	15-Tetracosenoic acid, methyl ester	99	$C_{25}H_{48}O_2$
49.447	31561137	0.3	Tetracosanoic acid, methyl ester	99	$C_{25}H_{50}O_2$
50.549	15152898	0.1	Stigmasterol, 22,23-dihydro-	74	$C_{29}H_{50}O$

The fatty acids in microalgae oil are much higher than waste and rapeseed oils. Table 10 and the microalgae biodiesel chromatogram (Fig. 9) show that the amount of methyl ester and its derivatives for microalgae biodiesel are much more than the previous two samples. Due to the interaction of microalgae biodiesel with the stationary phase, the components of microalgae biodiesel are in Table 11. The highest concentration is related to octadecanoic acid methyl ester with an area below 65%. The concentration of the desired component in the sample depends on the surface below the graph. For example, methyl laurate with an area below the peak of 0.03% has the lowest concentration in the sample.

The basis of separation depends on the boiling temperature and the polar properties of biodiesel and its components. In chromatogram analysis, it is important to know the chemical and physical properties such as the degree of polarity and boiling point of the material. The components get out at different rates because their speed of interaction with the stationary phase is different. The velocity of the sample depends on two factors: the interaction with the stationary phase and the linear velocity of the carrier gas. Table 10 shows that the exit rates of biodiesel components from the GC-mass column are different. Methyl octanoate was removed from the column as the first component in 9 minutes due to having the lowest stability and highest velocity. Methyl cholesterol was removed from the column in 38 minutes as the last component due to its higher stability than other components. The rate at which components leave the column decreases by their increasing retention time. The faster the component leaves the column, has less interaction between it and the stationary phase. In this analysis, methyl octanoate left the column in a shorter time because of the least interaction. Similarly, methyl cholesterol remained for a long time in the column due to more interaction. The same situation has happened for all components of microalgae biodiesel.

Table 10
Results of GC-Mass chromatography for microalgae biodiesel

RT (min)	Area (Ab*s)	Area%	Hit Name	Quality	Molecular Formula
9.065	39043796	0.11	Methyl octanoate	97	$C_9H_{18}O_2$
12.568	16302159	0.05	2,4-Decadienal	95	$C_{10}H_{16}O$
13.019	35549050	0.10	2,4 DECADIENAL	97	$C_{10}H_{16}O$
15.188	30183980	0.09	Methyl azelaaldehydate	91	$C_{10}H_{18}O_3$
16.739	11728541	0.03	Methyl laurate	97	$C_{13}H_{26}O_2$
18.068	25875195	0.07	Laural dimethyl acetal	53	$C_{14}H_{30}O_2$
20.076	87959348	0.25	Methyl myristate	99	$C_{15}H_{30}O_2$
21.58	20398918	0.06	Methyl pentadecanoate	96	$C_{16}H_{32}O_2$
23.256	8601715769	15.00	Methyl palmitate	99	$C_{17}H_{34}O_2$
25.882	15850026419	65.00	10,13-Octadecadienoic acid, methyl ester	96	$C_{19}H_{34}O_2$
27.506	93160151	0.26	7,7-dimethoxy-2-endo- methylbicyclo [2.2.1]heptane-2-exo-carboxylic acid	43	
28.279	2363124386	6.06	11-Eicosenoic acid, methyl ester	99	$C_{21}H_{40}O_2$
28.517	1294619727	3.65	Eicosanoic acid, methyl ester	99	$C_{21}H_{42}O_2$
29.425	203896578	0.57	Z,Z-3,16-Octadecadien-1-ol acetate	41	$C_{20}H_{36}O_2$
30.323	419799342	1.18	Methyl erucate	95	$C_{23}H_{44}O_2$
30.598	590984309	1.66	Docosanoic acid, methyl ester	99	$C_{23}H_{46}O_2$
31.35	13488783	0.04	Methyl oleate	98	$C_{19}H_{36}O_2$
31.6	54286118	0.15	Tricosanoic acid, methyl ester	99	$C_{24}H_{48}O_2$
32.419	791735134	2.23	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	95	$C_{21}H_{40}O_4$
32.674	279875561	0.79	Methyl lignocerate	99	$C_{25}H_{50}O_2$
33.405	10607204	0.03	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester	94	$C_{20}H_{38}O_2$
33.633	54569415	0.15	1-Octen-4-ol	38	$C_8H_{16}O$
34.479	67309471	0.19	Methyl oleate	93	$C_{19}H_{36}O_2$
34.733	36873739	0.10	Cerotic acid methyl ester	95	$C_{27}H_{54}O_2$
35.844	11766996	0.03	Cholesta-3,5-diene	83	$C_{27}H_{44}$
36.415	29360924	0.08	.gamma.-Tocopherol	96	$C_{28}H_{48}O_2$
36.767	13543892	0.04	15-Nonacosanone	93	$C_{29}H_{58}O$

RT (min)	Area (Ab*s)	Area%	Hit Name	Quality	Molecular Formula
37.136	27483240	0.08	2,8-diisopropyl-peri-xanthenoxanthene-4,10-quinone	83	
38.179	52738751	0.15	5,5'-(tetrahydro-1H,3H-furo[3,4-c]furan-1,4-diyl)bis-1,3-benzodioxole	98	$C_{20}H_{18}$
39.502	153293713	0.43	23 S-METHYLCHOLESTEROL	99	
40.104	10469366	0.03	Stigmasterol	99	$C_{29}H_{48}O$
41.474	292524319	0.82	(23S)-ethylcholest-5-en-3.beta.-ol	99	$C_{29}H_{50}O$
43.139	12501943	0.04	CAPNELLANE-5.ALPHA.-OL	60	

If the boiling point of components is very different from each other, it causes their better separation. The boiling points of the components are very close to each other because the peaks are adjacent to each other. Also, the existence of hydrocarbon impurities such as Benzodioxol, Cholesta causes the noisy baseline in the existing chromatogram.

4. Conclusions

Performed experiments on four parameters, and their results illustrate that microalgae oil has a high yield and is more suitable than waste oil and rapeseed oil. Comparing previous studies show that the optimal conditions in this study for all three samples have been more appropriate and cost-effective with more efficiency. According to the standards and the results of the performed combustion analysis (Table 11), all three samples are appropriate for application in jet engines. They reduce emissions and enhance fuel properties along with fossil fuels. Also, microalgae biodiesel has better effects on engine performance than the other two samples.

Table 11
Combustion analyzes of waste biodiesel, rapeseed biodiesel, microalgae biodiesel besides the standard mode

Factors Biodiesel Type	Moisture Content (%)	Acidity	Density (g/mL) At 15°C	Viscosity (mm^2/s) At 40°C	Thermal Value (Mj/Kg)	Flash Point (°C)	Cloud Point (°C)	Pour Point (°C)
Standard	< 0.5	< 0.5	0.88	1.9 to 6	37 to 44	> 130	-3 to -12	-11.6
Waste	0.3	0.38	0.901	7.98	39.566	162	6	0
Rapeseed	0.1	0.45	0.883	4.85	39.932	174	2	-6
Microalgae	0.01	0.41	0.882	4.6	40.2	188	-3	-12

Declarations

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Competing Interests

The authors declare that they have no competing interests.

Author Contributions

Valiullah Babaeipour designed and directed this research and corrected the article. Zahra Habibzadeh has performed all the tests under the supervision of Valiullah Babaeipour and also has written the initial version of the manuscript. Shahram Ghanbari has helped to perform and interpret combustion data analysis. Peyman Sazandechi has assisted in experiments with microalgae biodiesel production and data analysis. All authors have read and approved the article.

Data Availability

The all of generated data during the current study are available in this article.

References

1. F. Rosillo-Calle et al accessed 03 March 2014 The potential and role of biofuels in commercial air transport – Biojetfuel. Task 40. Sustainable International Bioenergy Trade. IEA Bioenergy. www.bioenergytrade.org.
2. T.D. Hong et al (2013) A study on developing aviation biofuel for the tropics: Production process - Experimental and theoretical evaluation of their blends with fossil kerosene. Chemical Engineering and Processing: Process Intensification 74, 124-130.
3. J.I. Hileman, and R.W. Stratton (2014) Alternative jet fuel feasibility. Transport Policy 34, 52-62.
4. J.I. Hileman et al (2013) The carbon dioxide challenge facing aviation. Progress in Aerospace Sciences 63, 84-95.
5. J. Popp et al (2014) The effect of bioenergy expansion: Food. energy, and environment. Renewable and Sustainable Energy Reviews 32, 559–578.
6. M. Elmoraghy (2013) Production of bio-jet fuel from microalgae. M.S of Chemical Engineering, Faculty of Engineering, University of New Hampshire.
7. S. Rajvanshi, and M. Pal Sharma (2012) Microalgae: A potential source of biodiesel. Journal of Sustainable Bioenergy Systems. 2, 49-59.
8. M.M. Brutyan (2017) Foresight of microalgae usage for the production of third-generation biofuel. Indian Journal of Science and Technology. 1-10.
9. C. Dixon, and L.R. Wilken (2018) Green microalgae biomolecule separations and recovery. Dixon and Wilken Bioresource, Bioprocess. 5:14.
10. J. Cong Ge et al (2017) Using Canola oil biodiesel as an alternative fuel in diesel engines. Appl. Sci. 7, 881.
11. A. Sales, and Z.R. Vigouroux (2011) Production of biodiesel from sunflower oil and ethanol by base catalyzed transesterification. MSc of chemical engineering, Department of Chemical Engineering Royal Institute of Technology (KTH).
12. K.M. Shereena, and T. Thangaraj (2009) An alternative fuel produced from vegetable oils by transesterification. Electronic Journal of Biology, Vol.5 (3): 67-74.
13. S.S. de Jesus et al (2019) Biodiesel purification by column chromatography and liquid-liquid extraction using green solvents. Fuel 235, 1123–1130.
14. I.M. Atadashi (2015) Purification of crude biodiesel using dry washing and membrane technologies. Alexandria Engineering Journal 54, 1265–1272.
15. sup> N. Aljabarin, and A. Al Jarrah (2017) Production of biodiesel from local available algae in Jordan. Journal of Ecological Engineering, 18, 8–12. doi: 10.12911/22998993/76830.
16. A.P. Cercado et al (2018) Ultrasound assisted transesterification of microalgae using synthesized novel catalyst. Sustainable Environment Research, 28, 234-239.
17. R. Manurung, D.A. Ramadhani, and S. Maisarah (2017) One Step Transesterification Process of Sludge Palm Oil (SPO) by Using Deep Eutectic Solvent (DES) in Biodiesel Production. AIP Conference Proceedings 1855, 070004, https://doi.org/10.1063/1.4985531.

18. sup> F. Anguebes-Franseschi, A. Córdova-Quiroz1, J. Cerón-Bretón1, C. Aguilar-Ucan1, G. Castillo-Martínez, R. Cerón-Bretón1, A. Ruíz-Marín1, and C. Montalvo-Romero (2016) Optimization of Biodiesel Production from African Crude Palm Oil (Elaeis guineensis Jacq) with High Concentration of Free Fatty Acids by a Two-Step Transesterification Process. Open Journal of Ecology, 6, 13-21, http://dx.doi.org/10.4236/oje.2016.61002.
19. A.P.P. Pires, Y. Han, J. Kramlich, and M. Garcia-Perez (2018) Chemical composition and fuel properties of alternative jet fuels. Bioresources 13(2), 2632-2657.
20. H.N. Bhatti, M.A. Hanif, U. Faruq, and M.A. Sheikh (2008) Acid and Base Catalyzed Transesterification of Animal Fats to Biodiesel. Iran. J. Chem. Chem. Eng. Vol. 27, No. 4.
21. J. Quesada-Medina, and P. Olivares-Carrillo (2011) Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol. J. Supercrit., Fluids 56, 56–63.
22. K.G. Georgogiannia, M.G. Kontominas, P.J. Pomonis, D. Avlonitis, and V. Gergis (2008) Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. Fuel Processing Technology, 89, 503 – 509, doi:10.1016/j.fuproc.2007.10.004.
23. sup> A. Aladetuyi et al (2014) Production and characterization of biodiesel using palm kernel oil; fresh and recovered from spent bleaching earth. Biofuel Res. J., 4, 134–138.
24. M. Klabsong, N. Kungskulniti, C. Puemchalad, N. Charoenca, and V. Punsuvon (2017) Feasibility study of biodiesel production from residual oil of palm oil mill effluent. Int. J. GEOMATE, 12, 60–64, http://dx.doi.org/10.21660/2017.33.2568.
25. N. Hindryawati, Erwin, and G.P. Maniam (2017) Esterification of oil adsorbed on palm decanter cake into methyl ester using sulfonated rice husk ash as heterogeneous acid catalyst. AIP Conf. Proc., 1813, 1–11, doi: 10.1063/1.4975965.
26. R.N. Ricca, M.Z. Alam, and M.S. Jami (2013) Enzymatic biodiesel production from sludge palm oil (SPO) using locally produced Candida cylindracea lipase. Afr. J. Biotechnol., 12, 4966–4974, doi:10.5897/AJB2013.12075.
27. Y. Tang, Y. Zhang, J.N. Rosenberg, M.J. Betenbaugh, and F. Wang (2016) Optimization of one-step in situ transesterification method for accurate quantification of EPA in Nannochloropsis gaditana. Appl. Sci. 6, 343, doi:10.3390/app6110343.
28. P.D. Patil, and S. Deng (2009) Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel 88, 1302–1306, doi:10.1016/j.fuel.2009.01.016.
29. J. Zeng, X. Wang, B. Zhao, J. Sun, and Y. Wang (2009) Rapid In Situ Transesterification of Sunflower Oil. Ind. Eng. Chem. Res., 48, 850–856.
30. K.A. Salam, S.B. Velasquez-Orta, and A.P. Harvey (2016) In situ transesterification of wet marine and fresh water microalgae for biodiesel production and its effect on the algal residue. journal of sustainable bioenergy systems, 6, 17-30, http://dx.doi.org/10.4236/jsbs.2016.62003.
31. S. Hashmi, S. Gohar, T. Mahmood, U. Nawaz, and H. Farooqi (2016) Biodiesel Production by using CaO-Al2O3 Nano Catalyst. International Journal of Engineering Research & Science (IJOER), Vol-2, ISSN:2395-6992.
32. Prasad CMV et al (2000) Performance evaluation of non-edible vegetable oil substitute fuels in low heat rejection diesel engines. IMech E Part D; 214: 181-87.
33. Prasad CMV et al (1998) Performance evaluation of semi- adibatic diesel engine with vegetable oil as substitute fuels. National conference on advances in automobile engineering, Chennai, India: 313-21.
34. J. Najar et al (1998) Performance and Emission characteristics of a diesel engine using pre-heated vegetable oils. XVIII National conference on advances in automobile engineering, Chennai, India: 313-21.
35. A. Zschocke (2012) High biofuel blends in aviation (HBBA). Final Report, Wehrwissenschaftliches Institut für Werk- und Betriebsstoffe, 1-168.
36. G. Knothe, and L.F. Razon (2017) Biodiesel fuels. Progress in Energy and Combustion Science, 58, 36.

37. G. Wu et al (2019) Emission characteristics for waste cooking oil biodiesel blend in a marine diesel propulsion engine. Pol. J. Environ. Stud. Vol. 28, No. 3, 2911-2921.

Figures

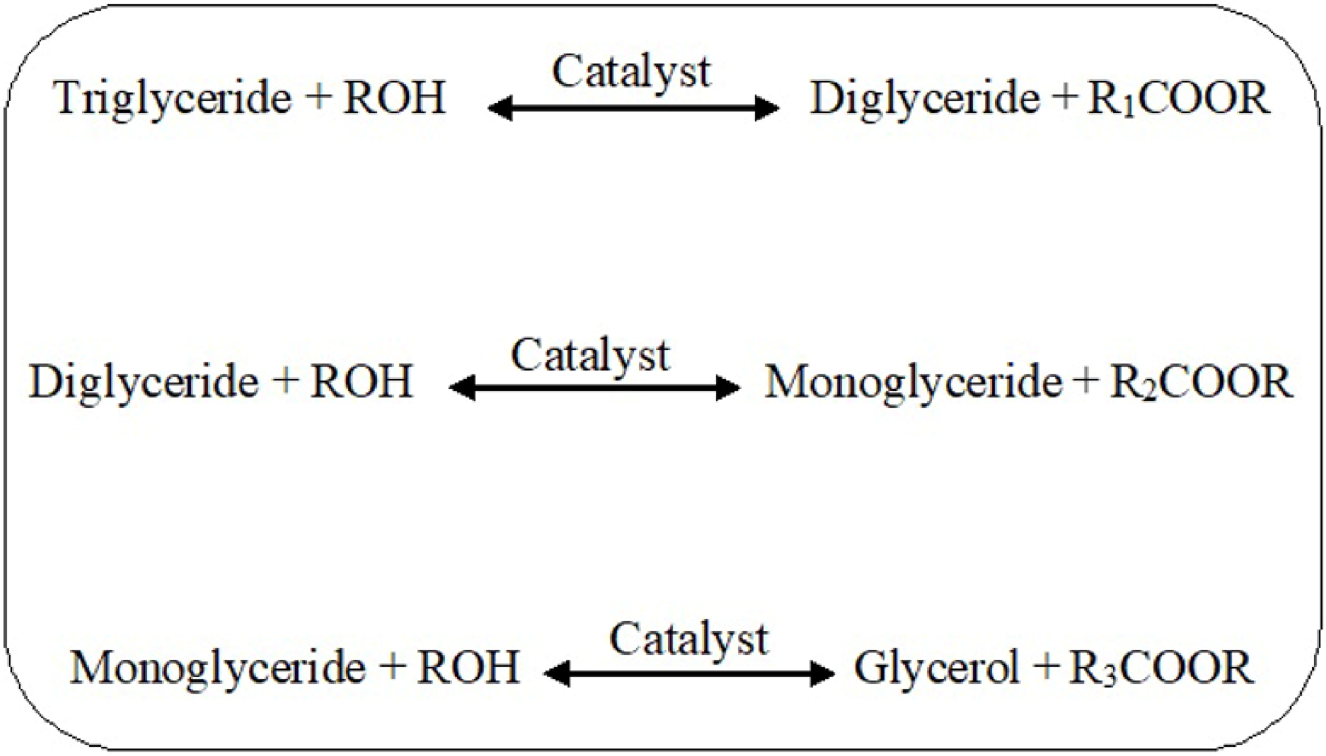

Figure 1

Transesterification reaction [12]

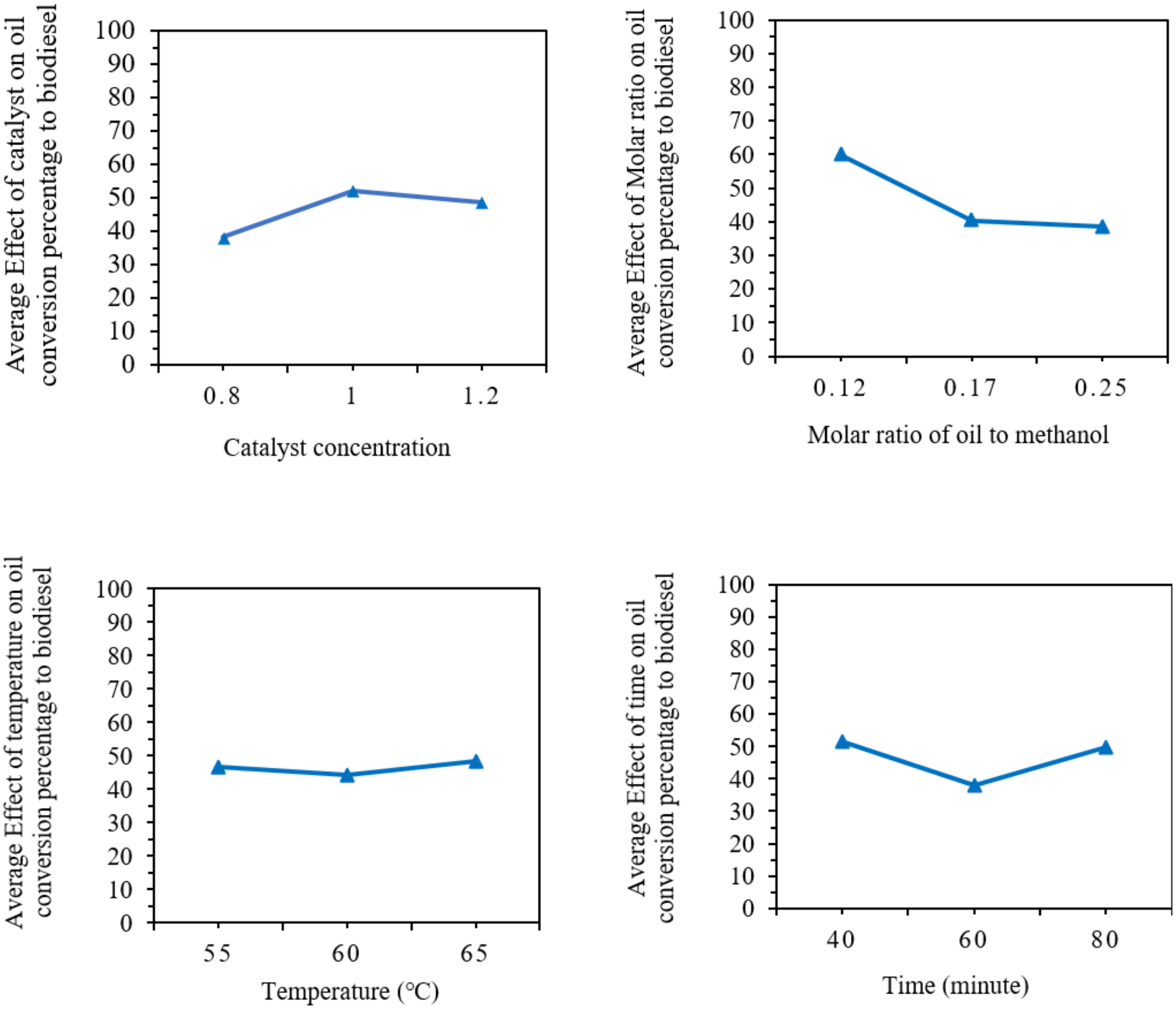

Figure 2

Average effect of different factors on the conversion percentage of rapeseed oil to biodiesel (methyl ester)

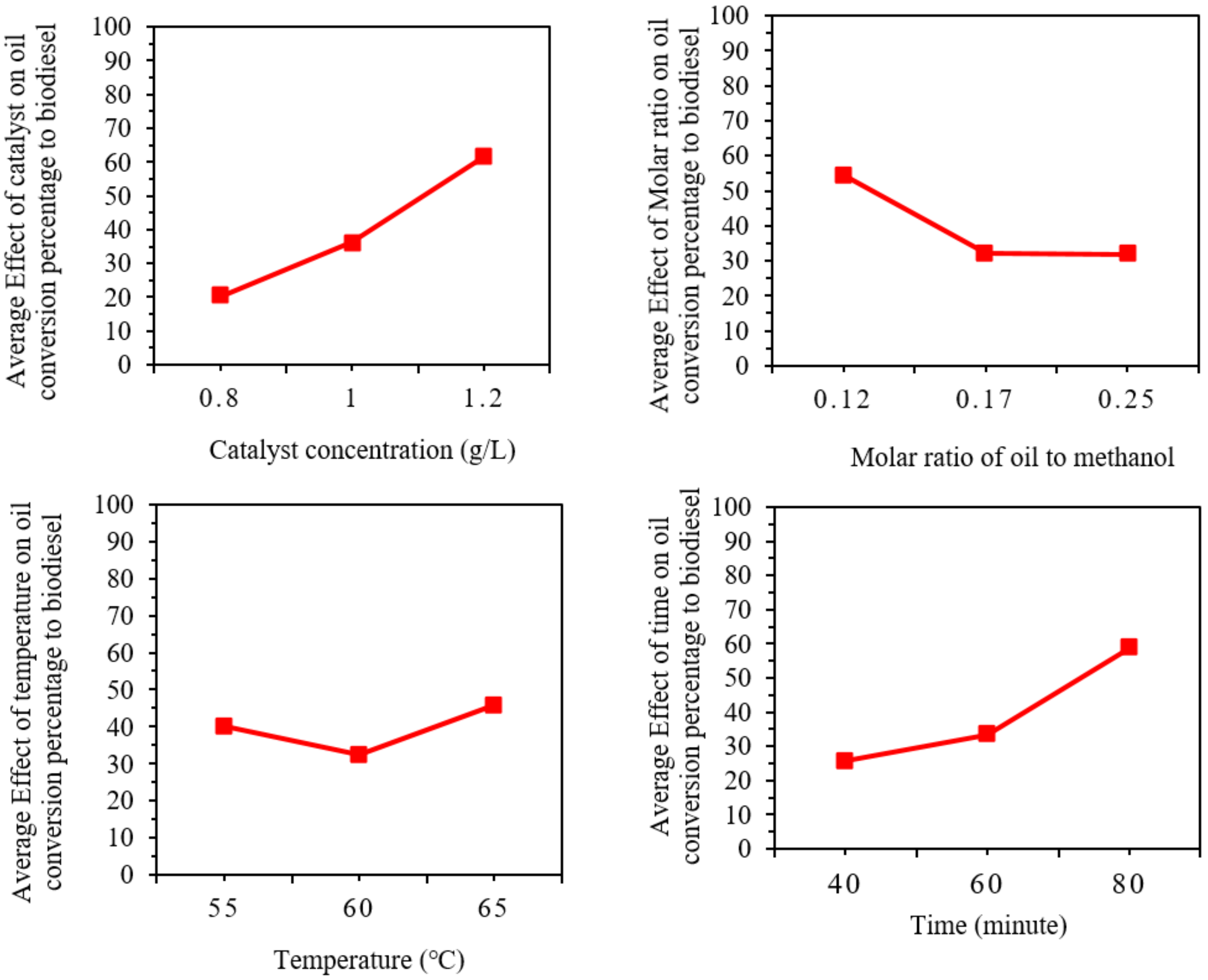

Figure 3

Average effect of different factors on the conversion percentage of waste oil to biodiesel (methyl ester)

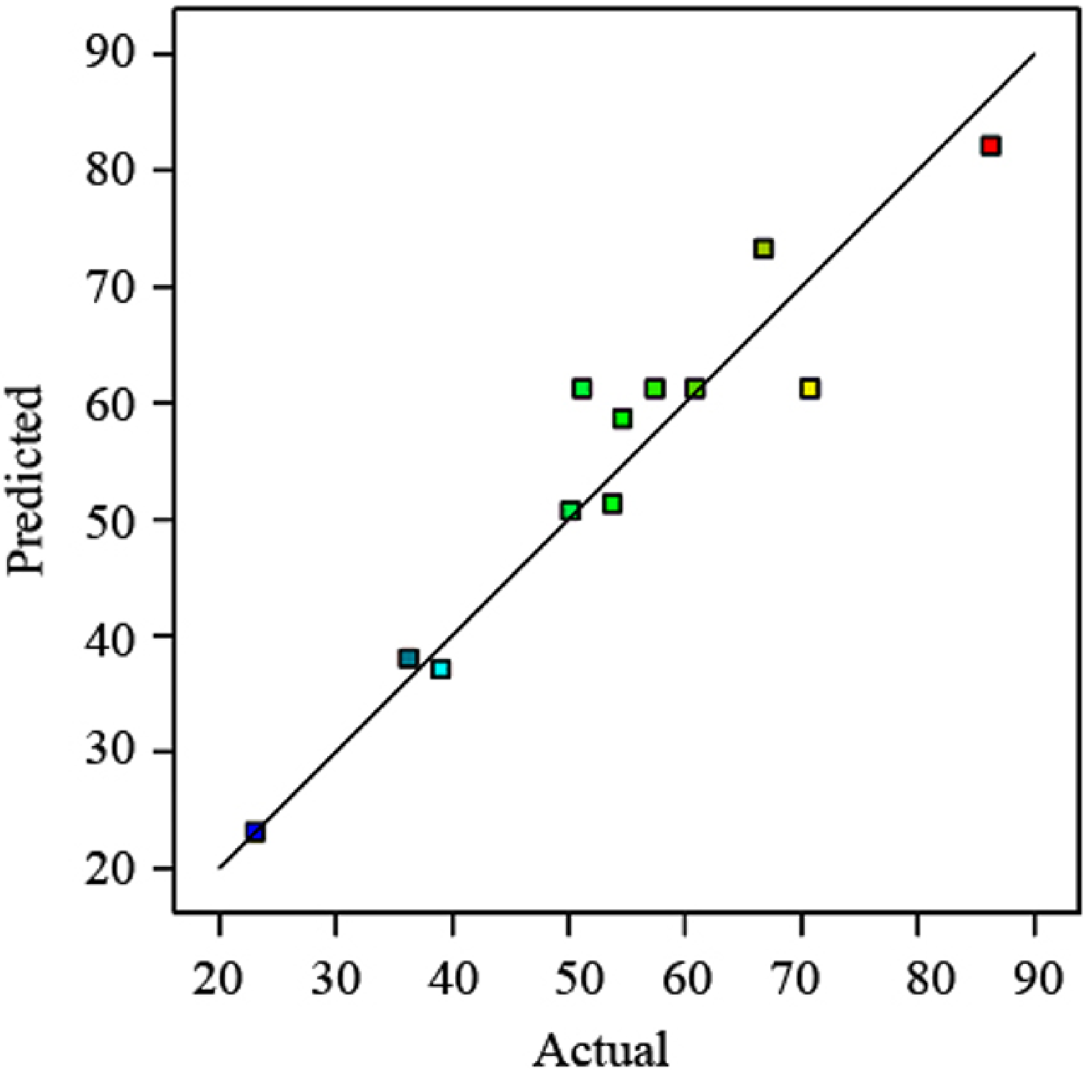

Figure 4

Experimental values and model predictions for biodiesel conversion rates

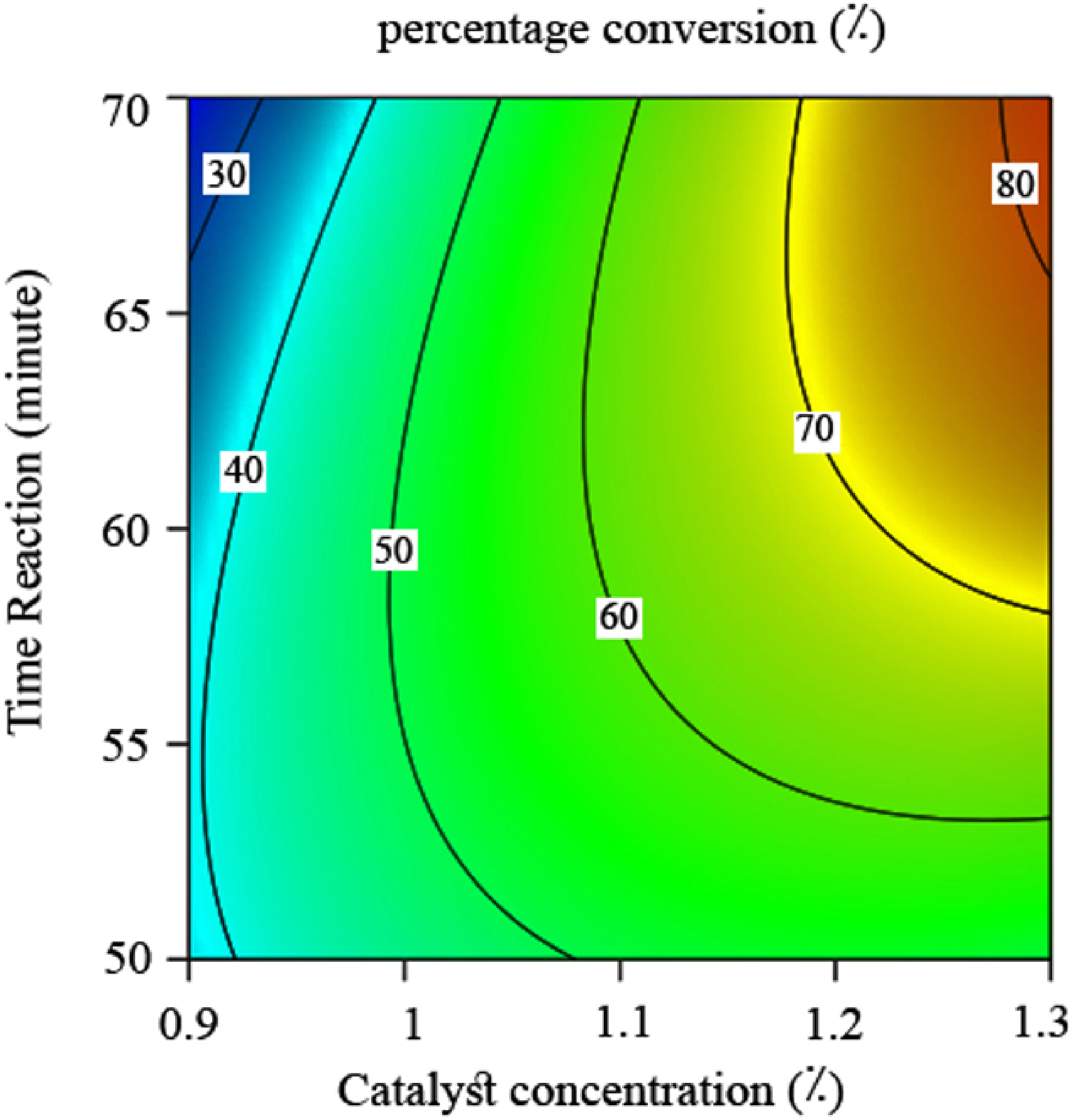

Figure 5

Effect of catalyst percentage and reaction time on biodiesel conversion rate

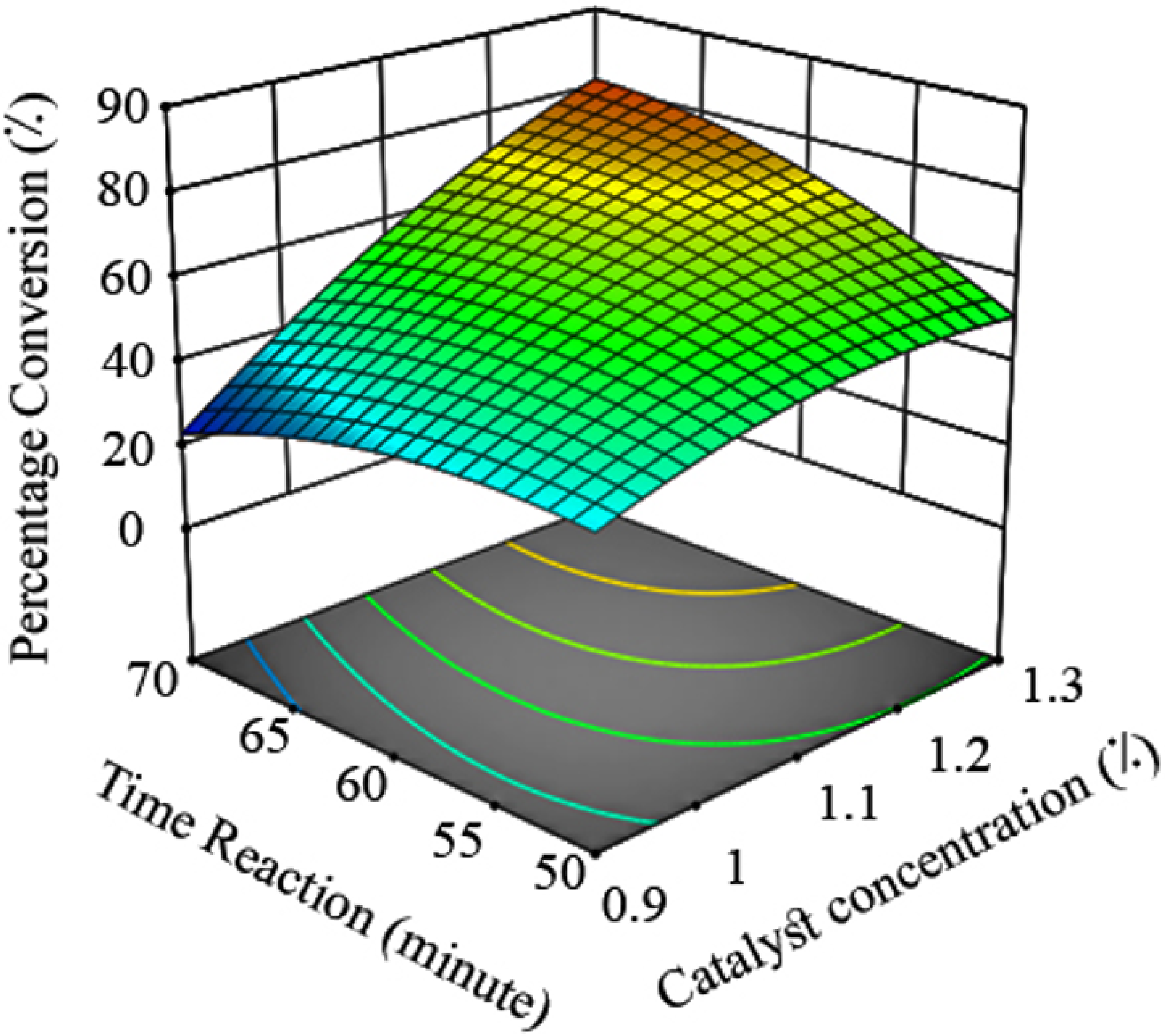

Figure 6

Changes in biodiesel conversion rate with catalyst percentage and reaction time in three dimensions

Figure 7

Waste oil biodiesel chromatogram

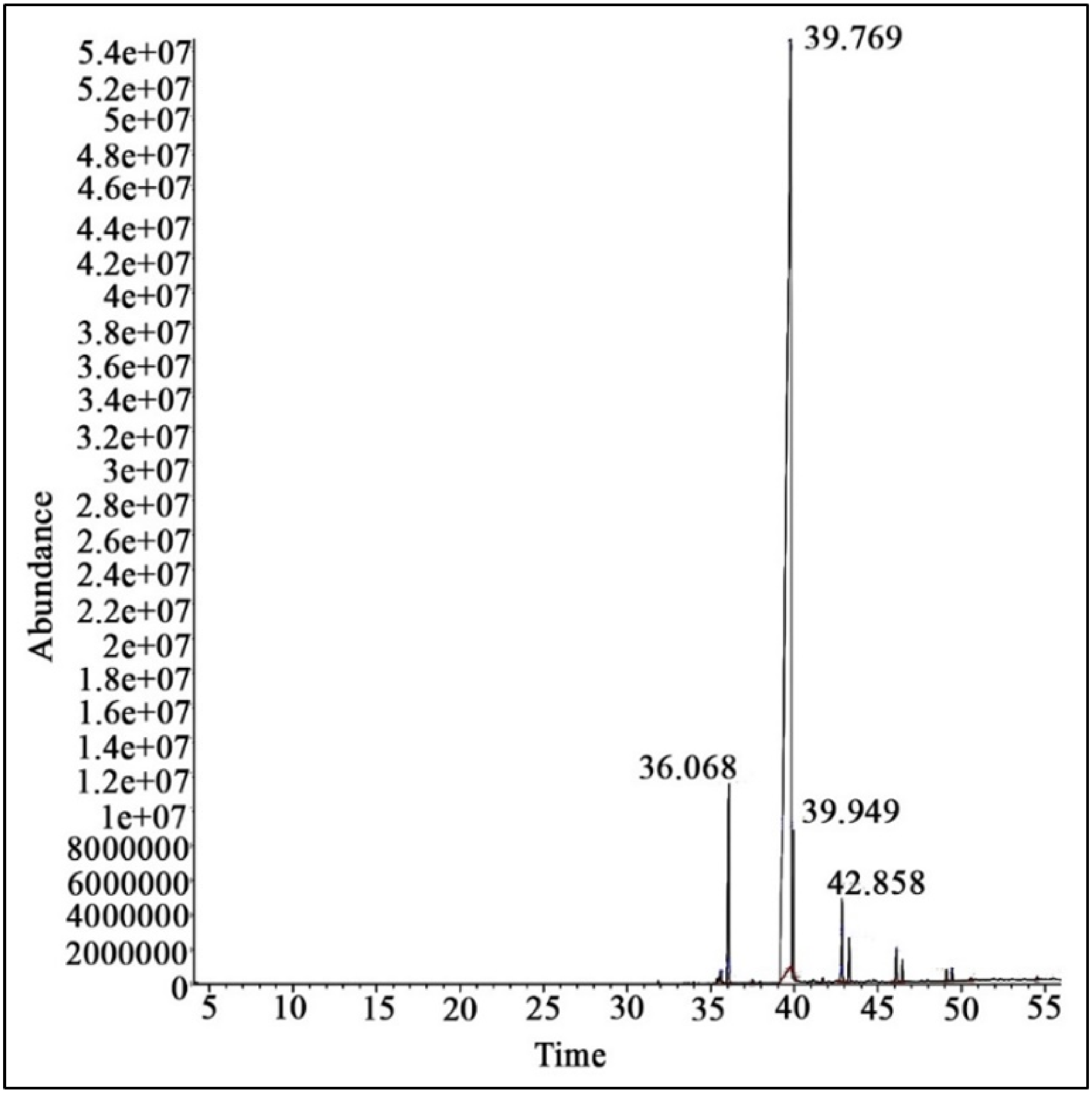

Figure 8

Rapeseed oil biodiesel chromatogram

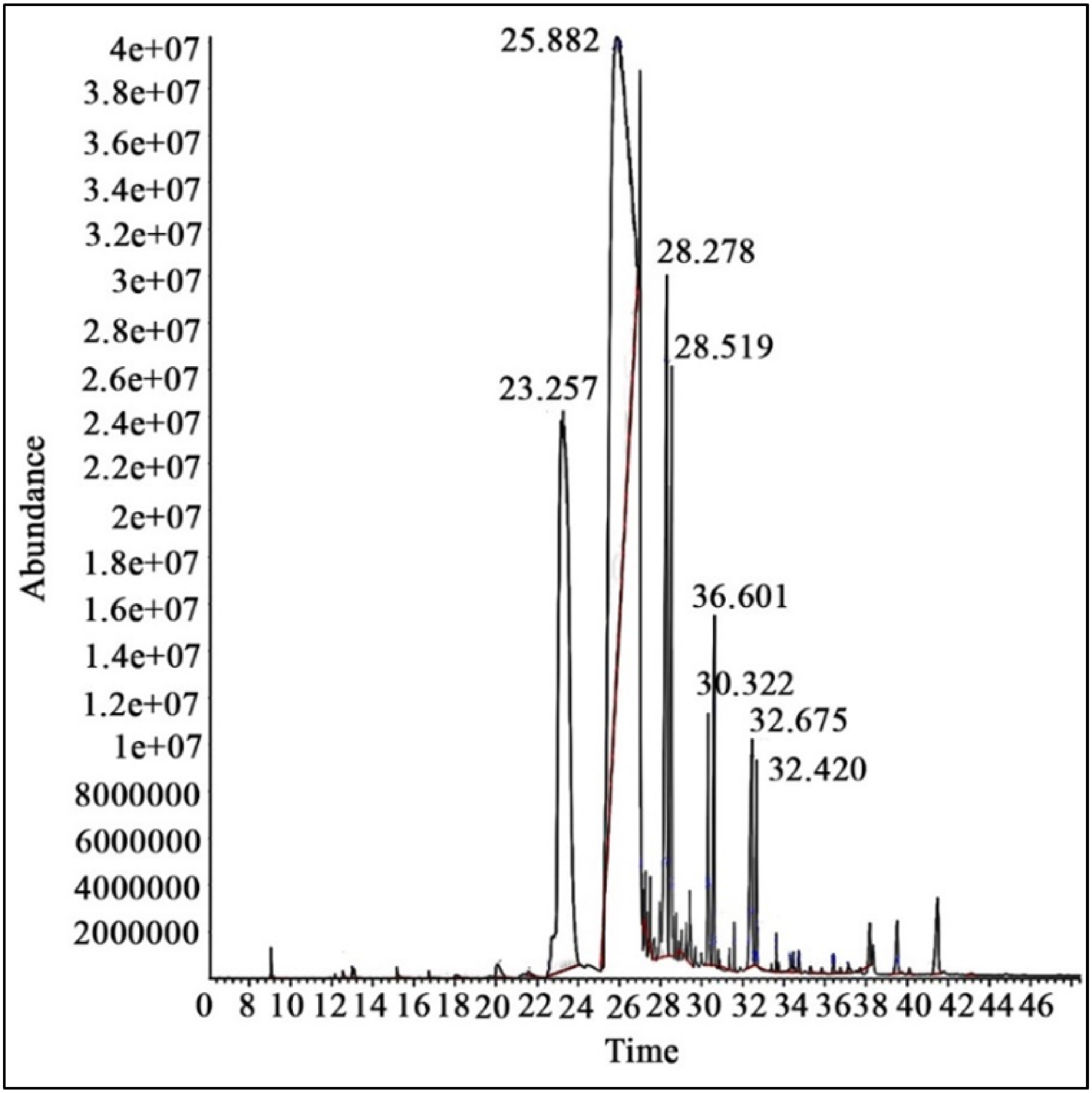

Figure 9

Microalgae oil biodiesel chromatogram