Optimization of the Parameters Affecting on the Conversion Rate of the Used Frying Oil

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Abstract

Biodiesel is an alternative fuel for diesel engines consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Most of the biodiesel that is currently made uses vegetable oil, methanol, and an alkaline catalyst However, there are large amounts of low–cost oils and fats such as used frying oil and animal fats that could be converted to biodiesel. In this study biodiesel, which is produced of used frying oil by using transesterification method. The transesterification reaction of used frying oil (UFO) by means of methanol, using sodium hydroxide, as catalysts, is studied. Under lab conditions transesterification method is used to statistical analysis the parametres of the used frying oil biodiesel upon the effective rates of the conversion rate. In order to put forth the effects of the catalyst amount, reaction temperature, alcohol/oil molar ratio parametres of the used frying oil methyl ester (UFOME) production the experiments are carried out in 50°C, 55°C and 60°C reaction temperature, the alcohol/oil molar ratios are 1/4, 1/6, 1/8 and 1/10 and the oil mass rates are stated as 0.5%, 1% and 1.5% using NaOH catalyst. At the end of the statistical analysis the derived UFOME amount which makes the experimental conditions in a maximum level is stated as 0.5% catalyst amount, 50°C reaction temperature and the molar ratio is given as 1/10. Under these optimal conditions the maximum methyl ester conversion rate is 98%. The important properties of used frying oil and its methyl ester (biodiesel) such as ester content, density, kinematic viscosity, flash point, iodine number, pour point, cetane number, heating value and sulphur content are found out and compared to those of No. 2 petroleum diesel and EN 14214 biodiesel standards. The comparison shows that the methyl ester has relatively closer fuel properties to diesel than that of used frying oil.

Key words: Used frying oil, methyl ester, transesterification, conversion rate, ANOVA

1. Introduction

World energy demand continues to rise. Several policies have been launched by the government to respond to the energy price dynamics and to encourage the use of alternative energy sources including biodiesel fuel. The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. In 1911, Rudolph Diesel presented an engine based on compression-ignition: the diesel engine. At that time there was no specific fuel to feed this engine. Rudolph Diesel used groundnut oil. There have been many problems associated with using vegetable oils directly in diesel engines, problems such as: decrease in power output and thermal efficiency of the engine; carbon deposits; oil ring sticking; thickening or gelling of the

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lubricating oil as a result of contamination by vegetable oils. Other disadvantages to the use of vegetable oils and especially animal fats are the high viscosity (about 11–17 times higher than diesel fuel) and lower volatility that result in carbon deposits in engines due to incomplete combustion. Beside that, vegetable oils contain polyunsaturated compounds. Some chemical or physical modifications have been tested to overcome these problems: pyrolysis, microemulsification, dilution and transesterification. Transesterification is widely used to reduce vegetable oil viscosity. Most industrial processes employ alkaline catalysis and methanol

Biodiesel is a renewable, biodegradable, environmentally benign, energy efficient, substitution fuel which can fulfill energy security needs without sacrificing engine's operational performance. Biodiesel refers to a diesel-equivalent, processed fuel derived from biological sources. Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The source for biodiesel production is chosen according to the availability in each region or country. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute [1]. There are concerns that biodiesel feedstock may compete with food supply in the long-term [2]. Hence, the recent focus is the use of non-edible plant oil source as the feedstock for biodiesel production meeting the international standards.

The new process technologies developed during the last years made it possible to produce biodiesel from recycled frying oils comparable in quality to that of virgin vegetable oil biodiesel with an added attractive advantage of being lower in price [3, 4, 5]. From a waste management standpoint, producing biodiesel from used frying oil is environmentally beneficial, since it provides a cleaner way for disposing these products; meanwhile, it can yield valuable cuts in CO_2 as well as significant tail-pipe pollution gains. Beside the rural produced low grade vegetable oil, the utilization of used frying oil as raw material for biodiesel production should also be taken into consideration.

The preparation of biodiesel is generally carried out using vegetable oils or animal fats as a starting material. The transesterification reaction is preferred to the direct esterification of fatty acid because triglycerides are more available than free fatty acids. Biodiesel is produced by transesterification of the triglycerides with short chain alcohols in the presence of a suitable catalyst. Transesterification reaction is shown in Figure 1. The stoichiometry requires 3 mol of alcohol and 1 mol of triglyceride to give 3 mol of fatty acid esters and 1 mol of glycerine [6, 7].

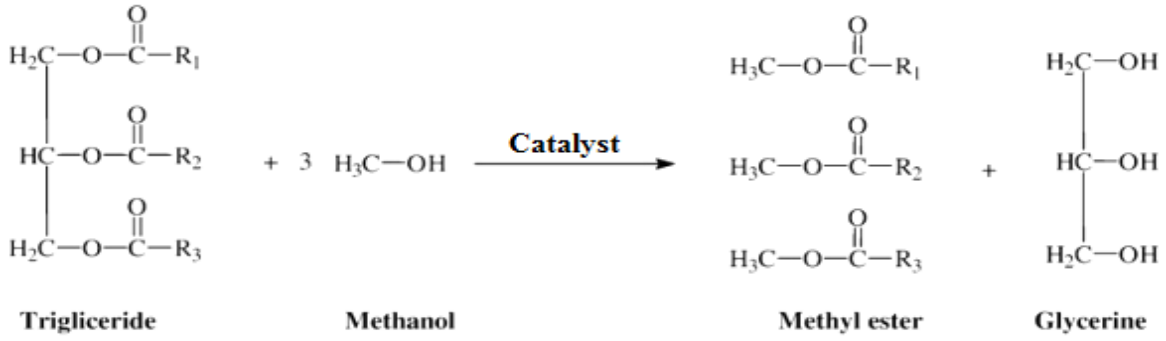

Figure 1. Transesterification reaction of triglyceride

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The overall process is a sequence of three consecutive reversible reactions where diglyceride and monoglyceride are intermediate products. The transesterification reaction can be catalyzed by both acid and alkaline catalysts, using a homogeneous or heterogeneous catalytic process. Sodium and potassium hydroxide are commonly used as industrial catalysts, since they are relatively cheap and also very active. On the other hand, their utilization in vegetable oil transesterification produces soaps by neutralizing the free fatty acid in the oil and by triglyceride saponification. The soap formation is an undesirable side-reaction, because it partially consumes the catalyst, decreases the biodiesel yield and complicates the separation and purification steps. The removal of these catalysts is technically difficult and brings extra cost to the final product. In addition, the difficulty for recycling and the generation of large waste amounts make the traditional catalysts less favourable.

Although transesterification using a conventional alkali catalyzed process gives high conversion levels of triglycerides to their corresponding methyl esters in short times, the reaction has several drawbacks: it is energy intensive; recovery of glycerine is difficult; the catalyst has to be removed from the product; alkaline waste-water requires treatment and free fatty acids and water interfere with the reaction. In order to minimize homogeneous process problems, attempts to use heterogeneous catalyst systems in alcoholysis of triglycerides have been made.

A study was performed of the transesterification reaction of used frying oil by means of methanol, using sodium hydroxide as catalysts. The objective of the work was to characterize the methyl esters for use as biodiesels in diesel engines. The operation parametres used were alcohol/oil molar ratio (1/4, 1/6, 1/8 and 1/10), catalyst concentration (0.5%, 1% and 1.5%) and reaction temperature (50°C, 55°C and 60°C). Conversion rate was determined after each parametric study. The optimal transesterification reaction conditions that produce the maximum conversion rate.

2. Materials and methods

2.1. Materials

Raw materials used in the research were used frying oil from local restaurants. The chemicals used were dry methanol and NaOH for analysis. The equipment used were rotary vacuum evaporator, magnetic stirrer, Erlenmeyer flask, separating funnel, pH meter and other equipment for analysis. The research was performed at Sakarya University Fuel Research Laboratory.

2.2. Production of used frying oil methyl ester

This study was conducted in two stages: 1) Characterization of raw material, 2) Optimisation on the transesterification process. The procedure of this researchs are presented on Figure 2.
To 100 g of used frying oil, a known amount of catalyst NaOH, (0.5, 1, and 1.5 wt%) dissolved in the required amount of methanol was added. The temperature i.e. 50, 55 and 60^{o}C was maintained as desired. The whole mixture was then transferred to a separation funnel; and the heavy, decanted phase was separated in the bottom outlet. Furthermore methyl ester was put again into a separating funnel and washed with warm pure water four times that cause removal of soap and excessive methanol. Reaction conversion rate was determined by weighing the remaining solution and taking into account the reaction stoichiometry.

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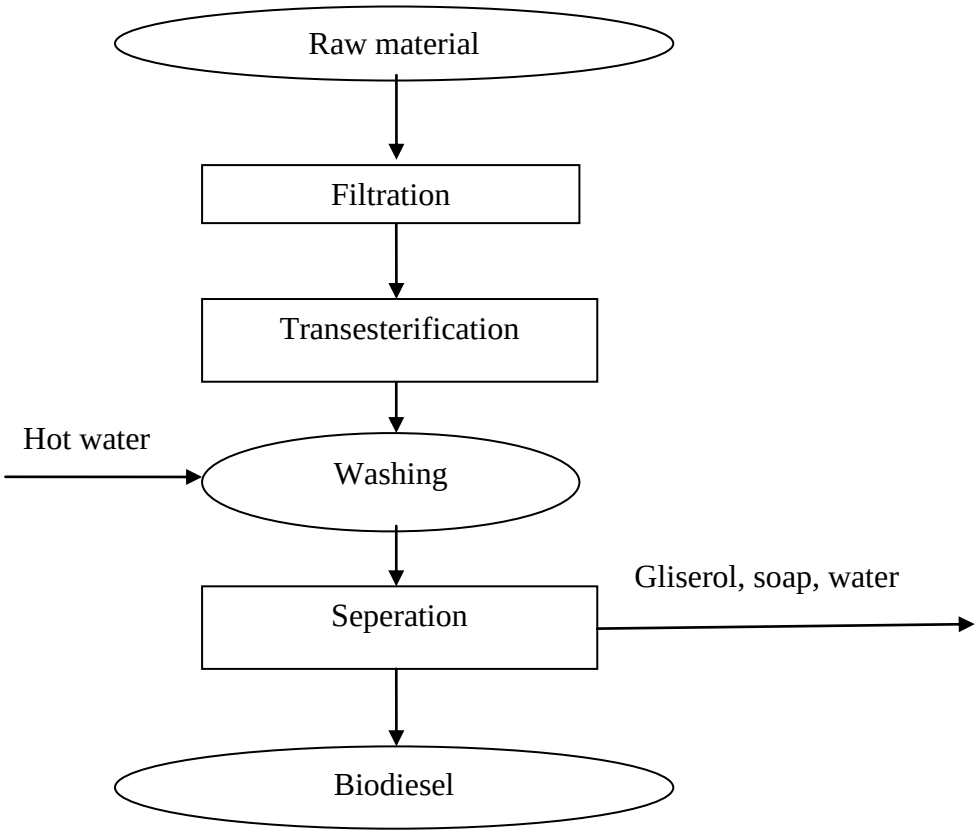

Figure 2. Flow chart of the production of biodiesel

Analysis of ANOVA was adopted considering the variables reaction temperature, catalyst amount and alcohol/oil molar ratios.

3. Results and Discussion

3.1. Characterization of used frying oil

The analysis results of used frying oil are presented on Table 1. After the fatty acid composition analysis, used frying oil was found as composed from saturated 13.79% and unsaturated fatty acids 86.21%. The used frying oil presents the following composition of fatty acids (in wt.%); oleic (43.72), linoleic (40.84), palmitic (8.62), stearic (4.13), and behenic (1.04). According to the acidity index, the free fatty acids composition is 0.85 wt.%, expressed as oleic acid.

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Table 1. Fatty acids composition of used frying oil

Fatty acids		Fatty acid composition (wt %)
Palmitic	**(C16:0)**	8.62
Stearic	**(C18:0)**	4.13
Behenic	**(C22:0)**	1.04
Oleic	**(C18:1)**	43.72
Linoleic	**(C18:2)**	40.84
Others		1.65

The physicochemical properties of used frying oil are listed in Table 2. The testing of free fatty acid (FFA) was intended to find out the not damage degree of used frying oil as raw material. Results of the test showed that frying oil had the lowest FFA average i.e 0.85%.

Table 2. Physicochemical properties of used frying oil

	Used frying oil
Density, g/mL	0.840
Free fatty acid (g/100 mL)	0.85
Peroxide value (kg 0_2)	690
Kinematic viscosity (mm^2/s)	35.42
Acid value (mgKOH/g)	1.7
Refractive index	1,480

3.2. Characterization of used frying oil methyl ester

The nine important fuel properties of methyl esters of UFO are presented on Table 3. Both these properties meet the specifications of EN 14214 European biodiesel standards and No 2 diesel fuel. The determined properties of the UFOME are suitable for EN 14214 standards.

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Table 3. Properties of used frying oil biodiesel in comparison with EN 14214 and diesel fuel

Analys	Unit	Method	UFOME	EN 14214	Diesel No 2
Ester content	%(m/m)	EN 14103	97.5	min 96.5	-
Density, 15 ^{o}C	g/cm^{3}	EN ISO 3675	0.87	0.86 - 0.90	0.82 – 0.86
Kinematic viscosity	mm^{2}/s	EN ISO 3104	4.0	3.5-5	2.5 – 3.5
Iodine value	g iodine/100 g	EN14111	115	max 120	-
Pour point	^{o}C	ISO 3016	-4	max 0	- 33
Flash point	^{o}C	ASTM D93	128	min 120	> 55
Heating value	MJ/kg	ASTM D 240	40.02	min 35	42.7
Cetane number	-	EN ISO 5165	52	min 51	49 - 55
Sulphur content	mg/kg	EN ISO 20846	1	max 10	0.05

3.3. Effect of the parameters on the conversion rate

In this study the amount of catalyst on the amount of the conversion rate was found to be effective. Synthesis of methyl ester as a result of parametric studies highest amount of the catalyst 0.5% NaOH, the reaction temperature is 50°C and 1/10 molar ratio was conditions. Under these conditions maximum ester conversion rate was found 98%. ANOVA results is shown in Table 4.

Table 4. The results of ANOVA

Factors	Degree of Freedom	Sum of Squares	Per Squares	F	P
Amount of catalyst	2	7402.0	3701.0	30.60	0.000
Temperature	2	582.0	291.0	2.32	0.124
Molar ratio	3	1398.0	699.0	3.02	0.011
Error	28	3282.4	120.2		
Total	32	12664.4			

Multi-way analysis of variance table is analyzed on the amount of UFOME, amount of the catalyst, reaction temperature, and alcohol/oil molar ratio were found to be effective in a statistically significant ($P < 0.05$). Found no significant difference between the groups as a result of ANOVA test groups, the difference between the two groups to determine which Tukey HSD multiple comparison test was performed. Tukey test results are shown graphically in Figure 3.

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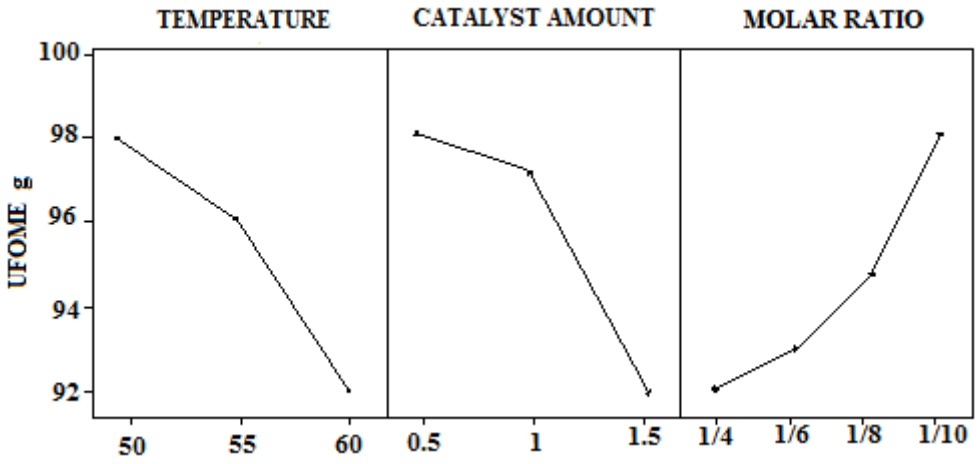

Figure 3. The factors and their levels of influence on the conversion rate

4. Conclusions

Used frying oil was transesterified using NaOH as catalyst and methanol to form biodiesel. The conversion rate was 98% at 50^{o}C with 1/10 molar ratio for NaOH (0.5% by wt) catalyzed transesterification. Conversion rate is the parameter of success on the process since it is immediately related to economical value. In this study, the alcohol/oil molar ratio has increased with the increase in the amount of ester. Rates in excess of 1% of a catalyst in increasing the use of used frying oil methyl ester has no effect on the conversion rate was statistically. With the increase in temperature decreases the amount of ester was obtained.

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