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Optimization of Biodiesel Production by Chemical Trans-esterification of Sunflower Oil

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Abstract

Vegetable oils and fats in comparison with diesel fuel have high viscosity, by transesterification method the viscosity of oil can be decreased. Transesterification of triglyceride with alcohol is one of the methods for production of biodiesel. In this study sunflower oil, methanol and ethanol, with molar ratio of (1:3, 1:4, 1:6, 1:8) and temperature (40, 50, 60 º C) were dependent parameters employing potassium hydroxide as a catalyst at the concentration of 1%. The reaction was carried out for 90 min at 600 rpm. The product viscosity was measured at 40ºC. Gas chromatogram showed that the highest yield of methyl and ethyl ester of sun flower oil at 1: 8 molar ratio of oil to alcohol at 60 º C could be obtained. The conversion rates were 96% and 85% for methyl ester and ethyl ester respectively. It was found that temperature and the ratio of oil to alcohol are two important factors in biodiesel production and thus increasing biodiesel yields. The result suggested that molar ratio of methanol to oil (1:8) at 60 º C for biodiesel production is optimal.

***Key words**: Biodiesel, Triglyceride, Gas Chromatography, Methyl ester, Ethyl ester*

Introduction

Biodiesel would be defined as mono alkyl ester of fatty acids derived from vegetable oils or animal fats. Due to biodiesel's renewable ability, non-toxicity, biodegradability, and better gas emission, it has been attracted much attention [1] recently. Due to limited fossil resources, demand for biodiesel has been increased. Biodiesel fuel is being used in compression ignition engines so that the

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transport system is almost entirely dependent on fossil fuels and biodiesel is an alternative for fossil fuels. High cost of biodiesel to diesel fuel would not be acceptable. But recent increase in gasoline price and uncertain access to gasoline in some countries, biodiesel has attracted much attention in diesel engines [2].

The use of biodiesel reduces the amount of uncombsted hydrocarbons, carbon monoxide and particulate exhaust. The nitrogen oxides output in biodiesel production shows low volatility. Having oxygen (11%) in the molecular structure of biodiesel due to its complete combustion and thus can cause reduction of carbon particles. These compounds do not contain sulfur and can be considered as an environmental friendly fuel [3].

Production of biodiesel has been developed due to the following reasons: (1) to provide a market for production of vegetable oils and animal fats. (2) although it can't eliminate the country's dependence on imported oil, but it can be reduced. (3) biodiesel is renewable and because of its complete carbon cycle that shall not participate in global warming and overall 78% of CO_2 emission compared to petroleum-based diesel fuels is reduced. (4) emission of carbon monoxide, unburned hydrocarbons and particulate matter emissions from biodiesel is lower than regular diesel fuel [4].

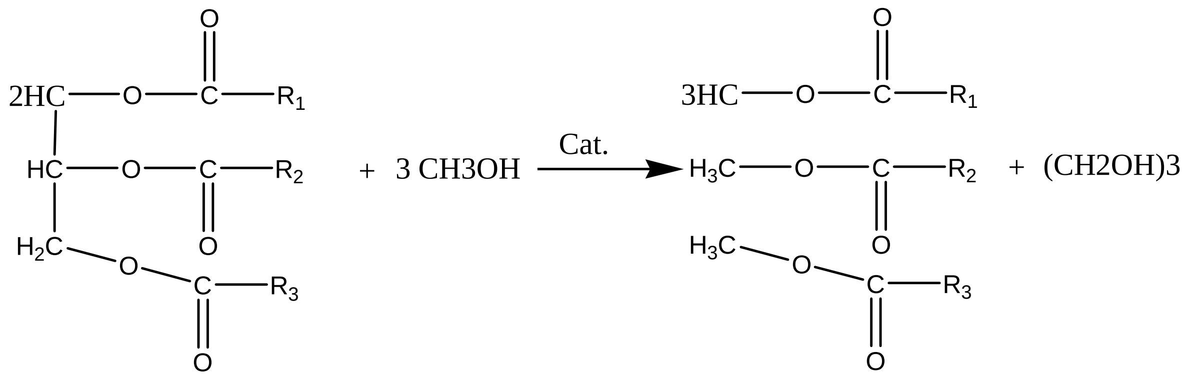
Biodiesel reduces CO_2 and other toxic compounds such as carcinogenic, mutagenic and damaging to the ozone layer that are caused by diesel fuel, so it can be a good idea to achieve cleaner air, less climate changes, clean fuel with a lower risk of cancer, respiratory diseases and other health issues [5]. Diesel fuel can be replaced with biodiesel made from vegetable oils. The main form of biodiesel is obtained by soybean oil and rapeseed oil. Soybean oil produced in the United States as the first source of biodiesel and rapeseed oil have a wider use in many European countries, but some countries prefer to use coconut and palm oils due to weather conditions [6].

Other sources used in production of biodiesel are animal fat and edible waste oils. Also today, scientists have developed methods for production of biodiesel from algal oil [7]. According to studies (FAPRI) demand for soybean oil to produce biodiesel from 264 million pounds in 2001 has been increased to 5/2 billion pounds in 2010 [5]. Table 1 shows the fatty acid composition of sunflower oil.

Table 1. Fatty acid content of sunflower oil.

Fatty acid	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)
Content , %	6.6	5.1	19.6	68.7

Because the viscosity of vegetable oils and fats are10 to 17 fold of diesel fuel therefore they are not suitable to be employed without treatment (directly). To reduce their viscosity in accordance to diesel fuel standard transesterification method can be employed [8].The most common method used in biodiesel production is transesterification. Transesterification is a reaction in which triglycerides present in vegetable oil reacts with an alcohol (usually methanol or ethanol) in the presence of alkaline catalyst yielding esters (biodiesel) and glycerol. Catalysts such as alkali metals, alkaline hydroxide (alkoxide) *viz* potassium hydroxide (KOH) and sodium hydroxide (NaOH) are used as the alkaline catalysts [9].Transesterification reaction is shown in Figure 1.



Triglyceride Methanol Mixture of fatty esters Glycerin

Figure 1. Transesterification reaction of triglycerides.

Vegetable oils contain few free fatty acids, when an alkali catalyst is added to them; catalyst reacts with free fatty acids to produce soap and water [4].

$$\underset{\text{Fatty acid}}{\text{R- COOH}} + \text{KOH} \longrightarrow \underset{\text{Pottassium soap}}{\text{R- COOK}} + \text{H2O}$$

Figure 2. Soap formation from free fatty acids.

Experimental

Materials

Sun flower oil was obtained from local market. Methanol, ethanol, n-hexane, methyl and ethyl mrystate were of Merck. Other reagents used were of analytical grade

Methods

Different molar ratios of alcohol were reacted with 1% KOH based on oil weight [10]. Trans-esterification process was carried out in a closed system and mixed on heater at the agitation speed of 600 rpm for 90 minutes. Sunflower oil as a source of oil, methanol and ethanol were used as alcohol. Studies carried out at three different temperatures (40, 50, and 60°C) and at molar ratios of oil to alcohol 1:3, 1:4, 1:6, 1:8 [11]. After 90 minutes the obtained product was further processed as, biodiesel was transferred to separating funnel in order to separate biodiesel from glycerol, catalyst and formed soap , the blend was washed successively with warm water. Then it was centrifuged at 5000 rpm for 15 min. The obtained product (biodiesel) was analyzed by gas chromatography (GC) under following conditions. The employed column was polar (0.25 mm× 100 m) and the flame thickness 0.20μm, which is unique to biodiesel fuel analysis. Nitrogen with a flow rate of 1.5ml. min^{-1} as a carrier and a FID detector were used. The temperatures were as 220°C, 250°C, for test, oven, injector and detector respectively. In accordance with the EN14103 standard for biodiesel analysis that in which the methyl mrystate and ethyl mrystate were used as internal standard. Methyl mrystate or ethyl mrystate in n-hexane at concentration of 10 mg ml^{-1} was prepared. Then 250 mg of sample containing biodiesel was dissolved in 5 ml of methyl or ethyl mrystate solution and finally 1μl of sample was injected into the column. The content of free fatty acid in sun flower oil was measured by titrimetric method employing 0.1N NaOH. Thus pH 10.5 was taken as an end point of titration. Density of the samples was measured at 25°C. The viscosity of biodiesel was determined at 40°C. All the experiments were performed in triplicate and analyzed with Tukey one-way ANOVA and the data reported as the mean value with the standard deviation of ±.

Results

The free acid content of sun flower oil was 0.66% as determined by titrimetric method. The results obtained for sunflower oil trans-esterification with methanol and ethanol (are shown in Figures 3-6) indicate the gas chromatograms of methyl ester and ethyl ester.

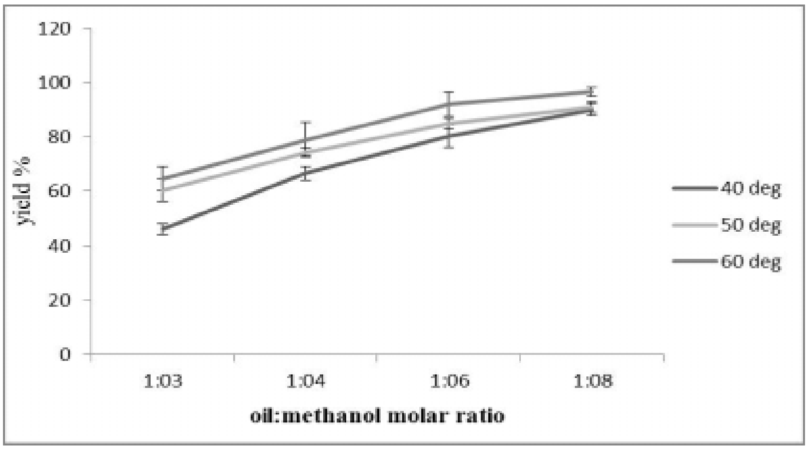


Figure 3. Effect of molar ratio of oil to methanol on yields of biodiesel at three different temperatures.The peaks from left are: of n-hexane, methyl mrystate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate.

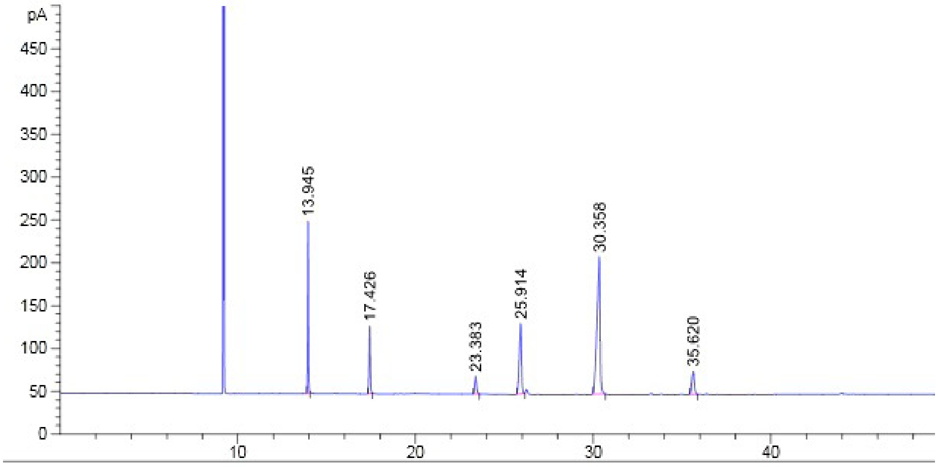


Figure 4. Chromatogram of B-100 biodiesel methyl esters of sunflower oil according to the EN14103 standard.

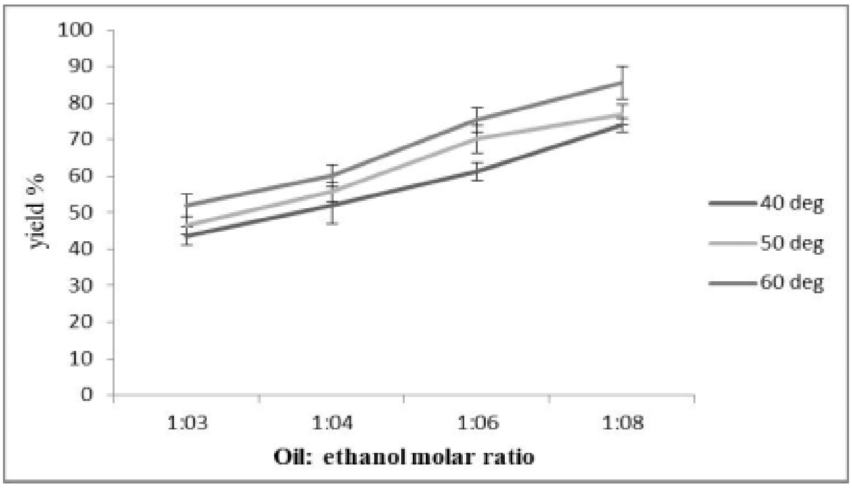


Figure 5. Effect of molar ratio of oil to ethanol on yields of biodiesel at three different temperatures.

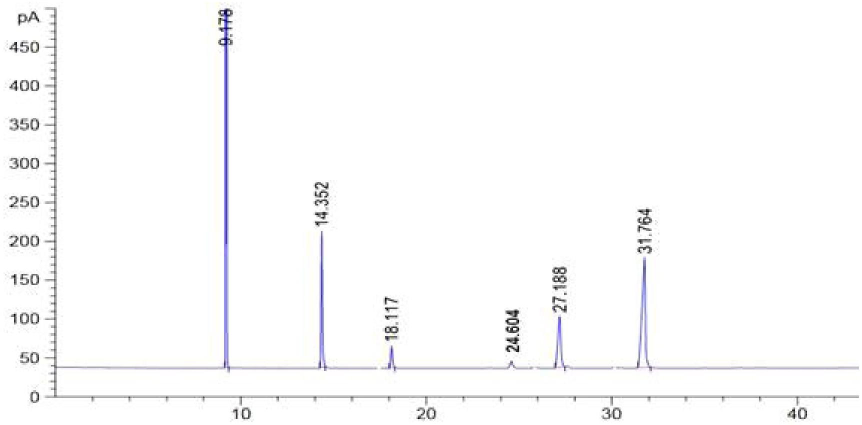


Figure 6. Chromatogram of B-100 biodiesel ethyl esters of sunflower oil according to the EN-14103 standard. The peaks from left are: n-hexane, ethyl mrystate, ethyl palmitate, ethyl stearate, ethyl oleate and ethyl linoleate.

Table 2. Data density and viscosity of sunflower oil biodiesel.

Viscosity	Density	Alkyl ester
mm^2/S 4.6	g/cm^3 0.867	Methyl ester
mm^2/S 5.6	g/cm^3 0.874	Ethyl ester

Discussion

According to the data obtained at temperature 40 º C up to molar ratio of 1:8, effect of increasing methanol ratio between 1:6 and 1:8 molar was significant, increasing efficiency does not show many differences as it is needed at high temperature. At 50˚C up to molar ratio of 1:8 yield of product is significant. By increasing the temperature and the amount of alcohol yield has been increased. At higher temperature (60˚ C) up to molar ratio of 1:6 (oil to methanol) there is a significant difference and after which the change occurs slowly.

Between the molar ratio of 1:6 and 1:8 molar the differences were not observed. Increasing the amount of methanol higher than 1:6 and 1:8 caused little effect on yield. The purity of the obtained biodiesel would be low at higher molar ratio of methanol. The main reason in reduction of the purity of biodiesel could be glycerin because at higher amount of methanol glycerin remains in biodiesel phase [9].Therefore, the purity and the apparent efficiency of biodiesel production are reduced. Theoretical basis for the perfect trans-esterification reaction the ratio of oil to alcohol must be at1:3 and increasing concentrations of alcohol can be helpful to synthesize more alkyl ester [12]. The results show a relationship between temperature and the molar ratio of oil to alcohol. Both factors have a positive effect on the reaction equilibrium thus causing higher production rate. At low temperature, increase in the methanol ratio can be helpful in production of biodiesel at high yield. In this study, the system contained oil and methanol at the molar ratio of 1:8 at 60 ºC thus the efficiency of biodiesel production was found to be 96%.

In production of biodiesel with ethanol at 40˚C between molar ratios of 1:3 to 1:4 and 1:4 to 1:6 there was no significant difference. But at 1:8 molar ratios the difference was significant, this indicated that the reaction needs temperature rather than higher molar ratio of ethanol, but in high proportion of ethanol, the ethanol effect was dominant and the reaction equilibrium proceeded toward more biodiesel production.

At temperature of 50 ˚ C amongst the three ratios of 1:3, 1:4 and 1:6, there were significant differences but the difference between 1:6 and 1:8 was insignificant. Hence the increases in temperature and molar ratio of ethanol could increase the product. At high proportions of ethanol, high temperatures were required in order to obtain more products. At 60°C the resulted rate was higher than the other two temperatures and by rising the temperature, reaction equilibrium proceeded towards the product which the need for ethanol would be more. Highest yield at 60°C and at 1:8 molar ratio of oil to ethanol was 85%. In production of biodiesel employing methanol and ethanol by rising the ratio of alcohol and temperature, the obtained yield increased, thus revealing that the temperature and molar ratio of alcohol in biodiesel production could be complementary therefore temperature had a positive effect on the alcoholise reaction [13].

Rashid and Anwar obtained similar results to optimize the production process of biodiesel from rapeseed oil [9].Henceforth, biodiesel can be used as mixture of 20% biodiesel and 80% gasoline in diesel engines that will reduce the air pollution caused by diesel fuel. According to viscosity test, the viscosity of methyl ester is less than ethyl ester. Figure (3-5). And both of them are in standard range of ASTM D6751 (1.9 – 6 $mm^2.sec^{-1}$) [14].

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