Optimization of Biodiesel Production from Waste Cooking Oil

Seid Yimer, Omprakash Sahu^{*}

Department of Chemical Engineering, KIOT Wollo University, Kombolcha (SW), Ethiopia *Corresponding author: ops0121@gmail.com

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Abstract Energy is basic need for growth of any country. The world energy demand is increasing so rapidly because of increases in industrialization and population that limited reservoirs will soon be depleted at the current rate of consumption. Both the energy needs and increased environmental consciousness have stimulated the researching of an alternative solution. So an attempted has been made to investigation of biodiesel production using transesterification reaction with solid or heterogeneous catalyst at laboratory scale and to compare the physical properties with the standard biodiesel properties. The selected process parameters are temperature ranged from 318 K to 333 K, molar ratio of methanol to oil from 4:1 to 8:1, mass ratio of catalyst to oil from 3% to 5% and rotation speed at optimum biodiesel yield was produced at 600 rpm.

Keywords: alcohol, bioenergy, methanol, oil, waste

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1. Introduction

"Sustainable" second generation biofuels don't yet exist on any useful scale but small quantities particularly from other existing waste streams - may be available by 2020. To meet the 10% target, and assuming the world carries out all the other measures above and if the quadruple waste counting comes into effect as proposed in the new commission proposal, an extra 22.7 Petajoules (PJ) of waste energy would be required to get us the rest of the way to the 10% target. In theory, there's quite a lot of waste energy out there. Food waste could be an aerobically digested to produce methane although this preferentially should be burnt to produce electricity. Much of this energy is in the form of wood, energy crops, forestry residues or agricultural straw, which isn't easy to transform into vehicle fuel and costly to transport. There's a risk that creating demand for waste as a fuel can reduce the incentive to reduce waste in the first place and reducing waste always saves more energy in the long term. As with all wastes, the primary focus should be on waste avoidance, then recovery, and finally disposal. In the waste management hierarchy, energy-from-waste comes fairly low down. Materials may have other more sustainable uses and have all sorts of unintended knock-on effects. So some solution should be required to minimize the cost like production of biodiesel [1]. Biodiesel is the name for a variety of ester based fuels (fatty ester) generally defined as monoalkyl ester made from renewable biological resources such as vegetable oils (both edible and non edible), recycled waste vegetable oil and animal fats [2]. This renewable source is as efficient as petroleum diesel in powering unmodified diesel engine. Today's diesel engines require a clean burning, stable fuel operating under a variety of conditions. Using biodiesel not only helps maintaining our environment, it also helps in keeping the people around us healthy [3,4,5]. Biodiesel is miscible with petrodiesel in all ratios. In many countries, this has led to the use of blends of biodiesel with petrodiesel instead of neat biodiesel [6]. There are different types of feed stocks that are used for the production of biodiesel. These includes linseed oil, palm seed oil, waste cooked vegetable oil, sunflower seed oil, cotton seed oil, cooking seed oil and animal fats [7,8,9]. Oilseed plants are used for the production of biodiesel through the process called transesterification reaction which is a process by which alcohol reacts with vegetable oil in the presence of catalyst. Triglycerides are major components of vegetable oils and animal fats. Chemically, triglycerides are esters of fatty acids with glycerol. Fatty acid ethyl esters are mostly involved because ethanol is the cheapest alcohol, but other alcohols, namely methanol, may be employed as well [10]. In this way, highly viscous triglycerides are converted in long chain monoesters presenting much lower viscosity and better combustion properties to enhance the burning. Homogeneous or heterogeneous catalysis are used to enhance the reaction rate [11.12.13].

However, the synthesis of biodiesel from these low quality oils is challenging due to undesirable side reactions as a result of the presence of FFAs and water. The pretreatment stages, involving an acid catalyzed preesterification integrated with water separation, are necessitated to reduce acid concentrations and water to below threshold limits prior to being processed by standard biodiesel manufacturing [14,15]. Besides catalyzing esterification, acid catalysts are able to catalyze TG transesterification, opening the door for the use of acid catalysts to perform simultaneous FFA esterification and TG transesterification [16,17]. The most common approach for processing waste oil in the biodiesel synthesis is a two-step acid-pretreatment before the successive base-catalyzed transesterification [18,19,20,21]. By using a two-step sulfuric acid-catalyzed pre-esterification, Canakci and Van Gerpen [20] were able to reduce the acid levels of the high FFA feedstocks (reaction mixtures containing 20-40 wt% FFA) below 1 wt% within 1 h, making the feedstocks suitable for the subsequent alkali-catalyzed transesterification.

Recently, the two-step catalyzed processes was shown to be an economic and practical method for biodiesel production from waste cooking oils where the acid values of 75.9 mg KOH/g were presented [18]. Employing a ferric sulfate catalyzed reaction followed by KOH catalyzed transesterification, a yield of 97.3% fatty acid methyl ester (FAME) was achieved within 4 h. By integrating the heterogeneous catalyst in the pretreatment process, several advantages have been introduced such as no acidic wastewater, high efficiency, low equipment cost, and easy recovery compared to corrosive liquid acids. Another reaction route for a two-step process was proposed and proven by Saka and his co-workers [22,23], where the first step involves hydrolysis with subcritical water at 270°C and subsequently followed by methyl esterification of the oil products at the same temperature. In this process, triglycerides were hydrolyzed with subcritical water to yield FFAs, which further reacted with supercritical methanol, resulting in a completed reaction within 20 min. Besides catalyzing the esterification, acid catalysts are able to perform TG transesterification; however, acid catalysts are 3 orders of magnitude slower than basic catalysts [24], thus allowing FFA esterification and TG transesterification to be catalyzed simultaneously [25]. The slow activity can be traded off with a decrease in process complexity, equipment pieces, and the amount of waste stream. For instance, Zhang et al. [3,8] have shown that, in biodiesel production using waste cooking oils, a one-step acid catalyzed process offered more advantages over the alkali-catalyzed process with regard to both technological and economical benefits. It was also proved to be a competitive alternative to a two-step acid preesterification process. Hence, it is imperative for this. The main aim of this work is to utilized the waste cooking oil for the production of biodiesel which is collected from the cafeteria, restaurant. The effect of temperature, effect of alcohol to oil molar ratio and effect of catalyst weight on the yield of biodiesel has also studied.

2. Material and Methods

2.1. Material

The waste cooking oil has been collected from the restaurant.

2.2. Method

2.2.1. Central Composite Design

Experimental design was analyzed and done by the Design Expert 7.0.0 software application. Experimental design selected for this study is CCD and the output measured is biodiesel yield gained. Process variables revised are reaction temperature, molar ratio of ethanol to oil and weight percentage of catalyst. To get maximum conversion; reaction period and rotation speed was set at 2 hours and 500 rpm respectively and at constant atmospheric pressure. The operating limits of the biodiesel production process conditions are reasons to choose levels of the variables Three level three factors CCD was made use of in the optimization study, needing 20 experiments to be done. Catalyst concentration, ethanol to oil molar ratio and reaction temperature were the independent variables selected to optimize the conditions for biodiesel production by using sodium hydroxide as main catalyst for performing transesterification reaction. Twenty experiments were done and the data was statistically analyzed by the Design Expert 7.0.0 software and to get suitable model for the percentage of fatty acid methyl ester as a function of the independent variables. The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared (R2), adjusted R-Squared and predicted R-Squared having a value of 0.9966, 0.9936 and 0.9788, respectively. The yield of the transesterification processes were calculated as sum of weight of FAME produced to weight of cooking oil used, multiplied by 100. The formula is given as:

Yield of FAME
=
$$\left(\frac{Weight \ of \ fatty \ acid \ methyl \ ester}{Weight \ of \ fat \ used}\right) \times 100\%$$
 (1)

2.2.2. Development of Model

The model equation that correlates the response to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of FAME content (R) in terms of the coded factors is given by Eq. 2.

Yield of FAME(%) = 86.07 + 13.34
$$xA$$
 + 0.75 xB
+2.13 xC - 0.66 $xAxB$ - 0.97 $xAxC$ - 0.68 $xBxC$ (2)
-5.62 xA^{2} + 0.090 xB^{2} - 0.55 xC^{2}

Table 1. Physicochemical	property of biodiesel

S. No	Biodiesel properties	Measured values	Units
1	Density at 20°C	950	kg/m ³
2	Kinematic viscosity 40°C	38.7	mm ² /s
3	Flash point (°C)	150	°C
4	Acid value	12.6	mgKOH/g
5	Saponification value mgKOH/g	180	mgKOH/g
6	Moisture content	0.019	(%)w/w
7	Ash content	0.04	(%)w/w
8	Iodine value	90.6	$I_2 g/100g$
9	Free fatty acidic	5.28	%
10	Melting point	30.2	°C

3. Result and Discussion

3.1. Physicochemical Properties

After transesterification biodiesel obtained, whose physical and chemical properties is mention in Table 1. The physical-chemical properties of generated biodiesel were found all satisfactoriness.

3.2. Effect of Methanol-to-Oil Molar Ratio

The methanol-to-oil ratio is one of the important factors that affect the conversion of triglyceride to FAME. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more FAME as products. The results obtained in this study are in agreement with this. As shown in Figure 1, the methanol-to-oil ratio showed positive influence to the yield of methyl ester, but the yield started to decrease as the ratio much increased. The increase is due to the positive sign in the experimental model. The decrease in the yield contrary to increase in molar ratio may be due to the separation problem resulted from excessive methanol. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst's active sites which could decrease the catalyst activity.



Figure 1. Interaction Effect of temperature and catalyst ratio versus yield (a) surface plot (b) contour plot

3.3. Effect of Catalyst Concentration

The RSM was used to optimize the conditions of biodiesel which is shown in Figure 2. It was observed that the catalyst concentration influenced the biodiesel yield in a positive manner up to a certain concentration. Beyond this concentration, the biodiesel yield decreased with increase in potassium hydroxide concentration. When the catalyst mount was improved, the interactive (active) site of the catalyst was increased; thus, the transesterification reaction was accelerated and biodiesel yield was increased.



Figure 2. Interaction effect of catalyst ratio and methanol ratio versus yield (a) surface plot (b) contour plot

3.4. Effect of Temperature

The effect of temperature with biodiesel conversion is shown in Figure 3. Temperature increase clearly influences the reaction rate and biodiesel yield in a positive manner. The temperature increase affected the biodiesel yield in a positive manner till 60°C and after that it decreased. The increase in the yield of FAME at higher reaction temperature is due to higher rate of reaction. From the experimental model analysis the p-value of the temperature term was nearer to the p-value limit. Hence, its effect on the biodiesel is almost constant.



Figure 3. Interaction effect of temperature and methanol ratio versus yield (a) surface plot (b) contour plot

The results above have shown that the three transesterification process variables and the interaction among the variables affect the yield of FAME. Therefore, the next step is to optimize the process variables in order to obtain the highest yield using the model regression developed. Using the optimization function in Design Expert, it was predicted that at the following conditions; 60°C of reaction temperature, methanol to cooking oil ratio of 4 and 5 wt% of catalyst, an optimum FAME yield of 95.08% can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 94.98% of FAME content agreed well with the predicted value. Therefore, this study shows that tribasic sodium phosphate is a potential catalyst for the production of biodiesel from cooking oil cooking oil via heterogeneous transesterification. The optimization result also tells the same result as the ANOVA output. The ANOVA output shows that the transesterification process is highly and significantly affected by the temperature, catalyst weight and the interaction between the temperature and the catalyst.

4. Conclusion

Biodiesel is alternative option in place diesel, the factors like profitability, availability, low sulfur content, low aromatic content, biodegradability and renewability makes biodiesel more advantageous. The result shows that biodiesel production using heterogeneous catalyst, is a considerable potential in biodiesel production process, mainly because of catalyst regeneration (decrease of catalyst cost),Simplification of separation process (decrease of production cost) and decrease of wastewater (development of environmental friendly process). At 333 K of reaction temperature, methanol to waste cooking oil ratio of 4 and 5 wt% of catalyst, an optimum fatty acid methyl ester yield of 95.10% was obtained. The sodium phosphate has excellent activity during transesterification. As a solid catalyst, sodium phosphate can decrease the waste water treatment and the steps of purification. It has potential for industrial application in the а transesterification of waste cooking oil to biodiesel. Hence, sodium phosphate has good catalytic performance

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