Vegetables Oil Waste Water as Solution for Air Pollution Reduction

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Abstract Any industries generate more waste water as compared to utilization. Waste water generated from the industry either treatment if treatment is feasible or simply discharges to nearby stream. Due that configuration of the environment disturb. It can be minimized if suitable step are take to recycle or use for positive direction. Waste water generated from vegetable oil more percentage oil in there effluent. Vegetable oils and their derivatives (such as methyl esters), commonly referred to as biodiesel, are prominent candidates as alternative diesel fuels. They have advanced from being purely experimental fuels to initial stages of commercialization in a number of countries. Biodiesel is technically competitive to conventional fossil diesel but relatively cheap fossil diesel prices have made the technology economically unfeasible for almost a century. However, recent high and rising world crude oil prices and claims that the world oil reserves are diminishing and environmental and political pressure have caused an urge in the development of the technology of biodiesel production. The goal of this work is to develop a two-step technique of biodiesel production from waste water oil of vegetable oil industry. The results showed the waste water oil containing 75.09% wt of high free fatty acid and the average molecular weight of fatty acid and waste water oil are 281 g mol-1 and 985 g mol-1 with the highest vegetableitic acid content.

Keywords: biodiseal, crude, dissolved, effluent, waste

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1. Introduction

Energy and Environment is big issue for now days. Pollution increase mainly due increase in industrial growth as well Energy will also require to run the industries. Basically for air pollution and water pollution Environmentalist are more serious to optimize and utilized them. More number of industry which generate the waste water more than there requirement. The waste water generation is due to processing, equipment cleaning, floor cleaning etc [1]. In that categories vegetable oil also have ranking to generate the huge amount of waste water. So many industry method are available in the literature but either they will generate the energy or minimised or have big project or equipment as well as non-economical. The demand for vegetable oils has increased rapidly in the past decade, catapulted by a combination of factors, including: i) increasing demand sparked off by higher consumption for edible oils, particularly in emerging countries such China and India caused by, among other things, population growth, improving living standards and changing diets; ii) the development of the biofuels industry (and more specifically biodiesel) around the world, particularly in the EU, USA, Brazil, Argentina, China and India, iii) price increases which have been due to varying factors e.g. increase in oil prices, low stock

worldwide, droughts, and speculation, iv) changing weather patterns which can have major geographical impacts and can be, potentially, quite large [2,3,4,5]. There are two major markets for vegetable oils: i) food which represents over 80%, and ii) industrial uses including biodiesel. The main driver for expansion is still the growing demand for edible oils for the food market, although an important part of this demand comes from the biodiesel sector. In recent years important new actors and trends in supply and demand have began to emerge e.g. i) China is rapidly emerging as the world leading importer of vegetable oils, ii) Indonesia, Malaysia and Argentina dominate the exports market, representing approximately 75%, iii) Brazil is also becoming one the world's largest exporters of soybeans 1, next to the USA, iv) Argentina, whose share of this market is growing rapidly, is rapidly becoming one of the world's top producer and exporter of soybean (meat and oil) [5-9].

Biofuels have largely been blamed for most of the increases in food prices. The reasons, however, are many and complex, with the major impact coming from the increases in oil costs and speculation on agricultural commodities. It has been shown that the cost of the raw material plays a comparatively small role in the retail of food in developed countries since price increases are largely determined by commercial and other issues rather than by raw material [10]. The vegetables oil market is bound for major changes, and will face substantial

challenges and opportunities. Improving living standards in emerging economies, population growth together with changing diets and the expansion of biodiesel, are new trends that will have a major impact in the future development of this sector. This market has very different features e.g. the Chinese market is characterised primarily by large imports, where in India it has been a rapid increase in production and demand of the domestic market [11]. Indonesia and Malaysia, the traditional palm oil producers and exporters, have major expansion plans as they face increasing competition from other countries, such as Thailand and possibly from Colombia. Traditional producers of soybean like the USA and Canada, face even greater competition from countries such as Argentina and Brazil. Crude vegetable oil from all of vegetable oil mill in Ethiopia has been losed into wastewater treatment pond about 1-2% from the milling process. This vegetable oil or waste vegetable oil was floated on the surface of wastewater in wastewater treatment pond and covered on the surface of wastewater which obstructe the direct contact with sunlight [12]. Due to which the treatment process was was very slow down. The waste vegetable oil is waste that must be treated before discharge from the mill plant. So, changing it to be raw material for making biodiesel fuels will be a green technology for a treatment of pond oil. In addition, it can diminish the environmental problems, too. Response surface methodology is a useful statistical technique which has been applied in research into complex variable process. It employs multiple regression and correlation analyses as tools to assess the effect of three independent factors on the dependent variables. Response surface methodology has been successfully applied in the study and optimization of biodiesel production in fat and oil feed stock [13,14,15]. So an attempted has been made for the utlized the wastewater oil convert into biodiseal. The esterification and transesterification steps was studied to optimize condition by response surface methodology. The free fatty acid in waste vegetable oil was reduced to less than 2% wt in the esterification step and the fatty acid methyl ester was produced in the transesterification step. After that fatty acid methyl ester was analyzed for properties of biodiesel quality by ASTM and EN standard methods.

2. Materials and Methods

2.1. Materials

The waste vegetable oil was collected from wastewater treatment pond of the vegetable oil mill plant in the southern part of Ethiopia. The chemicals for this research are ethanol, sulfuric acid, sodium hydroxide, potassium hydroxide, sodium chloride, N- heptanes (C_7H_{16}), methyl heptadecanoate, etc. They are analytical grade. The reference standards of fatty acid methyl esters are more than 99% purity.

2.2. Preparation for Material

The solid particles contained in waste vegetable oil was separated by mixing the pond oil with ethanol 1:2 by volume at 55°C for 10 min, after that the mixture product was filtrated on filter paper under vacuum filtration immediately to separate the solid particles from the mixture product. The ethanol solution in filtrate was evaporated by using the rotary evaporator. The water in filtrate was removed by heating operated at 500 rpm at 105°C for 4 hrs. The final product was investigated to find the fatty acid composition of pond oil by using gas chromgraphy and it was used as the feed stock for making biodiesel in the esterification and transesterification steps [16].

2.3. Apparatus and Reaction Procedures

The process for the production of biodiseal is shown in Figure 1. There is two steps involves to convert the waste oil into biodiseal [17].

2.3.1. Esterification Step

The reactions were conducted in 50 ml three-necked flask equipped with a reflux condenser and a thermometer. The flask was heated and stirred with magnetic stirrer on agitator heater, fixed stirred at 700 rpm and temperature reaction at 60°C. For esterification experiment, the flask was charged with 10 g of waste pond oil and heated to the setting temperature with agitation. A certain quantity of sulfuric acid catalyst was dissolved in the required amount of ethanol. After achieving the setting temperature of the reactant and catalyst, ethanol and catalyst were added to the flask. The reaction was timed immediately. When the reaction completed to separate the oil from excess ethanol, acid catalyst and water, the oil was washed with water and heated at 105°C. This final product was the feed stock for transesterification step.



Figure 1. Flow diagrame for biodiseal production

2.3.2. Transesterification Steps

Esterified oil obtained from esterification step was further reacted with ethanol and potassium hydroxide that was used as catalyst. The operation condition was 700 rpm of stirring rate and 60°C of temperature reaction. When the reaction completed, methyl ester was separated from glycerol. The methyl ester layer was washed with warm 1% NaCl and warm water. After washing, the methyl ester was subjected to heat at 105°C for removing excess water. Methyl ester was further characterized for physical and chemical properties followed ASTM and EN methods.

2.4. Experimental Design

2.4.1. Esterification Step

A five-level and three-factor central composite design with 20 experiments was employed in this study. Ethanol to free fatty acid in waste vegetable oil molar ratio, acid catalyst concentration and reaction time were the independent variables to optimize the reduction of free fatty acid in pond oil. The coded and uncoded levels of the independent variables, independent factor, levels, experimental design and predicted free fatty acid showed in Table 1. The central values (zero level) chosen for experimental design were 20:1 (wt/wt) of ethanol to free fatty acid in waste vegetable oil molar ratio, 5.00% (wt/wt) of acid catalyst concentration and 120 min of reaction time.

2.4.2. Transesterification Step

A five-level and three-factor central composite design with 20 experiments was employed in this study. Ethanol to esterified oil molar ratio, alkaline catalyst concentration and reaction time were the independent variables to optimize the conversion of triglycerides to fatty acid methyl ester or biodiesel from the pond oil. The coded and uncoded levels of the independent variables, independent factor, levels, experimental design and predicted fatty acid methyl ester showed in Table 2. The central values (zero level) chosen for experimental design were 10 (wt/wt) of ethanol to esterified oil molar ratio, 1.50% (wt/wt) of alkaline catalyst concentration and 30 min of reaction time. The experimental data were analyzed by the RSM regression procedure using a second-order polynomial as showed in Equation 1.

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{i=j+1}^{2} \beta_{ij} X_i X_j$$
(1)

Where *Y* is the response (% free fatty acid or % fatty acid methyl ester), β_0 , β_I , β_{ii} and β_{ij} are intercept, linear, quadratic and interaction constant coefficients, respectively. ANOVA and RSM were performed using the design expert software [18].

2.5. Engine and other Equipments

The performance tests were carried on a single cylinder, four strokes naturally aspirated, and water-cooled Kirloskar computerized diesel engine test rig. Diesel engine was directly coupled to an eddy current dynamometer. The engine and dynamometer were interfaced to a control panel, which was connected to a computer. This computerized test rig was used for recording the test parameters such as fuel flow rate, temperature, air flow rate, and load for calculating the engine performance such as mean effective pressure, power, brake specific fuel consumption, brake thermal efficiency, and emission like HC, CO, NOx and smoke [19]. The exhaust gas temperature, inlet and outlet water temperatures were measured through the data acquisition system and were fed to the computer. The exhaust gas was made to pass through the probe of Crypton computerized exhaust gas analyzer for the measurement of HC, CO, NOx and later passed through the probe of smoke meter of Bosch type for the measurement of smoke opacity. A whole set of experiments were conducted at the engine speed of 1500 rpm and compression ratio of 17.5:1.

3. Results and Discussion

3.1. Properties of Waste Oil

The waste pond oil had fatty acid contents of 65.09%. The average molecular weight (g/mole) of pond oil was determined by a weight average method utilizing the fatty acid profiles. The molecular weight of each fatty acid found in pond oil was multiplied by its corresponding weight percentage as determined by gas chromotography. This average molecular weight was used to calculate the mole ratio of ethanol to pond oil in transesterification step.

Table 1. Fatty acid composition of waste vegetable oil

S.No	Fatty acid	% wt		
1	Myristic	0.87		
2	Vegetableitic	47.40		
3	Vegetableitoleic	1.12		
4	Steric	4.29		
5	Oleic	36.30		
6	Linoleic	6.95		
7	Erucic	3.06		

After esterification and transesterification biodiesel obtained, whose physical and chemical properties is mention in Table 2. The physical-chemical properties of generated biodiesel were compared with ASTM value it was found all values are satisfactoriness.

Table 2. Comparatively result biodiesel with ASTM

S.No	Biodiesel properties	Measured values	ASTM Standard
1	Density at 20°C (kg/m ³)	839-843	875-900
2	Kinematic viscosity 40°C (mm^2/s)	2.90 -4.50	1.9-6.0
3	Flash point (°C)	132 - 150	<u>>130</u>
4	Acid value (mgKOH/g)	0.68 -0.89	<u>< 0.8</u>
5	Saponification value (mgKOH/g)	115.5-124.5	-
6	Moisture content % (w/w)	0.011 -0.019	< 0.03
7	Ash content% (w/w)	0.019 -0.029	< 0.02
8	Iodine value ($I_2g/100g$)	65.6-74.87	<120
9	Cetane number	70.25-76.46-	>47

3.2. Optimization of Esterification Step

The free fatty acid contents for etherification step at the design points, the statistical analysis model was performed to determine the variance. The linear regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for free fatty acid. The models characteristics and the coefficients were indicated that the predictability of the model is at 95% confidence level. The analysis of variance showed that the model F-values of 13.166 with significance was 0.000 which less than 0.05 for the models, implied the model was significant. The high correlation coefficient (R^2 =0.922) indicates that the model is suitable for represent the real relationships among the parameters

studied. The model to predict the free fatty acid content in esterification step is presented in Equation 2.

$$Y = 30.171 + 0.143M - 10.384C + 0.002T - 0.002M^{2} + 0.958C^{2} + 0.00001513T^{2}$$
(2)
-0.023MC + 0.001CT + 0.000MT



Figure 2. Response surface plots representing the biodiesel yields (a) temperature and catalyst weight versus biodiesel yield (b) catalyst weight and ethanol to oil molar ratio versus biodiesel yield and (c) temperature and ethanol to oil molar ratio versus on biodiesel yield

The optimized levels of variables were determined by constructing three-dimensional surface plots according to Eq. 2, which is shown in Figure 2. In Figure 2(a) shows the interaction effect of temperature and catalyst weight versus biodiesel yield, Figure 2(b) the interaction effect of catalyst weight and ethanol to oil molar ratio versus biodiesel yield and Figure 2(c) the interaction effect of temperature and ethanol to oil molar ratio versus on biodiesel yield. Generally, an increase in reaction temperature is found to increase the yield of biodiesel up

to some optimal value in all three cases. Additionally it was observed that at lower range of reaction temperature, higher weight of catalyst and higher molar ratio of ethanol to oil, always resulted in higher yield than when using lower weight of catalyst and lower ratio of ethanol to oil. Reactions which were carried out using lower ratio of ethanol to oil and lower weight of catalyst is found to have higher yield as compared to reactions using lower reaction temperature, higher molar ratio of ethanol to oil and higher weight of catalyst. However, at higher range of reaction temperature, the observations showed that using a combination of both, higher reaction temperature and higher molar ratio of ethanol to oil or higher weight of catalyst used is not beneficial in increasing the yield of biodiesel. This is probably because at these conditions, the higher reaction temperature is already sufficient to push the reaction forward. This phenomenon is further supported by the fact that reaction temperature is the most significant process variable that affects the yield of the biodiesel as indicated by graphs.

The optimum values in reducing free fatty acid to lower than 2% wt were 4.5-5.6% (wt/wt) of acid catalyst amount and 80-120 min of reaction time. Ethanol should be used between 23 to 28 moles of ethanol to free fatty acid in pond oil molar ratio which is obtained from the RSM. The optimized condition was predicted by using optimization function of the SPSS software at 28 moles ethanol to free fatty acid in waste vegetable oil molar ratio, 5.5% H_2SO_4 for 90 min of reaction time. This condition can reduce free fatty acid to 1.76% wt.

3.3. Optimization of Transesterification Step

The methyl ester contents for transesterification step at the design points are given in Table 4. The predictability of the model is at 95% confidence level. The analysis of variance (ANOVA) showed that the model F-values was 8.966 (FAME) with significance of 0.001 that less than 0.05 for the models. It implied the model was significant. The high correlation coefficient (R^2 =0.890) indicates that the model is suitable to represent the real relationships among the parameters studied. The model to predict the FAME is presented in Equation 3.

$$Y = 52.317 - 2.661M + 39.939C - 0.479T$$

+0.137 $M^2 - 10.446C^2 + 0.006T^2$ (3)
+0.363 $MC + 0.069CT$

The optimized levels of variables were determined by constructing three-dimensional surface plots according to Eq. 3, which is shown in Figure 3. Figure 3(a) shows the FAME on methanol/oil molar ratio and reaction temperature, Figure 3 (b) reaction temperature and catalyst concentration, and Figure 3(c) methyl ester production. From the Figure it was found that the strong interaction between ethanol/oil molar ratio (M), and KOH catalyst concentration (C). This can also be confirmed by the high p-values of the interaction parameters. It could also be seen from Figure 3(a) the FAME yield increased with increasing catalyst concentration at first. However, when the catalyst concentration reached a certain level, the reverse trend was observed. The similar pattern was followed when increasing methanol/oil molar ratio. This could be due to the fact that the positive coefficient for the linear parameters (M, C, and T) played the main role when the KOH catalyst concentration and ethanol/oil molar ratio

were at lower level, while at higher level, the interaction terms and the quadratic terms showed more significant negative effect, leading to the decrease of the yield. This was consistent with the physical explanation. Since the methanol and triglyceride in the oil are immiscible, addition of catalyst can facilitate the transesterification reaction, and rapidly increase the yield. However, when the catalyst concentration was too high, soap could be quickly formed which made the separation of glycerol from biodiesel more difficult, thus reducing the yield. Similarly, the increase of the methanol amount, on one hand, will drive the reaction to the right since the transesterification reaction is an equilibrium process; on the other hand, excess methanol will help increase the solubility of glycerol resulting in the reaction driven to the left, thus decreasing the yield. In Figure 3 (b) showed the effect of ethanol/oil ratio and the reaction temperature when the level of catalyst concentration was fixed. At low methanol to oil ratio, %FAME increased with reaction temperature increase. Also, the FAME yield increases with increased molar ratio certain level. Figure 3 (c) showed the effect of reaction temperature and catalyst concentration on the methyl ester yield when the level of methanol/oil molar ratio was fixed. At a certain level of catalyst concentration, the increase in reaction temperature T increases the ethyl ester yield. An explanation to this has been attributed to the fact that at a higher initial temperature helps in faster settlement of glycerol. However, the temperature increase affected the FAME yield in a positive manner until 600C. After that the effect was negative. This could be explained by the higher p-value nearly high p-value and the negative coefficient for the reactive and quadratic term in the model, indicating the non-significant effect.

The optimum values of amount of alkaline catalyst and the reaction time from RSM were 1.4-2.2 % of KOH and 30-55 min of reaction time. Mole ratio of ethanol to esterified waste Vegetable oil was 10 to 14 moles which is obtained from the RSM. The optimized condition was predicted using optimization function of the SPSS software at 14 moles ethanol to esterified oil molar ratio, 1.5% KOH for 55 min of reaction time. This condition can convert triglycerides to 84.05% of FAME.

3.4. Air Pollutant Reduction

The reduction of pollutants by using the biodiesel at various percentages is shown in Figure 4. It was observed that nitrogen oxide (NOx) percentage increase with maximum 10% was found when biodiesel was 100% used. Other parameters particulate matter (PM), carbon monoxide (CO), and hydrocarbon (HC) was decrease with increase in biodiesel percentage. The maximum reduction 55% PM, 54% CO and 73% of hydrocarbon was observed at 100% of biodiesel was used.



Figure 3. Response surface Plot of FAME yield (%) in terms of coded factors: the Effect of ethanol/oil molar ratio and catalyst concentration (a), ethanol/oil molar ratio and reaction temperature (b) reaction temperature and catalyst concentration (c), on ethyl ester production



Figure 4. Pollutant emission by heavy duty biodiesel engine

4. Conclusions

The waste oil generated from the pond with high free fatty acid could be used as raw material to produce biodiesel. The free fatty acid in pond oil can be reduced to less than 2% by optimizing the central composite design and response surface method in esterification step. The optimum conditions of esterification reaction were obtained at 28 moles of ethanol to free fatty acid in pond oil molar ratio, 5.5% sulfuric acid concentration in 90 min of reaction time and 55°C of reaction temperature. In transesterification step, the optimum conditions were 14 moles ethanol to esterified oil molar ratio, 1.5% KOH for 1h min of reaction time which can convert triglycerides to FAME. The result gave methyl ester content at 94.05% according to EN 14103 method. The fuel properties tested are within the ASTM and EN norms and were found to be very close to those of petroleum diesel. The results showed that transesterification improved the important fuel properties tested. The calorific value of the biodiesel is slightly lower than that of diesel but has a higher calculated cetane number. The density and the viscosity were indicators of the biodiesel quality against the process variables. Higher iodine value indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. Generally, the FAME of biodiesel has relatively closer fuel properties to petroleum diesel than the oil.

References

- Thompson, A.E., D.A. Dierig, E.R. Johnson, G.H. Dahlquist, and R. Kleiman. Germplasm development of vernonia galamensis as a new industrial oilseed crop 1994; 3: 185-200.
- [2] Perdue R.E. Jr. Carlson K.D. Gilbert MG. vernonia galamensis, potential new source of epoxy acid 1986; 40: 54-68.
- [3] African Journal of Biotechnology Vol. 8 (4) 18 February 2009; 635-640.
- [4] Alexander C.Dimian and Costin Sorin Bildea. Chemical Process Design, Computer Aided Case Studies 2008; 399-42.

- [5] IPMS Information Resources Portal Ethiopia (23 June 2005, accessed 3 March 2009); 12.
- [6] Perdue, R.E. Jr., K.D. Carlson, and M.G. Gilbert, vernonia galamensis, potential new crop source of epoxy acid 1986;40:54-68.
- [7] Ayhan Demirbas, Biodiesel, a Realistic Fuel Alternative for Diesel Engines, Energy Technology Sila Science and Energy Trabzon Turkey, Springer, 2008.
- [8] J.M. Encinar, J.F. Gonzalez, A.R. Reinares. Ethanolysis of used frying oil biodiesel preparation and characterization, Fuel Processing Technology 2007; 88: 513-522.
- [9] Baye, T. Variation in agronomic characteristics of vernonia galamensis, a new industrial oilseed crop of Ethiopia 2000. 49-53.
- [10] Y.C. Leung, W.Xuan. A review on biodiesel production using catalyzed transesterification, Applied Energy 2010; 87: 1083-1095.
- [11] Dennis Y.C. Leung, Xuan Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, Department of Mechanical Engineering, The University of Hong Kong, applied energy, 2009.
- [12] G. El Diwani, N. K. Attia, S. I. Hawash, Development and evaluation of biodiesel fuel and by products from jatropha oil, Chemical Engineering and Pilot Plant Department, National Research Center, Dokki, Egypt Spring 2009; 219-224.
- [13] B. Freedman, E.H. Pryde, T.L. Mounts. Variables affecting the yield of fatty esters from transesterified vegetable oils, Journal of American Oil Chemists Society 1984; 61 (10): 1638-1643.
- [14] G. Anastopoulos, Y. Zannikou, S. Stournas, S. Kalligeros. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters, Energies 2009; 2: 362-376.
- [15] L.C.Meher, D.Sagar, S. Naik. Technical aspects of biodiesel production by transesterification, Renewable and Sustainable Energy Review 2006; 10: 248-268.
- [16] Y. Zhang, M.A. Dubé, D.D. McLean, M. Kates. Biodiesel production from waste cooking oil: Process design and technological assessment, Bioresource Technology 2003; 89: 1-16.
- [17] B. Freedman, R.O. Butterfield, E.H. Pryde. Transesterification kinetics of soybean oil, Journal of American Oil Chemists Society 1986; 63: 1375-1380.
- [18] P. Nakpong, S. Wootthikanokkhan. Optimization of biodiesel production from jatropha oil via alkali-catalyzed methanolysis, Journal of Sustainable Energy and Environment 2010; 1: 105-109.
- [19] A.A. Refaat. Different techniques for the production of biodiesel from waste vegetable oil.International Journal of Environmental Science and Technology 2010; 7(1): 183-213.