International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 06 Issue: 07 | July 2019 www.irjet.net p-ISSN: 2395-0072

Biodiesel Production, Optimization and Fuel Properties Characterization of Waste Fish Oil

Shreehari P. Shaldar[1], Athith D[2], Abhishek H A[3]

[1,2,3]*Assistant Professor, Dept. of Automobile Engineering, Acharya Institute of Technology, Bengaluru, Karnataka, India*

Abstract - *The waste fish oil is used as the raw material for the production of biodiesel in this study. Crude oil was extracted from fish parts which pretreated and refined to get the oil. The weight proportions of the composition of the saturated and unsaturated fatty acids of waste fish oil were analyzed by a gas chromatography (GC-57) analyzer. It was found that the selected oil contains 28.15% saturated acid (Palmitic acid 23.31 % and Stearic acid 4.84 %) and 5.6%. unsaturated acid (Oleic acid 2.93%, Linoleic acid 1.62 % and Linolenic acid is 1.05 %). The Free fatty acid content was determined which was found to be 15, so a two stage transestrification process was employed for the biodiesel production. Central composite design is employed to get the maximum biodiesel yield. XLSTAT is used to generate linear model to predict the free fatty acid level as a function of methanol quantity, catalyst concentration and reaction time by keeping reaction temperature constant (55°C). MINITAB is used to draw the 3D response surface plot to predict the maximum biodiesel yield. A statistical model predicted the maximum fish oil methyl ester (94.091%) yield obtained at the maximum methanol quantity of 20 (%v/v of oil), catalyst concentration of 0.4(%w/v of oil) and reaction time of 60 minutes. Experimentally, 94.11% of waste fish oil methyl ester has obtained at the above parameters. The characteristics fuel properties of methyl ester and its blends have found to be close to those of conventional diesel oil.*

Key Words: **Waste fish oil, Methanol, Biodiesel, XLSTAT**

1. INTRODUCTION

Alternative fuels for diesel engines are becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines [1]. One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine. With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO2 [2]. The alternative diesel fuels must be technically acceptable, economically competitive, environmentally acceptable and easily available. From the viewpoint of these requirements, triglycerides (vegetable oils/animal fats) and their derivatives may be considered as viable alternatives for diesel fuels. Vegetable oils are widely available from a variety of sources, and they are renewable. As far as environmental considerations are concerned, unlike hydrocarbon-based fuels, the sulphur content of vegetable oils is close to zero and hence, the environmental damage caused by sulphuric acid is reduced. Moreover, vegetable oils take away more carbon dioxide from the atmosphere during their production than is added to it by their later combustion. Therefore, it reduces the increasing carbon dioxide content of the atmosphere. However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct-injection and indirect type diesel engines. The high viscosity, acid composition, and free fatty acid content of such oils, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening are some of the more obvious problems. Consequently, considerable effort has gone into developing vegetable oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. Problems encountered in substituting triglycerides for diesel fuels are mostly associated with their high viscosity, low volatility, and polyunsaturated character [3]. To overcome these drawbacks and allow vegetable oils and oil waste to be utilized as a viable alternative fuel pyrolysis, micro-emulsification, and transesterification process were investigated. Pyrolysis refers to chemical change caused by the application of thermal energy in the presence of an air or nitrogen. Thermal decomposition of triglycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, aromatics, and carboxylic acids. Different types of vegetable oils reveal large differences in composition when they are thermally decomposed [4]. Micro emulsions are isotropic, clear or translucent thermodynamically stable dispersions of oil, water, a surfactant, and often a small amphiphilic molecule, called a cosurfactant. Use of micro emulsions with solvents such as methanol, ethanol, and 1-butanol are useful for solving the problem of high viscosity of vegetable oils [5]. Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water. Suitable alcohols include

methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance [6]. Biodiesel is defined as mono-alkyl esters of vegetable oils or animal fats, obtained by transesterification of an oil or fat with an alcohol [7]. It is a biodegradable and nontoxic biofuel, so is environmental beneficial [8]. Fish oil is recommended in a healthy diet because of its content in omega-3 polyunsaturated fatty acids such as eicosapentaenoic (EPA) and docosahexaenoic (DHA) acids [9]. However, refining of fish oil extracted from fish wastes would result in low yields because of its high content of free fatty acids and oxidation products [10]. Moreover, waste fish oil might have a low amount of EPA and DHA reducing its application on the pharmaceutical and functional food fields [11]. Thus, biodiesel using waste fish oil as feedstock has been recently researched [12–17]. Nevertheless, biodiesel from fish oil has low oxidative stability, mostly due to its high content of polyunsaturated fatty acids (PUFA) containing more allylic methylene positions [18]. Biodiesel oxidation is undesirable because it can increase viscosity and may lead to formation of residues, which can lead to clog fuel lines and pumps [19]. In order to improve this property, antioxidants can be added to biodiesel or fish oil can be mixed with more stable oils and used as biodiesel feedstock [20]. Therefore, the aim of this work was to produce a biodiesel from the waste fish oil and determination of the optimal conditions for biodiesel production and property evaluation of the biodiesel produced so that it can be used in the diesel engine.

2. EXPERIMENTAL WORK

The fuel characteristics of biodiesel from waste fish oil were measured and compared with that of the diesel to investigate the possibilities of using the waste fish oil biodiesel as an alternative diesel fuel.

2.1 Production of the Biodiesel from waste Fish oil

The waste fish oil was extracted from the lipid content of the discarded parts of various fish. To prepare the fish oil, the stock was treated by a series of processes, starting with boiling in the water, squeezing it, and centrifugally separating the products. The waste fish oil produced from the fish was brown and contained various kinds of impurities, such as water, fish residue and saline compound. Therefore, it was refined by a set of pre-treatment processes. These processes included the absorption of the fish residue by active clay and storing at 4°C for 120 min, centrifuging at 3000 rpm for 10 min to remove the solid impurities, washing with water by 5 vol.% distilled water for 15 min, and heating to 105°C for 30 min. The weight proportions of the composition of the saturated and unsaturated fatty acids of waste fish oil were analysed by a gas chromatography (GC-57) analyser. Table 1 shows that fatty acid composition of waste fish oil from Gas Chromatography (GC-57) analysis.

Table -1: Free Fatty Acid Compositions (FFA in %) of waste fish oil

Type of fatty acids	Chemical structure	Waste fish oil
Palmitic acid	C16:0	23.31%
Stearic acid	C18:0	4.84%
Oleic acid	C18:1	2.93%
Linoleic acid	C18:1	1.62%
Linolenic acid	C18:3	1.05%

It was found that the selected oil contains 28.15% saturated acid (Palmitic acid 23.31 % and Stearic acid 4.84 %) and 5.6%. unsaturated acid (Oleic acid 2.93%, Linoleic acid 1.62 % and Linolenic acid is 1.05 %). The waste fish oil has low saturated free fatty acid ester. It reduces the cold point, cetane number, and stability. The content of saturated fatty acid increases with the cold filter plugging point. In this case saturated fatty acid content is low compare to unsaturated fatty acid. Increase in unsaturated contents lead to reduce the cetane number and increase in flash point. It also reduces the viscosity of the oil.

Two stages transesterification process was used for waste fish oil as its free fatty acid level was more than 15. Methanol has chosen as an alcohol for transesterification process because of its low cost. In the first stage, sulphuric acid (H_2SO_4) has used as an acidic catalyst because it appears to be quite effective at converting high FFA to esters, and this reaction is fast enough to be practical. In the second stage, sodium hydroxide (NaOH) was used as an alkaline catalyst because it is cheaper and reacts faster than acidic catalyst. Thus acid pre-treatment step followed by an alkaline catalysed step has used to convert waste fish oil samples into esters. The waste fish oil was converted into methyl 12 esters through acid transesterification process with sulfuric acid (H_2SO_4) in the presence of methanol and catalyst. For 1 litre of waste fish oil, 300ml of methanol and 15ml of concentrated sulfuric acid is used. This mixture is heated in a flask with constant stirring at 60°C for 35 min, and then it is taken out and allowed to settle for 6 to 8 hours in a separating funnel. Here, the Esterification acid layer is separated and it is to be removed from the oil. The FFA of oil is measured and taken for second stage. If FFA is more than 4% same process as discussed is done. The upper layer of the previous process having low free fatty acid (FFA) is used for this reaction. The product obtained in previous stage that is, triglyceride is made to react with 200ml of methanol and 4grams of NaOH catalyst for 1litre of test oil and is heated at 60°C with constant heating and stirring for 1 hour. The reacted products of this stage settled at the bottom of container due to gravity. The lower layer

contains glycerine and other impurities, which are to be separated later from the methyl ester.

3. OPTIMIZATION METHOD

In this work, experiments have been carried out according to Central composite design (CCD) to understand the relation between the process variables and biodiesel yield. A Central composite design method was used to find out the optimal experimental conditions for production of biodiesel. Central composite design has the advantage to predict yield based on few set of experimental results in which all the parameters varied within the range.

3.1 Parameter design Methodology

In order to optimize the transesterification process parameter a five- level-three factors CCD has used. Three control parameters such as methanol (D) in ml, sodium hydroxide (E) in grams and reaction time (F) in minutes have selected for optimization of biodiesel yield. Each of the three control parameters has treated at five levels. Table 2 shows the experimental matrix for CCD and biodiesel yield for alkaline catalyzed transesterification process. Twenty experiments have been conducted keeping reaction temperature constant (55°C to 60°C) and varying reaction time.

Table 2

Exp. NO	CH_3OH (% v/ v of oil)	NaOH (% w/ v of oil)	Reaction time (minutes)	Yield (%)	
				Experimental	Predicted
1	20	0.4	30	90.9	86.177
2	20	0.4	60	94.11	94.091
3	20	0.8	30	77.22	79.174
4	20	0.8	60	81.82	84.503
5	30	0.4	30	86.95	88.135
6	30	0.4	60	92.38	86.353
7	30	0.8	30	86.3	82.237
8	30	0.8	60	77.27	77.87
9	25	0.6	19.8	76.19	77.614
10	25	0.6	70.2	76.14	80.596
11	25	0.26	45	92.38	96.091
12	25	0.93	45	80.92	83.925
13	16	0.6	45	85	80.094
14	33.4	0.6	45	80.95	83.069
15	25	0.6	45	85.75	85.533
16	25	0.6	45	85.75	85.533
17	25	0.6	45	85.75	85.533
18	25	0.6	45	85.75	85.533
19	25	0.6	45	85.75	85.533
20	25	0.6	45	85.75	85.533

3.2 Statistical analysis

The experimental data was analyzed with XLSTAT for least quadratic square regression technique.In this work also, XLSTAT for quadratic least square technique with MINITAB software have used in the regression analysis and analysis of variance (ANOVA) and to generate surface plots using the fitted quadratic polynomial equation obtained from regression analysis. Few experiments have conducted to validate the equation using a combination of the independent variables. Selected variables are within the experimental range

4. RESULTS AND DISCUSSION

The waste fish oil samples are taken to conduct the experiment by use of an alkaline catalyzed transesterification process. For optimum conditions to maximize the waste fish oil methyl ester yield, the experiments are carried out based on the CCD experimental matrix the multiple regression coefficients have obtained by employing XLSTAT for least quadratic square regression technique to predict a quadratic polynomial model for waste fish oil methyl ester yield. A statistical model predicted the maximum fish oil methyl ester (94.091%) yield obtained at the maximum methanol quantity of 20 (%v/v of oil), catalyst concentration of 0.4(%w/v of oil) and reaction time of 60 minutes. Experimentally, 94.11% of waste fish oil methyl ester has obtained at the above parameters.

4.1 Effect of methanol and NaOH on experimental yield

Fig. 1 shows the 3D response surface plot and 2D contour plot between methanol quantity and NaOH concentration for different fixed parameter. From Fig. 1 it can be seen that the methyl ester yield increases with the increase in the methanol quantity but decreases with increase in catalyst concentration (NaOH).

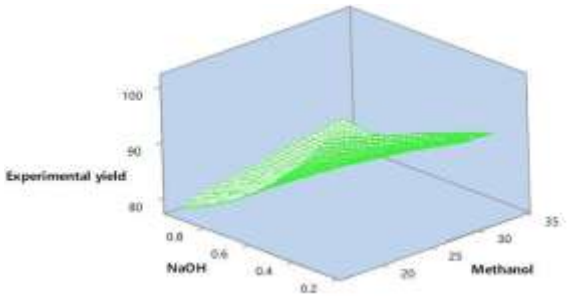

Fig-1: Response Surface Plot: Effect of NaoH and Methanol Quantity on Experimental Yield

This has reached the maximum yield 94.11% at NaOH concentration of 0.4 (%w/v of oil) and methanol quantity of 20 (%w/v of oil) and the yield decreases with the increase in NaOH concentration. This is due to there is less significant interaction between methanol quantity and NaOH concentration and negative concentration of

quadratic coefficient mostly caused by soap formation side reaction.

Fig. 2 shows the 3D response surface plot and 2D contour plot between methanol quantity and NaOH concentration for different fixed parameters. From Fig.2 it can be seen that the maximum yield 94.11% at NaOH concentration and methanol quantity of 20 (%w/v of oil) and the yield decreases with the increase in NaOH concentration.

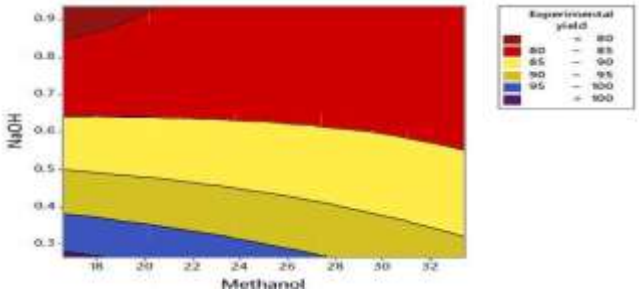

Fig-2: Effect of Methanol and NaOH on Experimental Yield in 2D Contour Plot

4.2 Effect of Methanol and Reaction Time on Experimental Yield

Fig. 3 show the 3D response surface plot and 2D contour plot between reaction time and methanol quantity for different fixed parameter. From Fig. 3 it can be seen that the methyl ester yield increases with the increase in reaction time and reaches maximum yield of 94.11% at methanol quantity of 20 (%w/v of oil) and reaction time of 60 minutes. Then the yield is decreases with the increase in methanol quantity and increase in the reaction time. This is due to there is less significant interaction between methanol quantity and reaction time and negative concentration of quadratic coefficient mostly caused by soap formation side reaction.

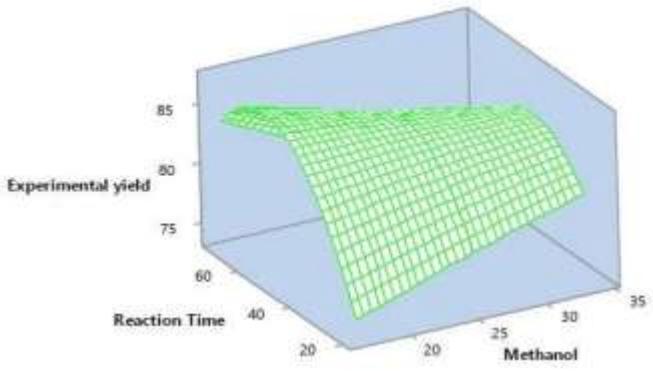

Fig-3: Response surface plot: Effect of reaction time and methanol quantity on experimental yield

Fig. 4 shows the 3D response surface plot and 2D contour plot between reaction time and methanol quantity for different fixed parameter. From Fig. 4 it can be seen that the methyl ester yield increases with the increase in reaction time and reaches maximum

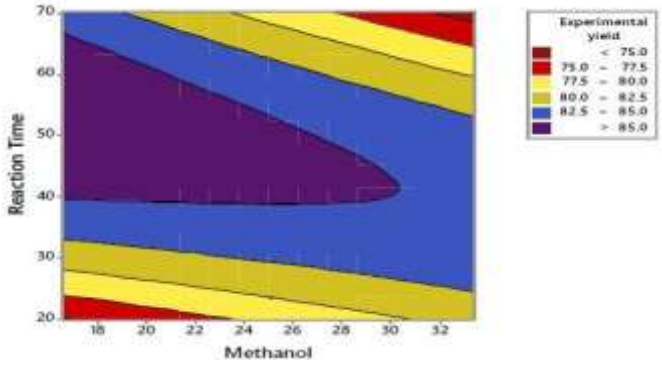

Fig-4: Effect of methanol and reaction time on experimental yield in 2D contour plot

4.3 Effect of NaOH and Reaction Time on Experimental Yield

Fig. 5 show the 3D response surface plot and 2D contour plot between reaction time and NaOH concentration for different fixed parameter. From the Fig. 5, it can be seen that the methyl ester yield increases with the increase in reaction time and reaches maximum yield of 94.11% at methanol quantity of 20 (%w/v of oil) and reaction time of 60minutes. Then the yield is decreases with the increase in NaOH concentration and increase in reaction time. This is due to there is less significant interaction between reaction time and NaOH concentration and negative concentration of quadratic coefficient mostly caused by soap formation side reaction.

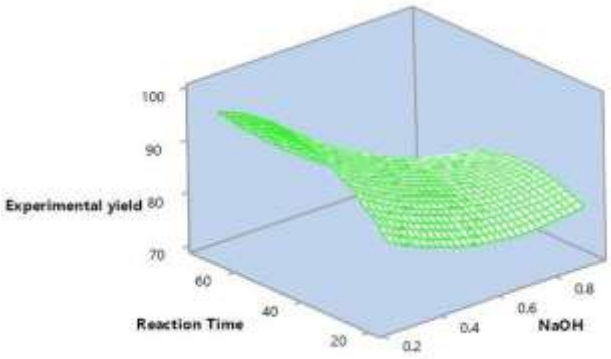

Fig-5: Response surface plot: Effect of reaction time and NaOH on experimental yield

The fig. 6 shows the 3D response surface plot and 2D contour plot between reaction time and NaOH concentration for different fixed parameter. From the Fig. 6, it can be seen that the methyl ester yield increases with the increase in reaction time and reaches maximum yield

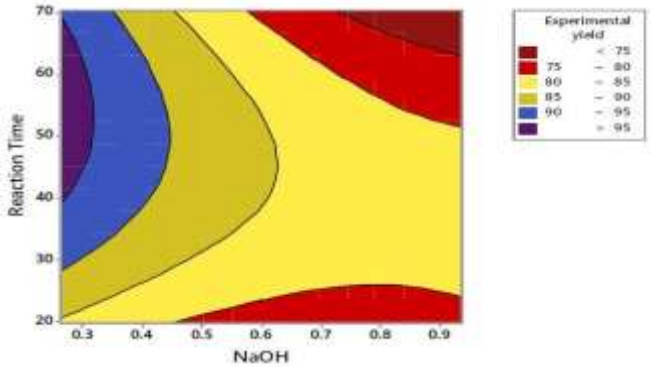

Fig-6: Effect of reaction time and NaOH on experimental yield in 2D contour plot

4.4 Analysis of the Fuel Properties of Waste Fish oil Biodiesel

There are a number of fuel properties that are essential for the proper operation of diesel engine. Therefore, before the engine testing was carried out, basic physical, chemical and fuel related properties of test fuels were evaluated according to the standard procedures as shown in Table 3.

Table 3

Properties	B20	B40	B60	B80	B100	Diesel
Flash point (°C)	69.6	85.2	101	116.4	132	54
Fire point (°C)	75.2	91.4	108	123.8	140	59
Cloud point (°C)	-5.6	-1.4	1.4	4.2	7	-7
Pour point (°C)	-6	-4	-2	0	2	-8
Kinematic viscosity (cSt)	4.38	4.66	4.95	5.23	5.52	4.1
Calorific values (MJ/kg)	42.69	40.59	38.5	36.39	34.29	44.8
Density (kg/m3@ temp 28 °C)	808	816	824	832	840	800
Specific gravity	0.808	0.816	0.82	0.832	0.84	0.8

The specific gravity of diesel, waste fish oil methyl ester (B100), B20, B40, B60, and B80 are as shown in the table 3. The observed values indicate that the specific gravity of diesel waste fish oil biodiesel blends are closer to that of diesel fuel. The specific gravity increased with increased volume of ester within the blend. It can be suggested that all waste fish oil methyl ester blends mixed in 80:20 to 20:80 proportion with diesel could be selected as alternative to diesel fuel. The waste fish oil biodiesel blends have their viscosity close to that of diesel oil. The Indian standard recommends the range of the viscosity of diesel from 2 cSt to 7.5 cSt for use in high speed diesel engines. The comparisons of viscosity of biodiesel and its blends suggests that it can be mixed with conventional diesel oil in any ratio to meet the requirement of IS standards. It as shown in the table 3 that the observed gross calorific value of WFO methyl ester and diesel fuel was 34.29 MJ/kg and 44.8 MJ/kg, respectively. The gross heat of ethyl ester blends have 42.69 MJ/kg, 40.59 MJ/kg, 38.49 MJ/kg, 36.39 MJ/kg, respectively for the blends prepared in 80:20, 60:40, 40:60 and 20:80 proportions. It is evident from the table 3 that the gross heat of combustion of WFO methyl ester is less than that of diesel oil. The decrease in gross heat of combustion could be attributed to the presence of few hydrogen atoms in the molecule. Esterification of WFO methyl ester increased the gross heat of combustion WFOME but lower than that of diesel oil. The gross heat combustion of methyl ester blends found closer to that of diesel fuel. The flash point of biodiesel is higher than that of diesel oil. Esterification of oil found to reduce the flash point of oil. For methyl ester blends, the flash point increased with the increased volume of ester within the blends. B100 has highest flash point of 130°C and B20 has lower flash point of 69.6°C.

5. CONCLUSION

The selection of transesterification process or reaction depends on the free fatty acid level of the selected source (waste fish oil). When free fatty acid (FFA) level is less than 1%, single stage (alkaline catalyzed) transesterification process is effective. If free fatty acid (FFA) level is greater than 1% the two stages (acid – alkaline catalyzed) transesterification process is effective. In this work, two stages (acid – alkaline catalyzed) transesterification process is used because selected source has FFA level 15%. The CCD is the most effective method of optimization of transesterification process parameters of biodiesel production from low free fatty acid (FFA) source, the results obtained from XLSTAT closely related to ANOVA. ANOVA results shows that the reaction time is the most influencing factor affecting WFOME, whereas NaOH concentration to be the second option. CCD is the most effective method for optimization of transesterification process produced from waste fish oil. A second order model has developed to predict the methylester in terms of methanol quantity, NaOH concentration (CATALYST concentration) and reaction time. It is concluded from the present work that the fuel properties of waste fish oil biodiesel blends have deviated from conventional diesel oil. With increase in percentage of methyl ester at any instant the property values of B20 slightly deviate from conventional diesel oil, whereas other blends like B40, B60, B80 and B100 largely deviate from the conventional diesel oil. Hence, the use of methyl ester with diesel may restrict lower proportion of methyl ester.

REFERENCES

[1] Fukuda, Hideki, Akihiko Kondo, and Hideo Noda. "Biodiesel fuel production by transesterification of oils", Journal of bioscience and bioengineering, pp. 405 - 416, 200.

[2] Ma, Fangrui, and Milford A. Hanna. "Biodiesel production: a review." Bioresource technology, pp.1-15, 1999.

[3] Ma, Fangrui, and Milford A. Hanna. "Biodiesel production: a review." Bioresource technology, pp.1-15, 1999.

[4] Alencar, J. W., P. B. Alves, and A. A. Craveiro. "Pyrolysis of tropical vegetable oils." *Journal of Agricultural and Food Chemistry*, pp. 1268-1270, 1983.

[5] Ziejewski, Mariusz, et al. "Diesel engine evaluation of a nonionic sunflower oil-aqueous ethanol microemulsion." Journal of the American Oil Chemists' Society, pp.1620-1626, 1984.

[6] Clark, S. J., et al. "Methyl and ethyl soybean esters as renewable fuels for diesel engines." Journal of the American Oil Chemists' Society, pp. 1632-1638, 1984.

[7] Knothe, Gerhard. "Biodiesel and renewable diesel: a comparison." Progress in Energy and Combustion Science, pp. 364-373, 2010.

[8] De Almeida, Vanessa F., et al. "Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: Optimization of fuel properties." Fuel Processing Technology, ppt.152-160, 2015.

[9] P.M. Kris-Etherton, W.S. Harris, L.J. Appel, "Fish consumption, fish oil, omega-3 fatty acids, and cardiovascular disease", pp.2747–2757, 2002.

[10] T.H.Wu, P.J. Bechtel, "Salmon by-product storage and oil extraction", Food Chemistry , pp. 868–871, 2008.

[11] A.P. Bimbo, "Current and future sources of raw materials for the long - chain omega - 3 fatty acid market", Lipid Technology, pp. 176–179, 2007.

[12] C.Y. Lin, R.J. Li, "Fuel properties of biodiesel produced from the crude fish oil from the soapstock of marine fish", Fuel Processing Technology, pp.130–136, 2009.

[13] C.Y. Lin, R.J. Li, "Engine performance and emission characteristics of marine fish-oil biodiesel produced from the discarded parts of marine fish", Fuel Processing Technology, pp. 883–888, 2009.

[14] R. Behcet, "Performance and emission study of waste anchovy fish biodiesel in a diesel engine", Fuel Processing Technology, pp. 1187–1194, 2011.

[15] D.Madhu, B. Singh, Y.C. Sharma, "Studies on application of fish waste for synthesis of high quality biodiesel", RSC Advances, pp. 31462–31468, 2014.

[16] A.B. Fadhil, M.M. Dheyab, L.A. Saleh, "Conversion of fish oil into biodiesel fuels via acid-base catalyzed transesterification, Energy Sources ", Part A: Recovery, Utilization, and Environmental Effects , pp.1571–1577, 2014.

[17] P. Jayasinghe, K. Hawboldt, "A review of bio-oils from waste biomass: focus on fish processing waste", Renewable and Sustainable Energy Reviews, pp. 798–821, 2012.

[18] P.J. García-Moreno, M. Khanum, A. Guadix, E.M. Guadix, "Optimization of biodiesel production from waste fish oil", Renewable Energy, pp.618–624, 2014.

[19] G. Knothe, "Some aspects of biodiesel oxidative stability", Fuel Processing Technology, pp. 669–677, 2007.

[20] L. CherngYuan, L. Jung-Chi, "Oxidative stability of biodiesel produced from the crude fish oil from the waste parts of marine fish", Journal of Food, Agriculture & Environment , pp. 992–995, 2010.