

Production of Fatty Acid Methyl Ester from Acid Oil an Edible Oil Refinery By-Product by Two Step Esterification Followed by Trans-Esterification Process

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Abstract - Energy is essential to life. In the current world scenario demand for fuels goes on increasing with an increase in population and industrialization, whereas the fossil fuel reserves are going on decreasing day by day. Fossil Fuels increases carbon emission and GHG in an environment. Due to the awareness of adverse effects of conventional fuels to environment and frequent rise in crude oil price, the need of renewable and sustainable fuels goes on increasing from last few decades. The source of energy should be environment friendly and also adoptable for the existing system. Biodiesel is proved to be the best replacement for diesel because of its unique properties like significant reduction in greenhouse gas emissions, non-sulfur emissions, non-particulate matter pollutants, low toxicity and biodegradability and also showing good properties of fuel i.e. Cetane number and octane number. This paper reviews the pretreatment step, the physical and chemical properties of Acid oil, Esterification, Esterification-2, Trans-esterification and production of Biodiesel from Acid oil by various methods and catalysts reported so far. The factors affecting the process parameters reported are studied and the point of interest focuses on their Alcohol to oil ratio, Reaction temperature, Catalyst both qualitative and quantitative scope. The optimum condition is investigated.

Key Words: Biodiesel, GHG (Green House Gases) Esterification, Trans-esterification, FAME (Fatty Acid Methyl Ester), FFA (Free Fatty Acid), Acid Oil, Cetane Number, Octane Number.

1. INTRODUCTION

In the current world scenario demand for fuels goes on increasing with an increase in population and industrialization, whereas the fossil fuel reserves are going on decreasing day by day. Nowadays due to a decrease in fossil fuel reservoir, an increase in environmental consequences, and an increase in petroleum price scientist are in search of renewable cost-effective energy fuel. Vegetable oil is one of the important sources of renewable energy substitute for diesel fuel. There are many alternatives as a renewable fuel like bio-methanol, ethanol, bio-butanol, dimethyl ether, vegetable oil, etc. (Bart et al., 2010) Vegetable oil can be used as a liquid fuel by modifying it by dilution with other oil, thermochemical conversion of oil, hydrogenation, and trans-esterification of vegetable oil. Trans-esterified vegetable oil also referred to biodiesel, and it is carbon-neutral renewable liquid fuel to petroleum fuel.

In the edible oil industry, the refined vegetable oil is produced by extraction of oil from oilseeds followed by the physical or chemical refining of oil. During this process, several by-products and wastes are generated. Degumming of oil is an important process for refining of vegetable oil to remove hydratable and non-hydratable gums. After solvent extraction, the hydratable gums are removed by simple hot water degumming process, during this process phospholipids and Free fatty acids (FFA) are separate out from oil these gums used for the lecithin production (Van Nieuwenhuyzen and Tomás, 2008). Remaining nonhydratable gums removed by chemical degumming or acid degumming process. During this process, phosphoric acid or citric acid are used for removal of non-hydratable gums. Usually, chemical degumming process is used after the water degumming process to remove remaining gums present in the oil. In this process, Soapstock produces by FFA neutralization & also due to some amount of saponification of oil results in an acceptable amount of oil losses for the further economically efficient refining process to produce the good final quality refined oil. Mostly, the gums from the chemical degumming are not utilized for lecithin production, for economic and technical reasons (Dijkstra and Van Opstal, 1989). Soapstock generated during the refining process is based on the presence of free fatty acids and oil losses during the alkali refining process.

Soapstock separated by centrifugal separator after the chemical degumming process are used for the production of acid oil. This soapstock mixed with wash water from the refinery use for soapstock splitting unit. This process also called as the acidulation reaction in which sulphuric acid added in the soapstock mixture at a temperature approximately 900- 950 C. After a complete splitting process, the product is separated by overnight setting in a tank or by a centrifugal separator (Harwood et al., 2007). The Acid oil use for this research work collected after complete separation of acid oil from the aqueous layer.

Acid oil obtained from Acidulation process having high FFA (50- 80 %) (Harwood et al., 2007). The cost of acid oil produced in the refining process is three times low as compared to the refined vegetable oil. Due to low-cost feedstock, this oil can be used for the production of fatty acid methyl ester (FAME). FAME is the esters (methyl) of fatty acid & its properties are similar to the diesel fuel, and a mixture of different fatty acid methyl esters are referred to biodiesel. Biodiesel production from acid oil by

base-catalysed trans-esterification is not possible due to the presence of high FFA. High FFA produces a large amount of soap; therefore, trans-esterification cannot be processed. To obtain more conversion from FFA to FAME two-step biodiesel production process were recommended by researchers (Mazumdar et al., 2013). In first step esterification of FFA were carried out followed by second step trans-esterification. In our research work, also carried out a two-step biodiesel production process but not obtained expected results from the two-step reaction process.

2.1 Materials:

Acid oil for this research work was collected from PFOL industry, Pune from there sunflower oil refinery plant. The sample was collected after overnight settling of acid oil in their plant. It contains a minimum amount of moisture due to overnight settling. Bleaching earth (Gallion V2) for the pretreatment process also collected from the same industry. Sodium methoxide (NaOCH₃) use for this work collected from the biodiesel industry. All other chemicals used for the research work and analysis are analytical grade. Sulfuric acid (98%), Sodium hydroxide pellet (NaOH), Potassium hydroxide pellet (KOH), Glycerol anhydrous (99.5% pure), Methanol (99% pure), Diethyl ether (99% pure), Toluene (99% pure), petroleum benzene (400- 600 C) (99% pure), are purchased from Merck. Zinc chloride (ZnCl₂) Hi-LR grade, and Stannous chloride anhydrous (SnCl₂) from Himedia Laboratories.

2.2 Characterization:

The Acid oil analysis done by AOCS methods involves Acid value, Iodine value, saponification value, unsaponifiable matters, and 1 H NMR procedures.

FAME was characterized by NMR, GC and FTIR. All other analytical part were done in lab such as acid value. Iodine value, saponification value as per AOCS method and results were compare with ASTM standard. The usual values for Properties like density, kinematic viscosity, saponification value, acid value and Iodine value are shown in the table 1.

Property	Unit	Acid oil	FAME	Specification
Acid Value	Mg KOH/g	98.1	0.3	AOCS
Saponification value	Mg KOH/g	197	189	AOCS
Iodine Value	g Iodine/g	98.9	97	AOCS
Specific Gravity at 25 C	CP	0.912	0.87	AOCS
Moisture Content	%	2.3	trace	AOCS
Unsaponifiable Matter	%	6 %	-	AOCS

Table 1. Analytical values for Acid oil and FAME by AOCS

Experimental procedure Biodiesel production from acid oil was carried out in three-step, due to the presence of high FFA and due to the presence of some impurities, two-step biodiesel production process is not suitable for conversion of FFA to methyl ester completely. For this purpose, experiments were carried out in the three-step process involves esterification, Esterification-2 & Trans esterification, before conducting reaction the oil received from industry were pre-treated.

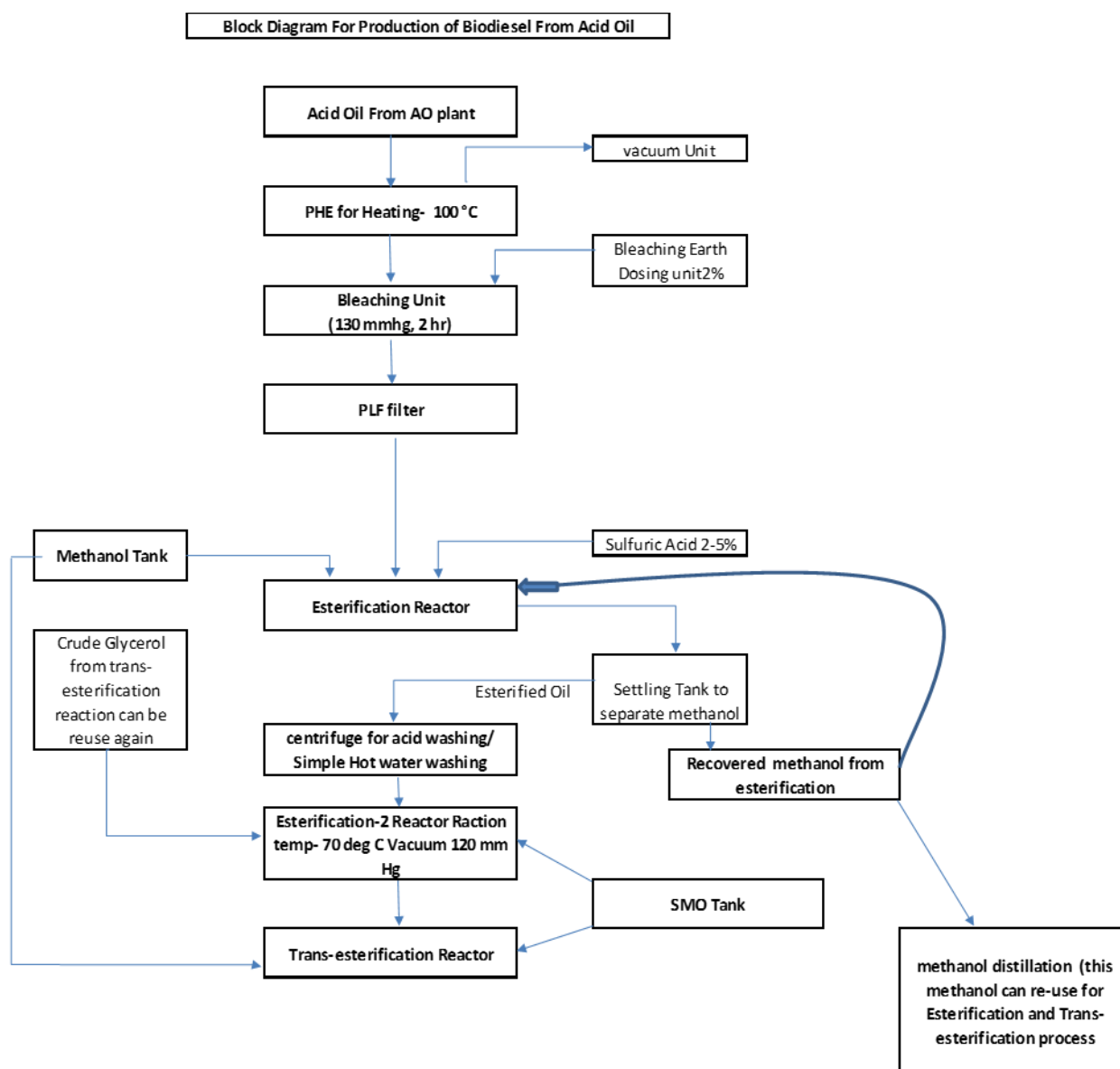


Figure 1. Flow Diagram for production of Biodiesel

2.2.1 Pretreatment:

Acid oil used for reaction initially pretreated with Bleaching earth, Bleaching of oil were carried out under 100 mmHg vacuum at 90 -1000C temperature and 2% bleaching earth (Galleon Earth V2).

During a bleaching process, oil first heated at 1000 C for 1 hrs. Under 120 mmHg vacuum. After complete removal of water from oil 2 wt. % Galleon V2 bleaching earth were added in oil for removal of impurities and improving oil color. After pretreatment, observe the change in FFA percentage of oil from 49% to 73 %. This change in FFA percentage due to the separation of impurities from oil by the bleaching process. Pretreatment of oil helps to obtained more conversion and maximum FAME yield.

2.2.2 Acid-catalyzed esterification reaction

The experiments of acid-catalyzed esterification were carried out in 250 ml three-neck round bottom flask with temperature control (silicon oil) bath & reflux condenser for methanol reflux several experiments were carried out for optimizing the esterification process, the parameter changes during the esterification reaction involves: molar ratio, temperature, catalyst quantity. During this reaction, oil to molar ratio varies from 3 to 15, temperature form 60 -70, catalyst quantity from 2 % to 8 %. And the time from 2 hrs. to 30 hrs. Percentage conversion of FFA to methyl ester can be represented as follows

$$\% \text{ Conversion} = \left\{ 1 - \left(\frac{\% \text{ FFA remains after esterification reaction}}{\text{Initial FFA of Oil}} \right) \right\} \times 100$$

After completion of esterification reaction. FFA remains in oil were 6-7%. The percentage of FFA is high due to which trans-esterification reaction cannot be continued further. To reduce the FFA percentage for trans-esterification reaction process modified and additional step of Esterification-2 reaction continued after esterification of oil. For this purpose, wash the acid and methanol present in it followed by centrifugation and vacuum drying to remove water content in it.

2.2.3 Base catalyzed Esterification-2 reaction

After the esterification reaction, Esterification-2 reaction was carried out to reduce FFA from 7% to 0.5 % so that Trans-esterification of remaining oil present in it can carry out by base-catalyzed Trans-esterification reaction. For this reaction, five catalysts were tested to reduce FFA, e.g., zinc chloride, stannum chloride, NaOH, KOH, and sodium methoxide with different wt. % and different oil to glycerol ratio. From these catalysts, NaOCH₃ was the optimized catalyst for a reaction as this catalyst can further use for a trans-esterification reaction. And this catalyst gives similar results as NaOH. Due to the presence of methanol in NaOCH₃, it avoids soap formation and easy glycerol separation for further reaction.

2.2.4 Trans-esterification of oil

After Esterification-2 reaction once FFA reduces below 0.5%, trans-esterification reaction was continued with NaOCH₃ catalyst already present in it, during Esterification-2 reaction. A mole ratio of oil to methanol for this reaction use as 1:6. Optimization study on Trans-esterification carried out by many researchers.

2.2.5 Glycerol purification

Glycerol purification is a step after separation of glycerol from both esterification-2 and Trans-esterification reaction. Separated glycerol purification by a conventional distillation process cost is too high. To avoid a high cost in purification sequential extraction process for purification was used (Contreras-Andrade et al., 2015). In this process, raw glycerine was purified by a discontinuous sequential liquid-liquid extraction process, in which glycerol first purified by petroleum benzene followed by toluene extraction in 250 ml round bottom flask with continuous stirring. After the extraction process, the decolorization of glycerol was carried out in flask by 5% activated carbon at 900 C for 4-10 minutes. Treated glycerol was separated by filtration under vacuum. Purified glycerol have several applications in medicine, cosmetics, foods, etc.

3. RESULT AND DISCUSSION.

3.0 Pretreatment of sunflower acid oil for biodiesel production:

Pretreatment is an initial process for the treatment of any material for production. In our process, bleaching of oil with bleaching earth (clay) was a pretreatment process for a reaction. During the bleaching process, most of the impurities removed by activated clay. And it is a well-established process in edible oil refining which helps in improving color, removing gums and soap contents and also remove traces of metals present in it. During the pretreatment process, FFA and unsaponifiable matter present in the oil was the focused parameters.

Optimized bleaching process parameter studied by many authors (David et al., 2017). Parameters used for our bleaching pretreatment process, e.g., 900 C temperature 130 mm Hg vacuum and optimized time 2 hrs. In this pretreatment, optimization in the percentage of bleaching earth for the process presented in fig.2

With an increase in the concentration of Bleaching earth USM percentage goes on decreasing and % FFA present in oil increases. Bleaching earth weight percentage in Oil can further increase, but above 5 % bleaching earth it will not be viable commercially. And expected results for the pretreatment process obtained by using 2 wt % bleaching earth. Hence, there is no need to increases wt. % of bleaching earth unnecessarily, which causes increases in oil losses in bleaching earth.

3.1 Acid-catalyzed esterification of sunflower acid oil

Acid-catalyzed esterification is a well-established technique (Mazumdar et al., 2013) for the conversion of high FFA oil to biodiesel. In some papers, this process also refers to the pretreatment process (Chai et al., 2014). In our experiments, high FFA (74 % FFA) oil esterification was carried out to and FFA reduces to 6-7 %. Even after conducting a continuous run of Esterification FFA were not reduce below 7 %. In the initial 2 hrs. FFA gradually reduce, and after 2 hours, reaction equilibrium shifted, and reaction rate reduces with increase in time.

Once equilibrium achieves, FFA would not reduce below 7 %. Even after excess addition of methanol reaction were unable to process further. Hence based on 7 % FFA, optimization of the esterification reaction were studied at atmospheric pressure by various parameters such as temperature, catalyst concentration, reaction time, the molar ratio of oil to methanol.

3.1.1 Effect of temperature on conversion

The esterification reactions were carried out at 60 °C and 70 °C to study the effect of temperature on the conversion of FFA. In the esterification reaction, the reaction rate is not that much affected by varying temperature range. As the molar ratio of methanol to oil was high, while increasing the temperature, methanol vapors cannot be condensed. This may lead to a decrease in the concentration of methanol. To maintain methanol concentration same throughout the reaction and maintain irreversibility in the reaction mixture reflux condenser should be applied over the reactor. Therefore, an increase in the temperature beyond 70 °C leads to loss of methanol or the increase in the cost condensation of methanol vapors. Due to this reason experiment was carried out at 60 deg C and 70 deg C. results in FFA Conversion presented in Fig. 3 and the conversion result is shown by NMR analysis Shown in figure 7

For our experiments, the optimized temperature is 70 °C, and the maximum conversion of about 91 % achieved. The reaction temperature can further optimized for Pilot plant / industrial scale based on the heating fluid used for the reactor and process economy conditions.

3.1.2 Effect of reaction time

The esterification reaction is slow, and it requires more time for complete conversion. While in our experimental run reaction achieve equilibrium at 7% FFA after 6 hours of reaction. Due to this unnecessary increase in reaction have no scope for a shift in reaction equilibrium. Fig 3 and 4 with respect to temperature and molar ratio shows a reaction time optimization study.

3.1.3 Effect of catalyst concentration

For Esterification reaction optimized catalyst concentration consider in the range of 2 – 5 %. (Marchetti and Errazu, 2008) In this experimental work also studied the esterification reaction catalyst concentration at our optimized temperature of 70 degree C. Effect of catalyst concentration represented in Fig 3. Optimized catalyst concentration for our reaction is 3 wt. % Sulfuric acid concerning the weight of oil.

3.1.4 Effect of Methanol to oil molar ratio

The esterification reaction is highly reversible, to proceed reaction towards right-hand side excess amount of methanol required. We optimize the amount of methanol on a molar basis, oil to methanol molar ratio required to proceed reaction further is 1:12. Experimental results for the molar ratio optimization shown in fig 4.

Methanol molar ratio for the two different temperature also shows a similar result. Even after an increase in molar ratio beyond 12 shows the same conversion. At lower molar ratio, the conversion occurs in the initial 2 hours is similar to that of higher molar ratio. But after an increase in time conversion for the higher molar ratio is high as that of lower molar ratio.

3.2 Base catalyzed Esterification-2 of Sunflower acid oil

Esterification-2 reaction is a well-known reaction for the conversion of FFA to glycerides (Kombe et al., 2013a), the reaction were carried out with four parameters to optimize process conditions and achieved the low FFA after the reaction. To optimization of a re-esterification reaction, different parameters were studied involves temperature, reaction time, type of catalyst, oil to glycerol molar ratio.

3.2.1 Effect of type of catalyst

Five different catalysts studied for the re-esterification reaction. Out of that, only two catalysts were shows expected results for the reaction. With Catalyst Zinc chloride (Jansri, 2015) and stannum chloride (Jansri, 2015), obtained conversion for our reaction was very less. Catalyst Zinc chloride and stannum chloride are a heterogeneous catalyst. While catalyst Sodium hydroxide (Kombe, 2015), Sodium methoxide & potassium hydroxide are the homogeneous catalysts for the reaction, out of this catalyst, KOH & NaOCH₃ shows the maximum conversion at low temperature as compared to the heterogeneous catalyst, while NaOH catalyst is not an effective catalyst for our Esterification-2 reaction. By using NaOH catalyst instead of re-esterification soap formation were observed in the reaction, which affects the conversion and makes further separation of glycerol from oil difficult. Effect of catalyst on re-esterification reaction shows in fig 5a.

From the reaction result and literature study, can conclude that NaOCH₃ catalyst is a more effective catalyst at low temperature (700 – 900 C). It may be due to OCH₃ ions present in it, which affect less water formation during the reaction. Our further reaction optimization based on NaOCH₃ catalyst.

3.2.2 Effect of reaction time

Reaction time for re-esterification reaction was studied using NaOCH₃ catalyst. As per reference data for NaOH catalyst (Kombe, 2015), maximum conversion obtained in the initial 90 minutes of reaction time. While in our esterified acid oil study, expected conversion after four hours of reaction was observed. In the initial period, the reaction rate is high. After 2 hours,

reaction moves towards equilibrium, and the rate of reaction decreases. Maximum conversion achieved at 4 hrs. of reaction time there after very few drop in FFA observed as the reaction processed further.

3.2.3 Effect of catalyst concentration

Five types of catalysts studied for the re-esterification reaction, as mention in para 3.3.1 effective & optimized catalyst at low temperature was NaOCH₃. Amount of catalyst required for the reaction studied at four different concentration, e.g., 1, 1.25, 1.5 & 1.75 wt. % to oil as shown in Fig 5d.

Out of the above mention concentration, 1.5 wt. % catalyst concentration gives the expected results for the optimized condition of reaction parameters.

3.2.4 Effect of Glycerol: Oil molar ratio

Same as esterification and Transesterification reaction re-esterification reaction is also a reversible reaction. To maintain irreversibility towards RHS excess amount of glycerol were added in the reaction. Oil to glycerol molar ratio varies from 1:1 to 1:9. Oil to glycerol molar ratio beyond 1: 5 ratio, gives similar results. Such an unnecessary increase in a molar ratio will increase in production cost while scaling up a reaction process. The Effect of glycerol to oil molar ratio shows in fig 5c.

3.2.5 Effect of Temperature

For the reesterification reaction using acid catalyst required high temperature and for base catalyst reaction achieve conversion at low temperature (Kombe et al., 2013b). In our experimental run, five different catalysts were tested, as mention in para 3.3.1. Out of this, NaOCH₃ gives the best result at low temperature. The Temperature range from 500 C - 1300 C were tested. In this temperature range, best results were obtained at 750 C & 900 C. The optimized temperature range for re-esterification can consider as 750 C. while further optimize reaction temperature for industrial-scale based on heating medium and process economy parameters.

3.3 Transesterification

The trans-esterification process is a well-established process for the production of biodiesel. Many authors studied the operating process temperature, molar ratio, and catalyst amount. Our research group also published the review paper on biodiesel production from renewable feedstock. Transesterification process parameter use for our experimental run used from the previous work done by many research group (OA et al., 2019).

Though this process conversion to biodiesel follows the purification esterification, Esterification-2, and Trans esterification in each stage the conversion analyzed by the NMR data shown in figure 9

4. CONCLUSIONS

The conversion of acid oil in to the biodiesel i.e. FAME has been observed by three steps esterification, esterification2 and trans-esterification. A pretreatment has given to crude acid oil remove unwanted impurities by bleaching process at 900 C temperature 130 mm Hg vacuum and optimized time 2 hrs. With 2 weight percent of Bleaching earth. Further experiments done by using different Temperature, reaction time, catalyst concentration and methanol: oil molar ratio for esterification reaction and the optimum conversion result get at 60 degree temp, 6 hrs. of reaction time, 3 percent of catalyst by using sulfuric acid as a catalyst and 1:12 molar concentration of methanol: oil. Then esterification 2 to optimization of a re-esterification reaction, different parameters were studied involves temperature, reaction time, type of catalyst, oil to glycerol molar ratio. The optimum reactions by using 1.5 weight percent sodium methoxide catalyst, 6 hrs. of reaction time by keeping 1:5 Glycerol to oil molar ratio at 90degree Celsius and 130 mmhg of vacuum pressure. Upto this steps remaining FFA in esterification step get converted into glycerides and that triglyceride converted to FAME by Transesterification reaction.

5. REFERENCES

- [1] Bart, J.C.J., Palmeri, N., Cavallaro, S., 2010. Biodiesel science and technology, Biodiesel science and technology. Woodhead Publishing Limited. <https://doi.org/10.1533/9781845697761>
- [2] Chai, M., Tu, Q., Lu, M., Yang, Y.J., 2014. Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry. Fuel Process. Technol. 125, 106–113. <https://doi.org/10.1016/j.fuproc.2014.03.025>
- [3] Contreras-Andrade, I., Avella-Moreno, E., Sierra-Cantor, J.F., Guerrero-Fajardo, C.A., Sodré, J.R., 2015. Purification of glycerol from biodiesel production by sequential extraction monitored by 1H NMR. Fuel Process. Technol. 132, 99–104. <https://doi.org/10.1016/j.fuproc.2014.12.016>
- [4] David, D.B., Berbesi, R., Hodgson, A.S., 2017. Optimization of Bleaching Process. [WWW Document]. Am. Oil Chem. Soc. URL <http://lipidlibrary.aocs.org/edible-oil-processing/optimization-of-bleaching-process> (accessed 7.25.19).
- [5] Dijkstra, A.J., Van Opstal, M., 1989. The total degumming process. J. Am. Oil Chem. Soc. 66, 1002–1009. <https://doi.org/10.1007/BF02682627>

[6] Harwood, John, Gunstone, F., Dijkstra, A., Harwood, J, Scrimgeour, C., 2007. Fatty Acid and Lipid Structure, The Lipid Handbook with CD-ROM, Third Edition. <https://doi.org/10.1201/9781420009675.ch1>

[7] Jansri, S., 2015. Preparation of Vegetable Oil as Biodiesel Feedstock Via Re-Esterification: A Suitable Catalyst. *Energy Procedia* 79, 143–148. <https://doi.org/10.1016/j.egypro.2015.11.451>

[8] Kombe, G.G., 2015. Re-esterification of high free fatty acid oils for biodiesel production. *Biofuels* 6, 31–36. <https://doi.org/10.1080/17597269.2015.1039453>

[9] Kombe, G.G., Temu, A.K., Rajabu, H.M., Mrema, G.D., Kansedo, J., Lee, K.T., 2013a. Pre-Treatment of High Free Fatty Acids Oils by Chemical Re-Esterification for Biodiesel Production—A Review. *Adv. Chem. Eng. Sci.* 03, 242–247. <https://doi.org/10.4236/aces.2013.34031>

[10] Kombe, G.G., Temu, A.K., Rajabu, H.M., Mrema, G.D., Lee, K.T., 2013b. Low Temperature Glycerolysis as a High FFA Pre-Treatment Method for Biodiesel Production. *Adv. Chem. Eng. Sci.* 03, 248–254. <https://doi.org/10.4236/aces.2013.34032>

[11] Marchetti, J.M., Errazu, A.F., 2008. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. *Biomass and Bioenergy* 32, 892–895. <https://doi.org/10.1016/j.biombioe.2008.01.001>

[12] Van Nieuwenhuyzen, W., Tomás, M.C., 2008. Update on vegetable lecithin and phospholipid technologies. *Eur. J. Lipid Sci. Technol.* <https://doi.org/10.1002/ejlt.200800041>

[13] Aworanti OA, Ajani AO, Agarry SE (2019) Process Parameter Estimation of Biodiesel Production from Waste Frying Oil (Vegetable and Palm oil) using Homogeneous Catalyst. *J Food Process Technol* 10:811. doi: 10.35248/2157-7110.19.10.811.

[14] D. Kornack and P. Rakic, “Cell Proliferation without Neurogenesis in Adult Primate Neocortex,” *Science*, vol. 294, Dec. 2001, pp. 2127-2130, doi:10.1126/science.1065467.

[15] M. Young, *The Technical Writer’s Handbook*. Mill Valley, CA: University Science, 1989.

[16] R. Nicole, “Title of paper with only first word capitalized,” *J. Name Stand. Abbrev.* In press.

[17] K. Elissa, “Title of paper if known,” unpublished.

6. Figure ad Graphs

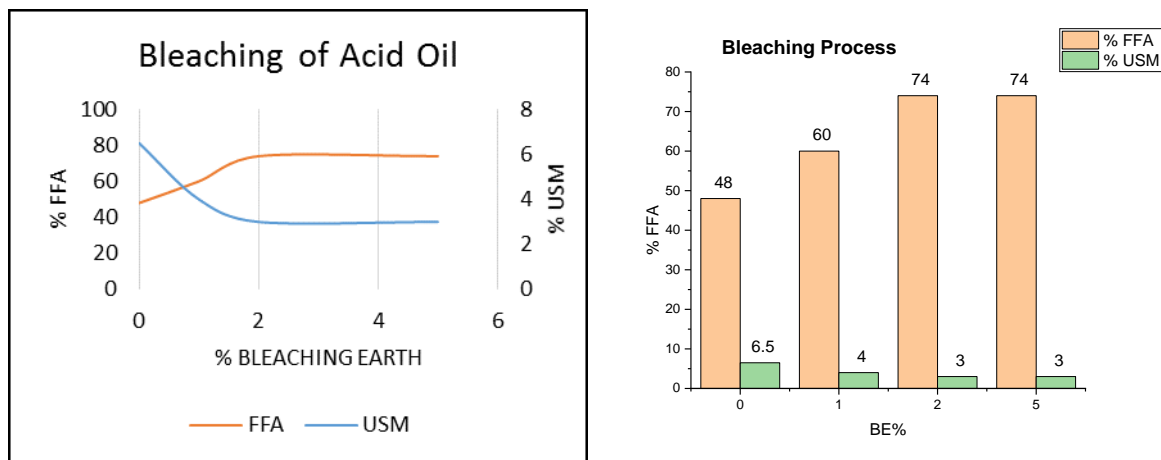


Figure 2: Effect of bleaching on FFA in Acid oil

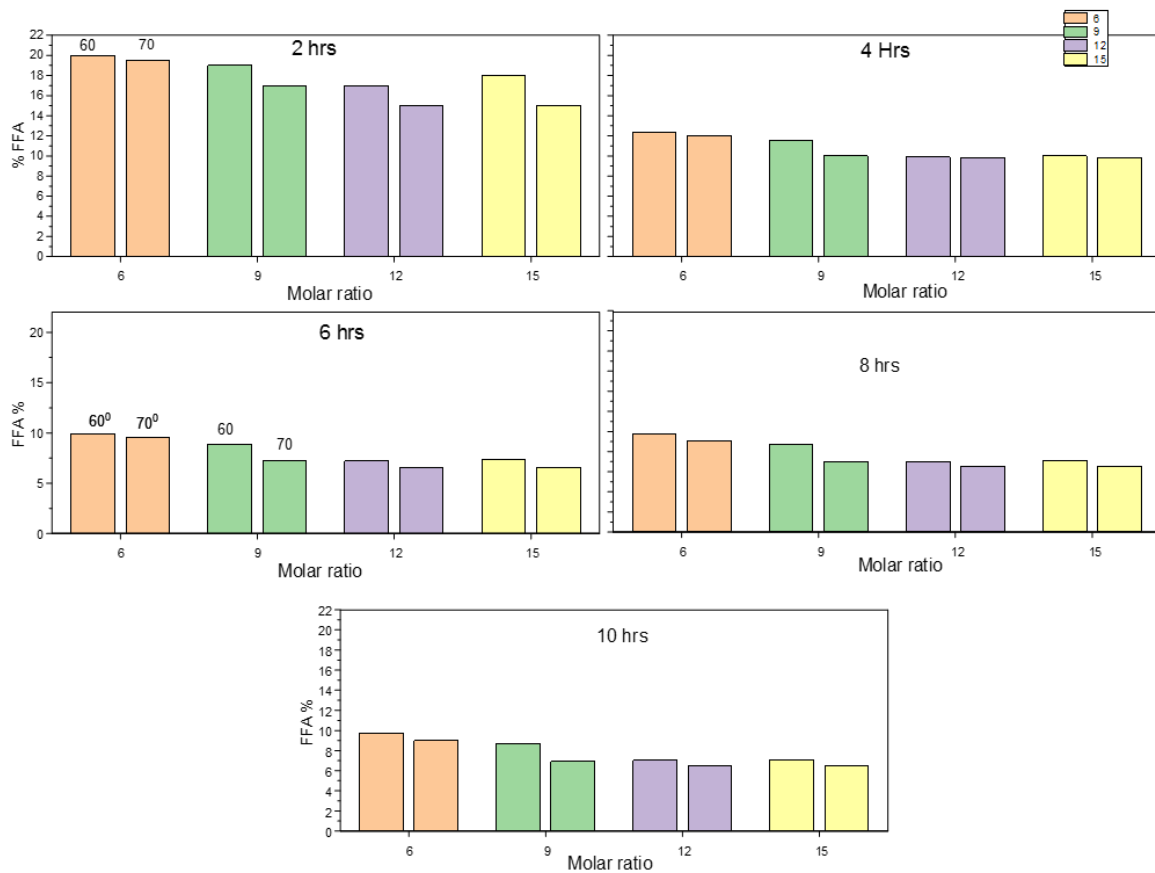


Figure 3- Effect of temperature on conversion in esterification reaction

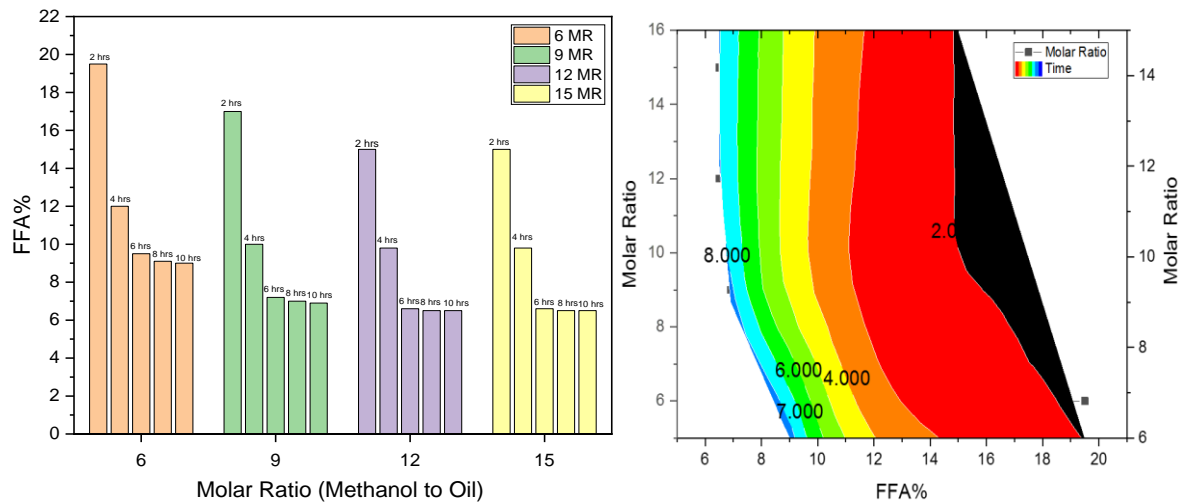


Figure 4- Effect of reaction time on Conversion in esterification reaction

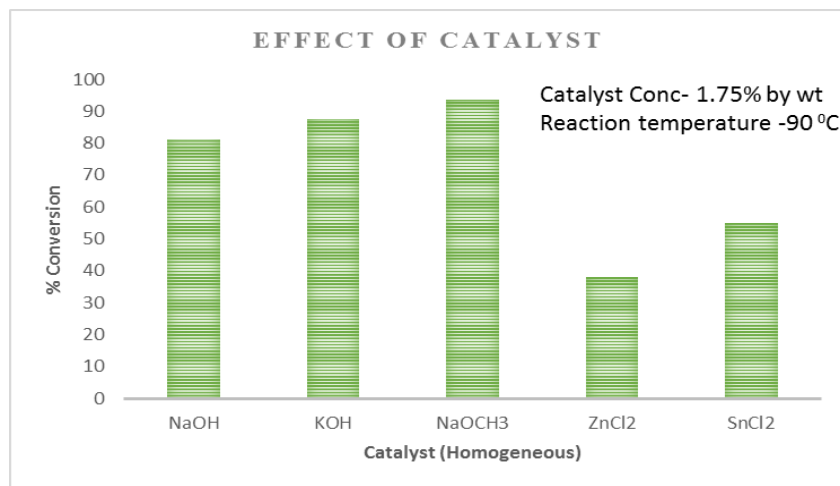


Figure 5 a- Effect of Different Catalyst in Esterification-2 reaction

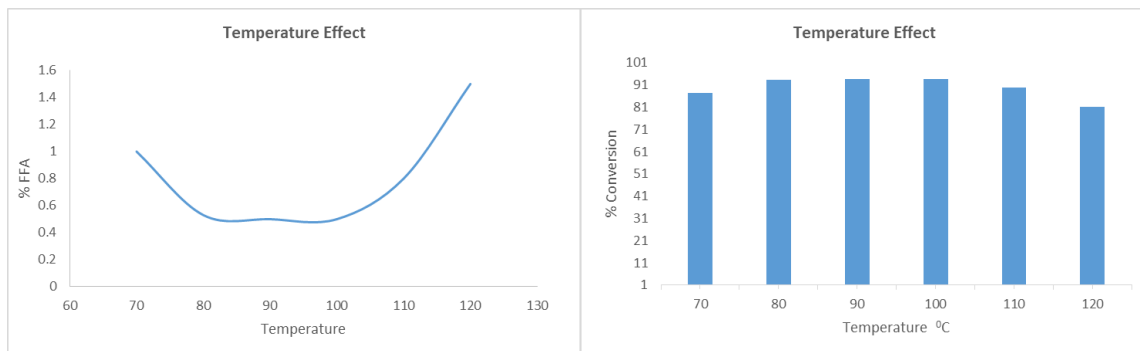


Figure 5 b- Effect of Temperature in Esterification-2 reaction

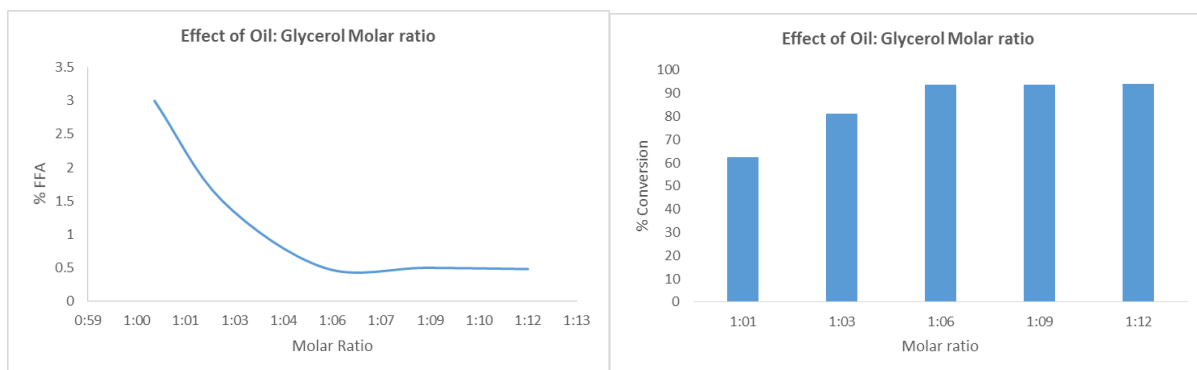


Figure 5c-Effect of Different Oil: Glycerol Molar Ratio in Esterification-2

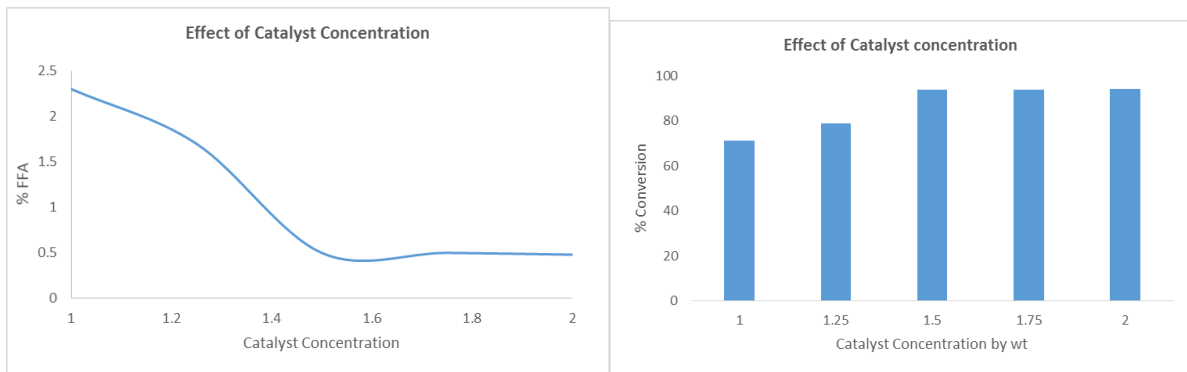


Figure 5d-Effect Of catalyst Concentration in Esterification-2

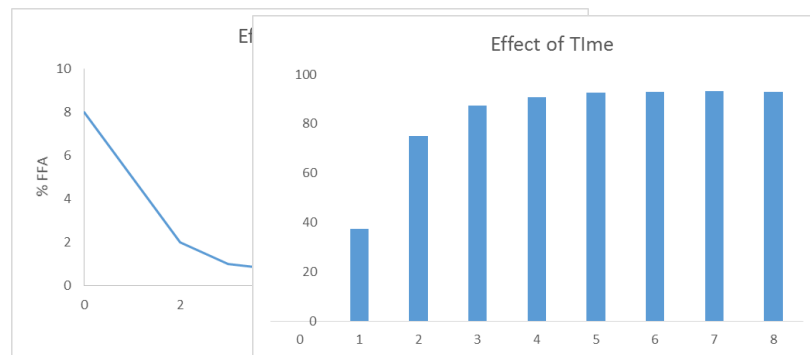


Figure 5e-Effect of Time in Esterification-2 reaction

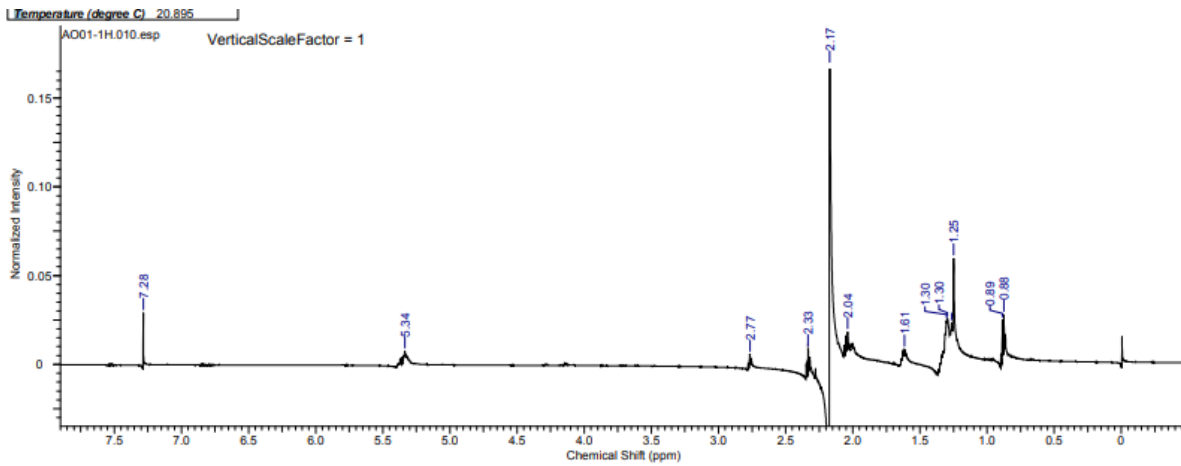


Figure 6-NMR plot for Acid Oil

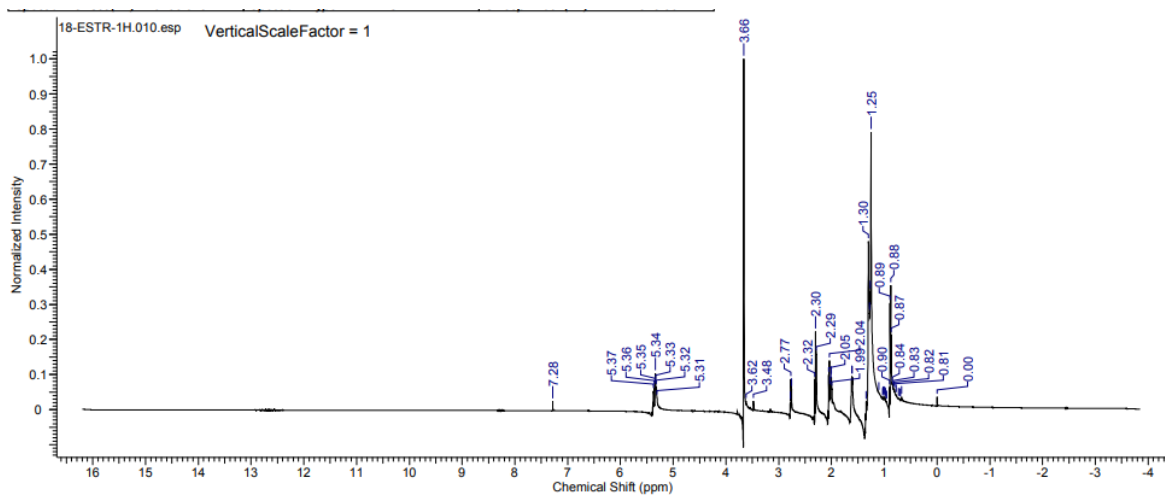


Figure 7- NMR plot after Esterification Reaction

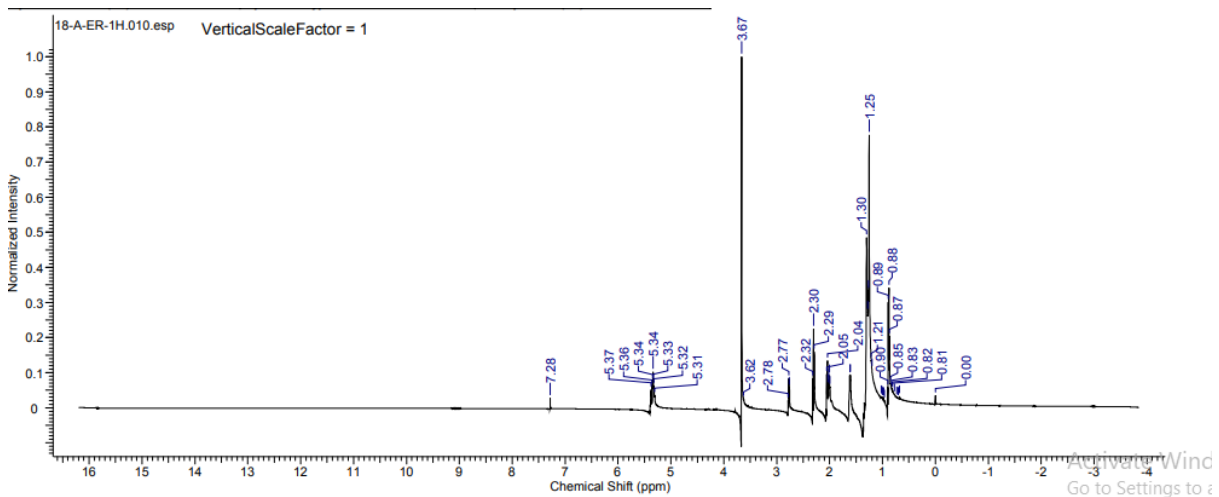


Figure 8-NMR after esterification-2 Reaction

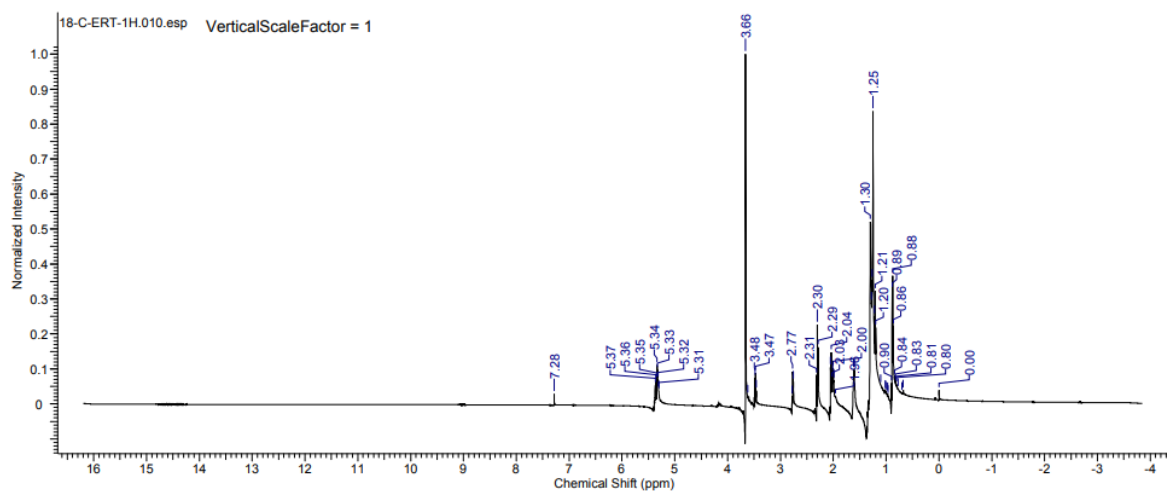


Figure 9- NMR after Transesterification reaction