

Bio Diesel Production from Vegetable Oil Refinery Industrial Waste by Transesterification Process

V.Sukumar, V.Manieniyam, P.Deivajothi and R.Senthilkumar

Abstract: *The present investigation aims to solve the twin problem of environmental pollution due to vegetable oil refinery waste and the need for an alternate fuel source. The main aim of this work is to find a solution to the mounting problem of vegetable oil refinery industry waste disposal, for which the vegetable oil refinery waste is converted in to biodiesel in usable fuel. In transesterification technique, breaking the molecule structure are accomplished with help alcohol and catalyst. In this investigation streamlined the catalyst, alcohol and response time for biodiesel production by transesterification process. The biodiesel is derived from vegetable oil refinery waste (Sunflower acid oil). Amid the transesterification method, menthol and ethanol were utilized with Sodium hydroxide (NaOH), Potassium hydroxide (KOH), and Sodium peroxide (Na₂O₂) as a catalyst. The results demonstrate the higher yield acquired utilizing ethanol with KOH impetus in all oil. The ethanol created higher yield of oil is acquired in 620 ml with ideal catalyst is 15g of KOH and 2ml of Sulphuric acid (H₂SO₄). The least response time got in response Na₂O₂.*

Index Terms: Biodiesel; Catalyst; Refinery waste; Transesterification

I. INTRODUCTION

Overall biodiesel generation is for the most part from eatable oils, for example, soyabean, sunflower and canola oils. Since, India isn't independent in eatable oil creation, consequently, tapping of non-consumable oil is up and coming for biodiesel generation. With plenitude of woods and plant based non-eatable oil being accessible in our nation, for example, Pongamia pinnata (karanja), Jatropha curcas (jatropha), Madhuca indica (mahua), Shorea robusta (Sal), Azadirachta indica A Juss (neem) and Hevea braziliensis (elastic), just couple of examinations (Giwa et al 2016) has been made to utilize esters of these non-eatable oils as substitute for diesel. Be that as it may, when contrasted with other non-palatable oils, very little work has been accounted for on biodiesel creation from mahua oil, which has an expected yearly generation capability of 181 thousand tons in India.

The generation and use of biodiesel is encouraged by two viewpoints first the farming arrangement of sponsoring the development of non-sustenance crops. Second, biodiesel is excluded from the oil impose (Mata et al 2010). Biodiesel has turned out to be appealing as of late due to its ecological advantages. The cost of biodiesel, be that as it may, is the principle obstruction to commercialization of the item. The monetary favorable circumstances of biodiesel are because of it's capacity to lessen ozone depleting substance emanations, decreases a nation's dependence on unrefined petroleum imports, and backings agribusiness by giving new work and market open doors for residential harvests (Rahman et al 2019). Biodiesel is a fuel for ordinary diesel motors, produced using plant or creature oils or fats that have been artificially changed into alkyl esters. It is a biodegradable transportation fuel, which emanates low sulfur and carbon monoxide and additionally particulate discharges to the environment (Honig et al 2017 and Bento et al 2019). Likewise, it is an inexhaustible, locally created fluid fuel that can diminish India's reliance on oil imports. The biodiesel was utilized as a part of pressure start motor, the outcomes revealed, that the emanation HC, CO and PM lessened. Be that as it may, NO_x outflow was higher because of higher oxygen displays in biodiesel likewise total burring contrasted with diesel (Chen, et al 2018). Oil from edit seeds are the principle hotspots for the ordinary vitality pick up and it is imperative asset for developing fuel. Biodiesel has been most prevalent since its condition repayment and the way that it is man made from ordinary sources. The cost of the vegetable oil and biomass is 60 to 70 % of the aggregate cost of the biodiesel fuel. This is a potential test with biodiesel fuel. The non-eatable oils are the attractive sources in India for the extraction of biodiesel. The some critical sorts of biodiesel creation techniques are transesterification process, warm splitting, supercritical process, ultrasonic reactor strategy, lipase-catalyzed technique, unstable unsaturated fats from anaerobic absorption of waste streams (Dhawane et al 2019). The Transesterification procedure is least expensive and high return of biodiesel generation contrasted with different techniques (Di Serio et al 2007 and Deivajothi et al 2016). In this paper talked about improvement of bio diesel creation and response time for transesterification process with three distinctive vegetable oil refinery squander, for example, ground nut, sunflower corrosive oil and unsaturated fat oil.

A catalyst is a compound that increases the rate of chemical reaction, but not consumed by the reactions, hence allows for the possibility that small amount of catalyst or its activity is lost in the reaction.

Manuscript published on 30 June 2019.

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The Catalysts are classified into two groups. One is the Homogenous catalysts and other for Heterogeneous catalysts. Heterogeneous catalyzed an emerging alternative technology is to use smart polymers (Laosuttiwong et al 2018). The transesterification reaction requires low water conditions otherwise the esters produced will be hydrolyzed back (Tang et al 2010). A number of lipase are commercially available and can be used after limited purification (Sharma et al 2012).

II. MATERIALS AND METHODS

Raw oil Sunflower acid oil was collected from vegetable oil refinery waste. There were two different by product from refinery industry, one for acid oil and other for fatty oil. The methanol and ethanol were used as the alcohol. The Acid based catalysts and Alkali based catalysts contemplated for their execution based on their yield and response time. The Acid based catalysts Sulphuric acid (H_2SO_4) and Alkali based catalysts for Potassium hydroxide (KOH), Sodium hydroxide (NaOH), Sodium peroxide (Na_2O_2) the were utilized. The methanol and ethanol were utilized as the alcohol. The optimization of catalyst and reaction time was conveyed in one litter of crude vegetable oil refinery waste (Sunflower acid oil). The Optimization work was conveyed in two segment initially was improved the catalyst from different proportion of catalyst included oil and second advanced the response time from different response time in best impetus proportion. In both stage the methanol and ethanol was changed in the 180ml to 200ml. The Sunflower acid oil have higher corrosive esteem, so biodiesel was set up by transesterification process in two fold phase process was embraced. In the main period of this work the pretreatment procedure was connected with utilizing 2ml to 6ml of H_2SO_4 to decrease the corrosive esteem and took after by Alkali catalyst transesterification utilizing NaOH different 9g to 17g, KOH different 12g to 18g and Sodium peroxide (Na_2O_2) different from 6g to 12g. After the finish of response, alcohol catalyst was isolated from upper layer. Next, the transesterified oil is washed with refined water, until the point that the remaining parts of impetus were evacuated and warmed to expel water content. In second period of the work was improved the response time with best measure of impetus. The response time was varied from 2 hours to 6 hours in all alkali catalyst.

III. RESULTS AND DISCUSSION

Acid esterification is the compound response amongst FFA and alcohol within the sight of acid catalyst for the transformation of FFA into mono alkyl methyl ester (Sukumar et al 2015). Alkaline transesterification is the substance response between triglyceride (triester) and methanol within the sight of alkaline catalyst to create monoester (Wei Xu et al 2015). The long and stretched chain of triglyceride particles are changed into monoesters and glycerin. H_2SO_4 is utilized 2ml in steady rate at all proportion of alkaline catalyst.

3.1 Effects of Methanol and Ethanol

Figure 1 and 2 shows the two disparate alcohols a well known as methanol and ethanol are used in this transesterification process. In this analysis 200 ml of methanol and 185 ml of ethanol are used. One carbon atom and two carbon atom were containing in methanol and ethanol respectively. NaOH was slowly broken up with

methanol, because it was lye corrosive nature. The alcohol typically utilized is methanol, since it is the least expensive (Quresi et al 2018). The procedure was named as methanolysis, when the utilized alcohol was methanol. This procedure creates methyl esters from the unsaturated fats. Be that as it may, while consider the biodiesel yield the ethanol produces higher contrast with methanol. The molar proportion was the important factor for biodiesel conversion process (Piloto-Rodríguez et al 2014). It also decided for efficiency and production cost. The transformation productivity is characterized as the yield of the procedure to regarding rate. Some examination uncovers that ethanol with 3 ml sulfuric acid change over the oil to 64 % ester simply following 4 hours of warming around at $65^\circ C$. The higher boiling temperatures of the more extended chain alcohols enable higher response temperatures to be utilized. In the two alcohols, the response temperatures were chosen beneath the breaking points of the liquor. The higher ester yield found for the more extended chain alcohols contrasted and ethyl ester are presumably because of the higher response temperatures permitted by their higher breaking points. The nearness of water or free unsaturated fat supports the arrangement of cleanser (Halim et al 2011). Therefore the oils and alcohols must be basically anhydrides. The water can be evacuated by dissipation, before the transesterification.

3.2 Effect of catalyst concentration

Biodiesel yield was varied in various concentration of catalyst shown in figure 1 and 2. The alcohol and catalyst were homogeneously mixed with help of stirrer in a reactor. The raw oil is initial fed into the reactor than the mixture of catalyst/alcohol was pour into the raw oil. Sulfuric acid is employed to increase the catalyze reaction of both KOH and NaOH catalyst. The KOH catalysts offer high yield of biodiesel, however the reaction rates were slow. The alcohol to grease molar magnitude relation is that the main issue manipulating the reaction (Madani et al 2017). The steps involve throughout acid-catalyzed transesterification were initial protonation of the acid to convey associate oxonium ion, the oxonium ion associated associate alcohol endure associate exchange reaction to convey the intermediate and this successively will lose a nucleon to become an ester (Pawar et al 2015). Deficient quantity of sodium hydroxide reported in imperfect conversion of triglycerides into the esters as showed from its lower ester substance. Great quantity of soap was determined in surplus quantity of NaOH. This can be as a result of addition of surplus alkalic catalyst originate a lot of triglycerides' contribution within the chemical reaction with NaOH, most important to the assembly of a lot of quantity of soap and reduction of the organic compound yield (Attaphong et al 2012 and Honig et al 2015). The 15g NaOH concentration was found in optimum, and additional raise in catalyst concentration in all the suitcases, ester production quantity reduced. The reaction time was increased in while using in NaOH catalyst during the transesterification process. Certain amount of soap was mixed in the biodiesel, during the water wash the soap was pasted in the separator (Matwijczuk et al 2017 and Manieniyani et al 2016). The higher biodiesel yield was obtained in KOH catalyst, also reduced the reaction time.

The 16g of KOH was found in the optimum catalyst, it was produced 625ml of biodiesel in ethanol. The table 1 and 2

listed of biodiesel yield in various catalysts with 190 ml and 200 ml Methanol and Ethanol.

Table 1. Biodiesel yield in various catalysts with 190 ml Methanol and Ethanol

Catalyst	MESAO in ml			EESAO in ml		
	KOH	NaOH	Na ₂ O ₂	KOH	NaOH	Na ₂ O ₂
14	300	250	230	450	400	370
15	280	220	280	510	50	470
16	240	210	200	625	400	380
17	200	170	150	570	300	240

Table 2. Biodiesel yield in various catalysts with 210 ml Methanol and Ethanol

Catalyst	MESAO in ml			EESAO in ml		
	KOH	NaOH	Na ₂ O ₂	KOH	NaOH	Na ₂ O ₂
14	245	206	196	519	372	333
15	274	196	176	598	412	372
16	216	186	167	539	343	323
17	196	157	137	402	294	274

3.3 Effects of Reaction time

Figure 3 and 4 were shown the different response time with two diverse ratio of alcohol. Diverse response times of 2, 3, 4, 5 and 6 hours were chosen for the analysis. For each case, the response was performed with 4 ml H₂SO₄, 190 ml overabundance alcohol and at the comparing boiling temperature of alcohol. The impact of response time on the ester yield was appeared in Fig.3. The greatest ester yield for ethanol was acquired simply following 4 hour while for methanol it was gotten following 5 hours. After 4 hours the ester yield still increments for methanol and ethanol. Subsequently the ideal response time required for this response was observed to be 5 hours.

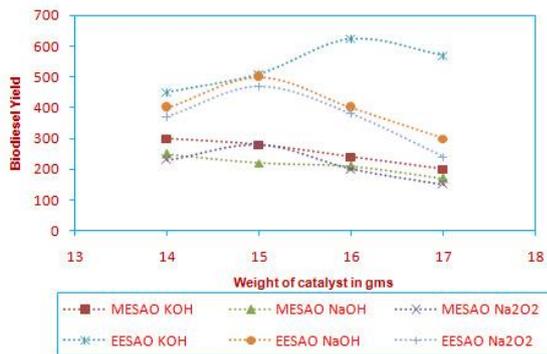


Fig 1 Biodiesel yield in various catalysts with 190 ml Methanol and Ethanol

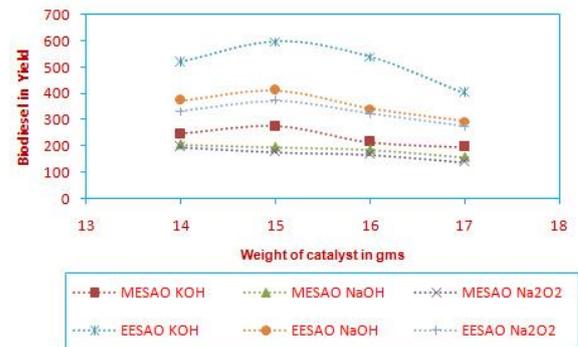


Fig 2 Biodiesel yield in various catalysts with 210 ml Methanol and Ethanol

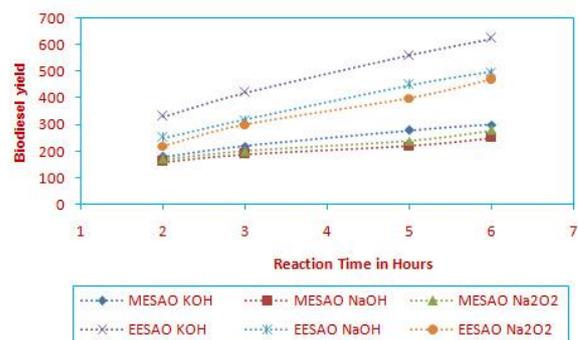


Fig 3 Biodiesel yield in various reaction times with 190 ml Methanol and Ethanol

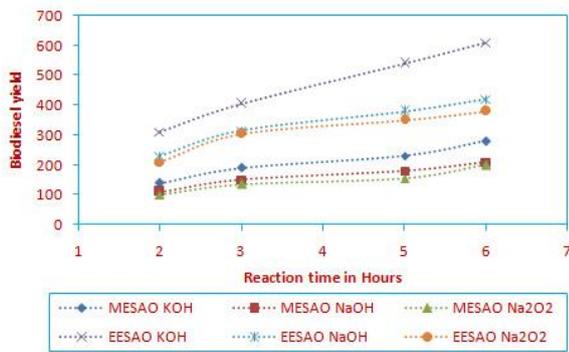


Fig 4 Biodiesel yield in various reaction time with 210 ml Methanol and Ethanol

The consolidation of the constant reaction time for best yield on oil is 625 ml with 190 ml volume of ethanol at 16 gm KOH and 6ml H₂SO₄. It shows that all oil higher yield in Potassium Hydroxide (KOH) with ethanol.

Table 4 Components found from GC-MS of EESAO

S.No	Name	Formula	RT (min)	Synonyms	MW
1	Phenol	C ₆ H ₆ O	4.731	Carbolic	94.11
2	Naphthalene, 1,6,7-trimethyl-	C ₁₃ H ₁₄	13.371	2,3, 5-Trimethylnaphthalene	170.25
3	9-octadecenoic acid(Z), methyl ester	C ₁₉ H ₃₆ O ₂	18.913	Oleic acid	296.48
4	9,12-octadecadienoic acid (Z,Z)-methyl ester	C ₁₉ H ₃₄ O ₂	718.876	Methyl octadeca-9,12-dienoate	294.47

Table 3 Properties of EESAO

Property of EESAO	
Specific gravity	0.870
Kinematic Viscosity at 40°C cSt	6.64
Flash Point °C	84
Fire point	90
Calorific value k.cal/kg	41782
Cetane Number	42

4.2 FT-IR Analysis

Figure. 6 shows the normalized FT-IR spectra obtained from the EESAO oil. Each spectrum was normalized by the intensity of the absorption band centered at 2921.60 cm⁻¹ (the strongest band). Characteristic vibrational modes are observed at 2921.60 cm⁻¹ (CH stretching, Linoleic acid), 2856.18 cm⁻¹ (CH stretching, Decanoic acid), 1744.94 cm⁻¹ (C=O stretching), and 1457.70 cm⁻¹ (C=C stretching, Palmitic acid). The carboxylic acid that is not present in the cracking products. It is worth mentioning that no vibration feature, characteristic of aromatic compounds, was observed in the FT-IR spectra, which is in good agreement with what was observed in the chromatography studies.

IV. BIODIESEL CHARACTERISTICS OF EESAO

4.1 Gas chromatography mass spectrometry (GC-MS) analysis

Some of the major physical properties were listed in table 3. The GC-MS analysis of the oil sample obtained from ethyl ester of sunflower acid oil is carried out to know the exact composition of the oil (Fig. 5) and seventy two compounds were detected which are summarized in the Table 4. Among the fifty five components, four components are major and others are minor. On the basis of the MS database, these peaks can be identified. With 9-octadecenoic acid (Z), methyl ester being present in highest amount (27.45 %), many derivatives of 9-octadecenoic acid (Z), methyl ester were also detected. On the basis of the MS database, these peaks can be identified (Phenol, Naphthalene, 1,6,7-trimethyl-, 9-octadecenoic acid(Z), methyl ester, 9,12-octadecadienoic acid, (Z,Z)- methyl ester Methyl stearate).

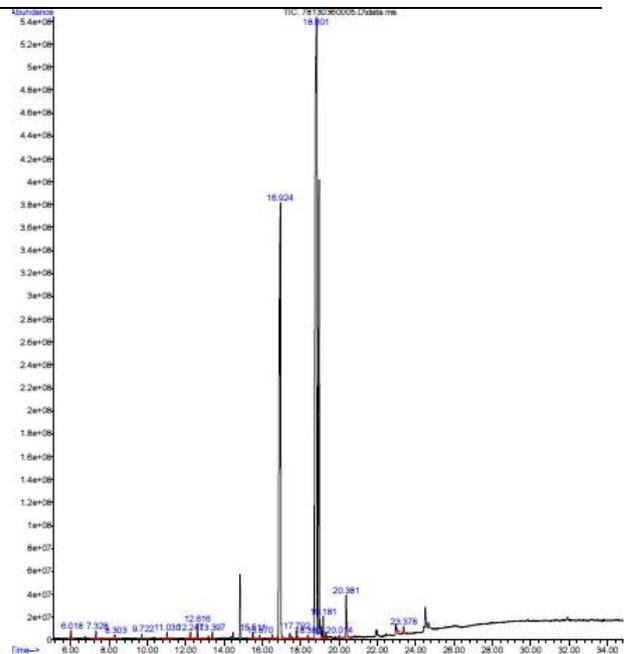


Fig. 5 GC-MS Analysis of EESAO



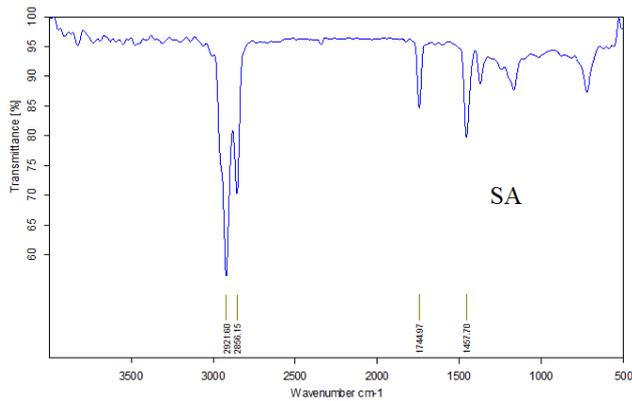


Fig.6 FT-IR Analysis of EESAO

V. CONCLUSION

This investigation was optimized the reaction time, catalyst, and alcohol for biodiesel production. The optimal estimations of these parameters for accomplishing most extreme conversion of oil to esters relied upon the chemical and physical properties of these oils. The accompanying conclusions are drawn from the investigation:

The molar proportion was the important factor for biodiesel conversion process. It also decided for efficiency and production cost. Addition of overabundance catalyst causes more triglycerides' support in the saponification response prompting a reduction in the ester yield. Biodiesel production process was lesser in lesser amount of alcohol. The higher biodiesel yield was obtained in KOH catalyst, also reduced the reaction time. The 16g of KOH was found in the optimum catalyst, it was produced 625 ml of biodiesel in ethanol. The 15g NaOH concentration was found in optimum, and additional raise in catalyst concentration in all the suitcases, ester production quantity reduced. After 4 hours the ester yield still increments for methanol and ethanol. Subsequently the ideal response time required for this response was observed to be 5 hours.

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