

Biodiesel from Palm Vegetable Oil

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Abstract

Energy obtained from a variety of non-renewable sources is considered unsustainable. Various fossil fuels, such as petroleum, coal, and natural gas, are among these sources. The combustion of fossil fuels resulted in the generation of greenhouse gases, which increased the amount of carbon dioxide in the atmosphere. Global warming and ozone layer degradation are the negative consequences. In a country like India, where consumable oils are still imported, it is sense to look at the possibility of using such unpalatable oils in CI engines that aren't often utilized as cooking oil. Palm oil is a vegetable oil obtained from the monocarp of the oil palm's crop. The main goal is to provide a low-cost, high-performance alternative to diesel. The possibility of palm oil as a realistic, modest, and effective hotspot for the generation of biodiesel is investigated in this research. The article is focused on the comparison of palm oil and diesel in terms of characteristics.

Keywords

Biodiesel, Transesterification, Palm Oil, Heterogeneous Catalyst, Methyl Esters, Sustainable Fuel, Energy

1. Introduction

The rapid depletion of crude oil, its increasing price along with the global concern for the environment has necessitated research into new and eco-friendly alternative fuels as energy sources. Fuels derived from non-crude oil sources, such as methanol, ethanol, biodiesel, liquefied natural gas (LPG), natural gas, and hydrogen, are commonly referred to as alternate fuels. Biodiesel made from edible and non-edible oil supplies has evolved as a technically viable, economically competitive, environmentally sustainable, and socially good diesel substitute. Chemically, biodiesel is a mono alkyl ester of vegetable oil and animal fats that can be made by combining any natural oil or fat with an alcohol in the presence of a

catalyst.

The choice of vegetable oil for biodiesel production depends on soil and climates conditions. So, each country has usually different choices, for example, in the United States soybean oil, in Europe rapeseed oil and sunflower oil, in Philippines coconut oil, and in Southeast Asia (Malaysia and Indonesia) palm oil. In India, demand for edible oils exceeds supply, and there is no means to redirect these oils for biodiesel production. In addition, their high cost prevents them from being employed in biodiesel production. Under Indian conditions, only plant sources that are not edible in large amounts and can be cultivated on a large scale on marginal/waste lands can be considered. Such oils should not compete with food supply in the long run as biodiesel feedstocks. There are many non-edible seeds which are rich in oil and can be treated as feedstock for biodiesel production example—*Jatropha Curcus*, *Pongamia Pinnata*, Palm, Mahua etc. Among all these palm oil also has a high potential to produce biodiesel that can be used to replace conventional diesel. The leading producer of palm oil is Malaysia. When compared to other vegetable oils, palm oil emerges as a superior and potentially useful feedstock for biodiesel synthesis. Palm oil is a perennial crop, which is one of its most appealing features. Seeds of rapeseed and soyabean are not perennial crops. Moreover, if we consider the production of oil as per hectare of plantation then palm oil has the highest oil yield. It is ten times greater than the yields from rapeseed, sunflower or soyabeans. Furthermore, enhanced crop yield, low plantation water, pesticide, and fertilizer requirements, and lower energy balance requirements to manufacture a unit of oil make palm oil a viable candidate for biodiesel production. The most common vegetable oils on the market today are crude palm oil and refined palm oil.

ElaeisGuineensis is the fruit from which palm oil is extracted. The fruit's mesocarp is processed to produce palm oil. The fleshy inner wall of the fruit is known as the mesocarp. **Figure 1** depicts the process of transforming palm fruit into crude palm oil step by step.

The presence of 51.9 percent unsaturated fatty acid and 45.5 percent saturated fatty acid such as oleic acid (C18:1), linoleic acid (C18:2), palmitic acid (C16:0), and stearic acid (C18:0) is characteristic of crude palm oil. The approximate molecular weight of refined palm oil was discovered to be 843 g/mol based on the fatty acid content data, which serves as the basis for calculating the amount of catalyst.

Crude palm oil cannot be directly used as fuel in internal combustion engines because various properties like viscosity, density and flash point are not in acceptable range to be a fuel. These properties could be improved to be in the acceptable range by various methods like: Dilution, Pyrolysis, Microemulsification, and Transesterification.

Dilution: Diesel fuel, a solvent, or an alcohol can all be used to dilute vegetable oil. Knothe *et al.* [1] found that diluting sunflower oils with diesel fuel (v/v) resulted in a fuel with a viscosity of 4.47 cSt at 400°C, which was significantly lower than the viscosity of plain sunflower oil (31cSt) reported by [2]. However,

owing of significant injector nozzle choking and sticking, the blend could not be recommended for long-term usage in diesel engines. Freedman [3] investigated the effect of combining ethanol with beef tallow to lower the viscosity of the methyl ester. The viscosity of tallow ester was 5.5 cSt at 30°C, while the viscosity of diesel fuel was 2.4 cSt at the same temperature, according to the researchers. The viscosity of tallow ester was lowered to 2.4 cSt by adding 35 percent ethanol. However, research have shown that using diluted vegetable oil directly in direct and indirect diesel engines is ineffective and inefficient. The main issues include excessive viscosity, lubricating oil thickening, carbon deposit, free fatty acid content, and gum production as a result of oxidation and polymerization during storage and combustion.

Pyrolysis: Lamba *et al.* [4] studied the thermal cracking or pyrolysis, a process of conversion of heavier hydrocarbon into simpler hydrocarbon by heating it in the absence of air. Vegetable oils, animal fat, natural fatty acids, and methyl ester of fatty acids can all be pyrolyzed. Vegetable oil was first pyrolyzed in an attempt to create petroleum from it. This method was used to create items appropriate for use as fuel from various vegetable oils. The lengthy chain is reduced into fragment mixtures of varied sizes when the hydrocarbons are heated to 300°C - 400°C. The length of the carbon chain affects the viscosity of hydrocarbons. The chain length and viscosity decrease after pyrolysis. Thermal cracking produces chemicals that are chemically comparable to petroleum-derived fuels, but because oxygen is removed during the process, the environmental benefits of using an oxygenated fuel are lost. Furthermore, the increasing equipment costs made the process costly for little throughput.

Microemulsion: Microemulsions, with or without an emulsifier, are liquids spread in an immiscible liquid, usually in droplets smaller than colloidal size. A micro emulsion can improve spray properties due to the explosive evaporation of low boiling components in the micelles [3]. Microemulsions can be made using vegetable oils, an ester, and a dispersant, or with vegetable oil, an alcohol, and a surfactant with or without diesel fuel. Methanol and vegetable oil microemulsions can behave similarly to diesel fuel. The problem of excessive viscosity in vegetable oils is solved with micro-emulsion. Micro-emulsions have been studied utilizing solvents such as methanol, ethanol, butanol, and others. In the short term, both ionic and non-ionic micro-emulsions of aqueous ethanol in Soyabean oil performed nearly as well as ASTM No. 2 diesel fuel despite having a lower cetane number and energy content. However the viscosity was reduced.

Transesterification: Transesterification is the reaction of a fat or oil with an alcohol to form fatty acid methyl ester (FAME) and glycerol, as seen in **Figure 2** [5]. Catalysts are frequently employed to speed up reactions and increase yields. To complete the transesterification, a 3:1 molar ratio of alcohol to triglycerides is necessary. In practice, a higher ratio is required to shift the equilibrium to the maximal ester yield. Three reactions are required to complete the transesterification of a triglyceride. In the first stage, a triglyceride and an alcohol molecule interact to generate a diglyceride and FAME. After that, a diglyceride reacts with

alcohol to form a monoglyceride and FAME. Finally, alcohol and a monoglyceride combine to form FAME and glycerol.

Alkalies, acids, or enzymes can catalyze the process, which can be homogeneous or heterogeneous. In homogeneous transesterification, basic catalysts such as KOH, NaOH, and NaOCH₃ are utilized, and the reactants are heated for roughly 1 hour at 60°C - 80°C. The product must next be washed thoroughly with water to remove the catalysts, which will taint the biodiesel if left in place. The use of homogeneous catalysts has been reported in the literature [6]-[15] and it has two advantages: high methyl ester yields under mild conditions and a shorter reaction time. However, environmental repercussions, production costs, and catalyst reusability must all be considered when using homogeneous catalysts for transesterification processes. To solve these challenges, heterogeneous transesterification, has received a lot of attention. Several heterogeneous catalysts have been investigated and reported [16] [17] [18] such as zinc oxide (ZnO), sulphated zirconia (SO₄²⁻/ZrO₂), sulphated stannous oxide (SO₄/SnO₂), KNO₃/KL zeolite and zirconia-supported potassium nitrate (KNO₃/ZrO₂). The reported literature suggests that for Palm oil, the most potential method is heterogeneous transesterification.

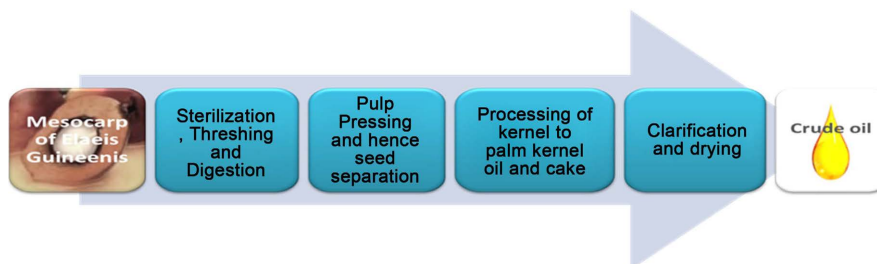


Figure 1. Conversion of palm fruit to palm oil.

2. Mechanism of Heterogeneous Acid-Catalyzed Transesterification

Solid catalysts catalyze processes by donating or receiving protons via acidic or basic functional groups in active areas. **Figure 3** shows the trans esterification of triglycerides using an acid catalyst. Triglycerides are protonated at the carbonyl group on the surface of a solid acid, and then a tetrahedral intermediate is formed by the nucleophilic assault of the alcohol on the carbocation (hemiacetal species). An unstable tetrahedral intermediate causes proton migration and tetrahedral intermediate breakup. After repeating the process three times, three new FAME compounds are produced, and the catalyst is regenerated. By increasing the electrophilicity of the neighbouring carbonyl carbon atom during the catalytic process, protonation of the carbonyl group increases the catalytic action of solid acid catalysts. Unlike Bronsted acids, Lewis acids receive electrons by generating a four-membered ring transition state [e.g., Fe₂(SO₄)₃, titanate complexes, tungstate, sulphate zirconia, carboxylic salts]. The Lewis complex formed by the reactant triglyceride and metal aids solid Lewis acids in activating

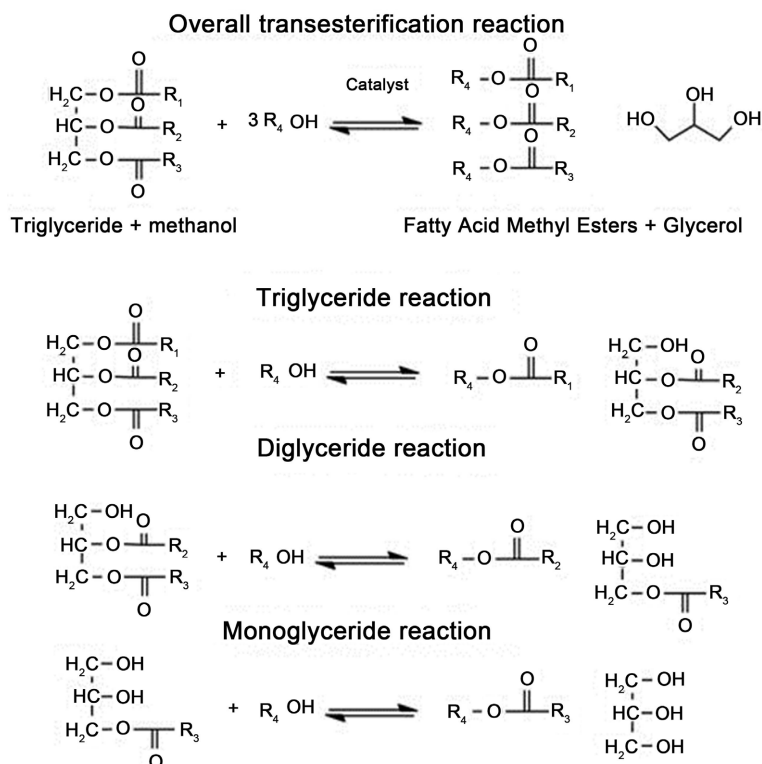


Figure 2. Basic Transesterification Process (Biodiesel Current Technology: Ultrasonic Process a Realistic Industrial Application—Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/Well-generalized-transesterification-pat-hway-3_fig2_264240361 [accessed 7 Feb, 2024], [5].

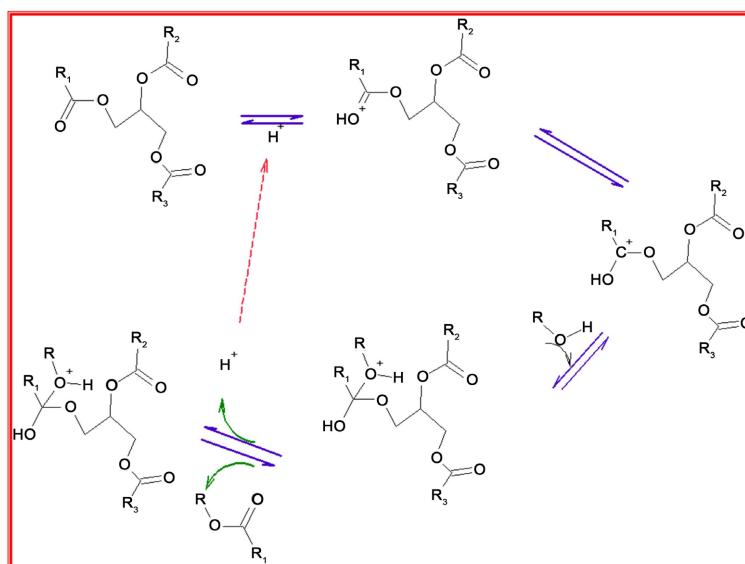


Figure 3. Acid-catalyzed reaction mechanism of transesterification.

carbonyl groups for nucleophilic attack by the reactant alcohol. The triglyceride carbonyl coordinates to a vacant place in the catalytic active species. The catalytic activity is due to the formation of a more electrophilic species [19].

3. Transesterification to form Palm Oil Methyl Ester (POME)

Palm oil usually has high free fatty acid (FFA), so, it involves two steps, esterification which is done to reduce the FFA and then transesterification to convert triglycerides into methyl esters. Esterification is catalyzed by sulfuric acid (H_2SO_4). A known weight of palm oil is heated to $50^\circ C$ on a hot plate magnetic stirrer in a three-necked glass flask with condenser as shown in **Figure 4**. Then, methanol is added to oil in a molar ratio of 12:1 followed by 1wt percent of sulfuric acid. The reaction mixture is heated for a period of 30 minutes.

This acid treatment brings the acid value in acceptable range. Water formed during the esterification process accumulates in the alcohol layer and part of acid, catalyst also remains in it. The alcohol layer containing sulphuric acid and water is rejected and the second (upper) layer is subjected to transesterification reaction. In this a known weight of crude oil is heated to $60^\circ C$ in the reactor. Then solid catalyst mixed with methanol is added into the oil, followed by addition of 20 percent by weight of tetrahydrofuran (THF). The various factors affecting the yield are methanol-to-oil molar ratio, reaction time, temperature, catalyst loading, amount of catalyst and catalyst calcination temperature. After completion of each batch, the catalyst particles are physically separated from the mixture by centrifuge. Then the methyl ester is washed with distilled water. The methyl esters are put into a separating funnel. An equal amount of distilled water is heated up to $50^\circ C$ and then added with a 0.1wt percent sulfuric acid. This mixture is added into methyl ester to wash all other impurities.

The washing operation is repeated until the waste water's colour changes to clear. After washing the methyl esters, a known weight of sodium sulphate (Na_2SO_4) is added to eliminate any remaining water, and the mixture is centrifuged to separate the solid from the methyl ester product. Following the European authorized procedure EN14103, Sinha *et al.* [20] the yield of biodiesel can be calculated by using the equation:

$$\frac{\text{weight of Biodiesel produced}}{\text{weight of feedstock (oil)}} \times 100 = \% \text{ Yield}$$

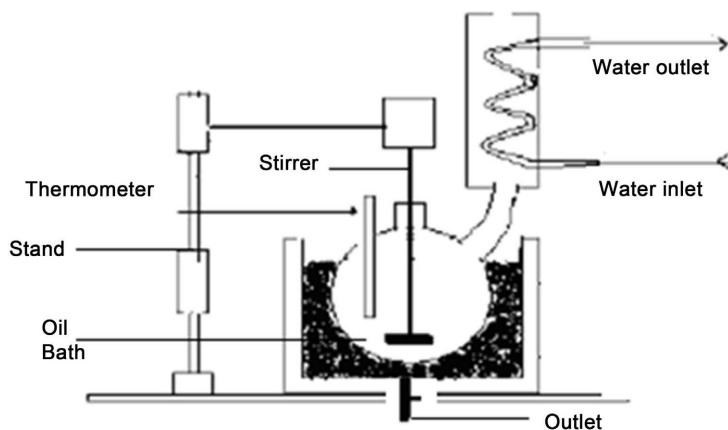


Figure 4. Schematic diagram of transesterification lab reactor.

4. Results

After purification and treatment, the fuel qualities of the resulting POME are assessed using ASTM standard procedures under optimal reaction circumstances and also subjected GCMS to determine the composition to check the POME suitability as an alternate fuel.

4.1. Physicochemical Characterization

The main physicochemical properties of prepared POME were determined and represented in **Table 1**. All the properties are in agreement to that reported in the literature. In terms of density, flash point and cetane value, POME has comparable physicochemical properties to that of EURO-IV HSD. However, the viscosity of the POME is more than that of commercial diesel (EURO-IV) that may further increases on storage. Also, the oxidation stability of the prepared methyl ester is even less the standard requirement value that indicates the less shelf life of the fuel.

Table 1. Physico-chemical Properties of POME.

	Palm oil	Palm oil methyl ester	EURO-IV HSD	STD limit	Test Method
Calorific value (MJ/Kg)		41.3			
Moisture content (mg/kg)		0.042%		0.05% max	ASTM D 2709
Cetane level	42	65	53	44	-
Flash Point (°C)	267	74	63	100	ASTM D93
Cloud point (°C)	31	16			ASTM D2709
Density at 15°C (g/cm ³)	0.91	0.88	0.822	0.82-0.89	ASTM D4052
Kinematic Viscosity at 40°C (cST)	38.2	4.5	2.6488	1.9-6	ASTM D445
Sulphur content (wt%)	-	0.04	--	--	-
Carbon residue (wt%)	-	0.02	-	-	-
Oxidation Stability (@ 140°C, h)	-	2.98	-	6 hrs minimum	ASTM D7545

4.2. GCMS of POME

The composition of prepared POME was analyzed using a GC (gas chromatograph) supplied by Nucon 5700 series with EOX column (serial no 5061; 30 m length, 0.25 mm ID and 0.25 mm outer dia). Helium (99.9% purity) was used as the carrier gas with a column flow rate of 1 ml/min and a pre-column pressure

of 49.7 kPa. The column temperature regime was 40°C for 3 min, followed by a 5°C/min ramp up to 230°C, followed by 40 min at 230°C. The injection volume and temperature were 0.2 ml and 240°C and the split ratio was 1/30. FAME (Fatty acid methyl ester) peaks were identified by comparison of their retention times with authentic standards by GC and quantified by area normalization. The GC of POME is shown in **Figure 5**. Analysis revealed that POME biodiesel contains mainly Methyl Myristate, Methyl Palmitate, Methyl heptadecanoate, Methyl Stearate, Methyl Oleate, Methyl Linoleate That have comparable calorific value and support the use of POME as energy source.

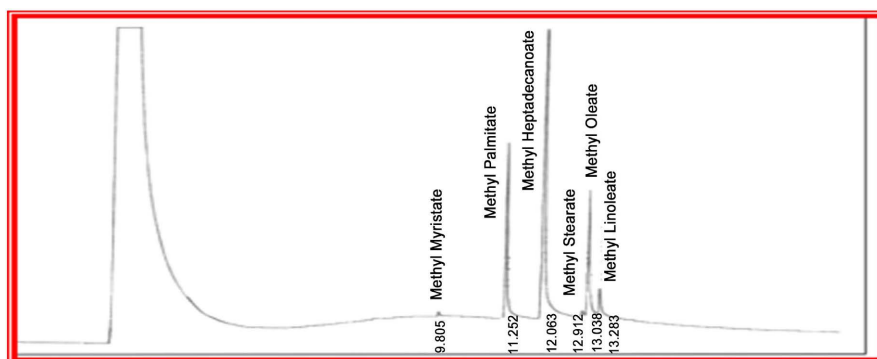


Figure 5. GC of POME.

5. Conclusion

The presented work focuses on biodiesel production from palm oil. Palm oil is well established as a potential feedstock which has advanced the diversification of production and usage of biodiesel as an alternative fuel. The conversion technologies for palm biodiesel have been extensively researched with a major emphasis on catalytic methods. The Homogeneous base catalysts are the most common, however it has many glitches if high free fatty acid appears in crude palm oil. A more efficient and greener method is the use of heterogeneous catalyst for production of palm biodiesel with a noteworthy yield. However, the method has its own flaws related to easy poisoning and deactivation making them less favorite for commercial scale production of palm diesel oil. Further research is desirable to improvise the techniques considering energy requirements and cost-effective benefits. The physiochemical analysis of the POME showed that research is also required to lower the viscosity and enhance the oxidation stability of the POME to make it a sustainable alternate fuel.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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