



Biodiesel Production from Karanj Crude Oil by Transesterification Process

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ABSTRACT: As the price of petroleum oil reaches a new high, the need of developing alternate fuels has become acute. Alternate fuels should be economically attractive in order to compete with currently used fossil fuels. Biodiesel, produced by the transesterification of vegetable oils or animal fats with simple alcohols and catalyst attracts more and more attention recently. Biodiesel is clean burning diesel alternative and has many attractive features including renewability, biodegradability, non toxicity and low emission. The aim of the present review is to study the biodiesel production from transesterification process and the effect of reaction parameters on conversion of biodiesel yield. It observes that the base catalysts are more effective than acid catalysts and enzymes. Biodiesel (fatty acid methyl esters) is a notable alternative to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural sources such as soybeans, waste cooking oil, coconuts and rapeseeds oil and thus reduces dependence on diminishing petroleum fuel from foreign sources. The problems with substituting triglycerides for diesel fuels are mostly associated with their low volatilities, high viscosities and polyunsaturated character. The main purpose of the transesterification process is to lower the viscosity of the oil. Over a number of years, the work of exploring different biodiesel as an alternative to diesel fuel has been carried out worldwide. The performance of biodiesel is closed to petroleum diesel fuel. The brake power of biodiesel fuel is approximately equal to diesel, while the specific fuel consumption is higher than that of diesel. The combustion characteristic of biodiesel fuels is similar to petroleum diesel fuel and blends provide small ignition delay, higher ignition pressure, and higher ignition temperature and peak heat release.

Keyword: *Biodiesel, Alternate fuels, Transesterification.*

I. INTRODUCTION

From 1973 to 2004 the global primary energy consumption increased from 252 to 463 billions MJ [1]. In addition, high emissions of CO₂, NO_x, SO₂ and particulate matter (PM) are produced during fossil fuel use, generating environmental problems. These facts have converged in the search of renewable energies, such as biofuels. The lack of conventional fossil fuels, their increasing costs and rising emissions of combustion-generated pollutants will make bio-based fuels more attractive [2]. Due to the rise in price of petroleum products, especially after the petrol crisis in 1973 and then the Gulf War in 1991, geographically reduced availability of petroleum and more rigorous governmental regulations on exhaust emissions, many researchers have studied alternative fuels and alternative solution methods [3, 4]. The ASTM (American Society for Testing and Materials) defined the biodiesel fuel is monoalkyl esters of long chain fatty acid derived from renewable lipid feedstock such as vegetable oil or animal fat. "BIO" represents its renewable and Biological source in distinguish to conventional petroleum-based diesel fuel; "Diesel" refers to its use in diesel engine. As a substitute fuel, biodiesel can be used in efficient form or in mixed form with petroleum-based diesel.

Biofuels are important because these can be used as an alternative petroleum fuel. It is predicted that the demand for biofuels will rise in the future. Biofuels are alternate fuel sources to petroleum; however, some still comprise a small amount of petroleum in the mixture [5]. Biofuels are generally considered as offering many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, and security of

supply [6]. Recently biodiesel has turned into more attractive because of its ecological benefits [7, 8, 9]. Biodiesel is a renewable energy source produced from natural oils and fats, which can be used as a substitute for petroleum diesel without the need for diesel engine modification [10]. At the present time, the high cost of biodiesel is the major problem to its commercialization. Biodiesel usually costs over US\$0.5/l, compared to S\$0.35/l for petroleum based diesel [11, 12]. It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil [13, 14]. The use of waste cooking oil in place of virgin oil to make biodiesel is an effective technique to reduce the raw material cost because it is estimated to be about half the cost of virgin oil [15]. The use of waste cooking oil could also help to solve the difficulty of waste oil disposal [16].

Biodiesel is essentially free of sulfur and aromatics, producing lower exhaust emissions than conventional fuel while providing similar properties in terms of fuel efficiency; moreover these methyl esters have considerably lower flash points than those of pure vegetable oils [5, 17-21]. Exploring the renewable energy resources such as biodiesel fuel is of growing importance in recent years [22]. Vegetable oils, also known as triglycerides, have the chemical structure vegetable oils comprise of 98% triglycerides and small amounts of mono- and diglycerides [23]. Figure (1) shows the viscosities of vegetable oils and their methyl esters. The injection and atomization characteristics of the vegetable oils are significantly different than petro-diesel fuels. Mainly these (vegetable oils) result of their higher viscosities [24]. Biodiesel, produced from different vegetable oils such as rapeseed, soybean, and sunflower etc. seems very attractive for various reasons.

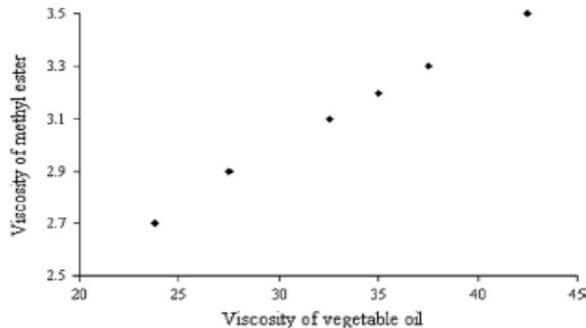


Fig. 1. Viscosities of vegetable oils and their methyl esters (mm²/s) at 38°C [23].

It can be substituted diesel oil for boilers and internal combustion engines without any major changes only a small decrease in performances of engine with negligible emissions of sulfates. A little contribution of CO₂ when the entire life cycle is considered including cultivation, production of oil, conversion to biodiesel and emission of pollutants analogous with that of diesel oil. For these reasons, many campaigns have been intended in many countries to introduce and promote the use of biodiesel [25]. The prices of edible vegetable oils are higher than diesel fuel therefore waste vegetable oils and non-edible vegetable oils prefer in place of edible vegetable oils for production of biodiesel [26].

Biodiesel (fatty acid methyl esters [FAME]) is a notable alternative to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural sources such as soybeans, rapeseeds, coconuts, and even recycled cooking oil, and thus reduces dependence on diminishing petroleum fuel from foreign sources. In addition, because biodiesel is largely made from vegetable oils, it reduces lifecycle greenhouse gas emissions by as much as 78% [27]. Due to the depletion of petroleum reserves and increases in environmental concerns the importance of biodiesel increases gradually [28]. Various non-edible oils, such as jatropha, honge, honne, rubber seed, mahua, hazelnut kernel, waste frying oil and cotton seed oils, are investigated for their suitability to diesel engine fuels [29-41]. Biodiesel used in compression ignition (diesel engine) like diesel which basically required very small or no engine modifications as biodiesel require a separate infrastructure. The use of biodiesel in diesel engines results in considerable reduction of carbon monoxide, unburned hydrocarbon, and particulate matter (PM) emission. Biodiesel considered is a clean fuel since it has no sulphur content, no aroma, and has about 10% oxygen content, which helps it to burn completely to biodiesel fuel. The higher cetane number (CN) of biodiesel fuel improves the ignition quality even when mix with diesel. Biodiesel can be used in CI (diesel) engines without blends with diesel or as blends with petroleum diesel fuel. A fuel containing 2% biodiesel for example is called B2; pure biodiesel is called B100 [42]. Biodiesel as an alternative fuel for CI engines is attractive increasingly important due to depletion of petroleum resources and the ecological consequences of exhaust emission from petroleum-fuelled engines. Biodiesel is the simple alkyl esters of fatty acids which are made from renewable energy resources. As a future prospective fuel, biodiesel has to compete economically with petroleum diesel fuels. India imports petroleum products at an annual cost of approximately \$50 billion in foreign exchange.

In view of this high demand/cost of fossil fuels associated with higher emissions, it is necessary to find an appropriate alternative to diesel oil. The use of 5% of biofuels in place of petroleum fuel enables India to save \$2.5 billion per year in foreign exchange [43]. The production costs of biodiesel is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and byproducts of the refining vegetables oils [44]. The major disadvantage of the biodiesel is its high manufacturing cost due to high cost of vegetable oil, which accounts to nearly 78% of the biodiesel production [45]. Reuse of WCO minimize the production cost of biodiesel significantly but also helps the government to disposing waste oils, maintaining treating oily waste water and public sewers. A lot of quantities of WCO are generated in food processing industries, fast food shops and house cooking every day. Waste cooking oil was selected as a substitute because it is cheap and also avoids the cost of waste product disposal and treatment [46]. The biodiesel production from acid-catalyzed (Transesterification) process using waste cooking oil proved to be technically feasible with less difficulties than the alkali-catalyzed process using waste cooking oil, thus production it a competitive alternative to commercial biodiesel making by the alkali-catalyzed process [22]. It is obvious that alkali-catalyzed transesterification process of biodiesel production is preferred for waste cooking oils (WCOs) than acid-catalyzed transesterification process [47-51]. The WCO was found to be 1.44% of FFA (Free fatty acids) content which was lower the limit of 5% for alkaline transesterification [52-54]. The most commonly used alkali catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH) but higher yield has been reported with KOH [55-56]. The most frequently used alcohols in transesterification process are Methanol and ethanol, but methanol was generally preferred for study due to its low cost and higher reactivity compared to ethanol [57, 58]. Transesterification process depends on various factors such as methanol-to-oil ratio, catalyst concentration, reaction temperature, reaction time and stirring rate. If any change on any factor at a time of studying its result on biodiesel production is tedious and time consuming. The variables affecting the transesterification process of peanut cotton seed and sunflower oil using sodium methoxide (as catalyst). The results revealed that the maximum biodiesel yield of 93% was observed with methanol-to oil molar ratio of 6:1, reaction temperature of 60°C and catalyst concentration of 0.5 wt% [59]. Optimization of biodiesel production from refined sun flower oil using design of experiments and RSM (Response Surface Method) was investigated [60]. Methanol-to-oil molar ratio of 6:1, reaction temperature of 20–50°C and high catalyst concentration of 1.3% were found to be the optimum conditions of biodiesel. The effect of process variables on acid catalyst (sulphuric acid) in transesterification of soybean oil results maximum biodiesel yield of 98.4% was noted with methanol-to oil molar ratio of 30:1, reaction temperature of 60°C and catalyst concentration of 5% [61].

Optimization of biodiesel production from sunflower oil in transesterification using KOH as catalyst was analyzed and results revealed that the maximum biodiesel yield of 96% was obtained under the optimum condition of methanol-to-oil molar ratio of 9:1, catalyst concentration of 0.28wt% and reaction temperature of 70°C [62].

The optimization of experimental conditions for biodiesel production from *Jatropha curcus* oil using NaOH as catalyst and found that the maximum biodiesel yield of 98 % was obtained for the methanol-to-oil percentage of 20, catalyst concentration of 1 wt%, reaction time of 90 min and reaction temperature of 60°C [63]. The methyl ester conversion of WCO (Waste Cooking Oil) in acid-catalyzed transesterification can reach up to 99%. This process was carried out using a very high methanol-to-oil ratio of 250:1 [22]. The conversion of WCO using sodium hydroxide as catalyst was approximately 86% [49]. The optimization study for the production of biodiesel from waste vegetable oil using NaOH and KOH as catalysts and it was found that the yield of biodiesel could reach up to 96.5% using KOH with the reaction temperature of 65°C; methanol-to-oil molar ratio of 6:1; reaction time of 180 min and catalyst concentration of 1 wt% [64]. The transesterification of waste rape seed oil with high FFA to biodiesel using response surface methodology (RSM) reported that the maximum biodiesel yield of 84.1% was observed with the reaction temperature of 45°C, KOH concentration of 1 wt%, methanol-to-oil molar ratio of 6:1 and reaction time of 65 min [65]. The effects of methanol-to-WCO ratio, potassium hydroxide (KOH) concentration and reaction temperature on the biodiesel conversion were investigated and established that the biodiesel yield of 88–90% for the methanol-to-oil ratios of 7:1–8:1, reaction temperatures of 30–50°C and 0.75wt% KOH [66]. The FFA and moisture content are key parameters for determining the viability of the vegetable oil transesterification process to carry the base catalyzed reaction to completion a free fatty acid value lower than 3% is needed [67]. In the transesterification process FFAs and water always produce negative effects, since the presence of FFAs and water causes soap formation, it consumes catalyst and minimize the catalyst effectiveness which results a low conversion in biodiesel production [68]. These FFAs react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water [69]. The alkali-catalyzed process using virgin oil (process I) was the simplest with the least amount of process equipment but had a higher raw material cost than other processes. Most of the optimization studies on the transesterification of vegetable oil; especially waste cooking oil (WCO) considered two or three process parameters at a time. However, there is a lack of research with regard to simultaneous effect of major process restriction such as methanol-to oil ratio, catalyst concentration, reaction temperature, reaction time and stirring rate on biodiesel yield. The engine performance analysis using sunflower methyl esters (biodiesel) exhibited characteristics very similar to conventional diesel fuel. The present studies were focused on performance and emission of biodiesel in CI (diesel) engines, wear performance on long term engine usage, combustion analysis, and economic feasibility [70, 68]. When using biodiesel there were no significant differences observed for torque, power, and exhaust smokiness [71-73]. BSEC (Brake specific Energy Consumption) is a more pertinent parameter than BSFC (Brake specific Fuel Consumption) because it is independent of the fuel. Hence, it is more appropriate to compare energy consumption rather than fuel consumption. BSEC is the energy input required to develop unit power. Biodiesel showed higher BSEC compared to that of diesel for all loads. At 100% load condition, BSEC of 15.5 MJ/kWh was observed with biodiesel, which was 3.1 MJ/kWh higher than that of diesel. This is mainly because of

lower calorific value of biodiesel. The brake thermal efficiency of biodiesel was slightly lower than that of traditional diesel fuel at 100% load condition. With the use of biodiesel the NO and smoke emission decreased as compared to diesel. Biodiesel showed lower heat release rate, a minute ignition delay and slightly higher combustion duration compared to diesel. [74].

The thermal efficiency of CI engine depends on the compression ratio and the fuel–air ratio. With fixed compression ratio, the thermal efficiency mainly depends only on the fuel–air ratio [75]. Maximum brake thermal efficiency of 23.1% was observed with biodiesel (WCO-ME), which is 6% lower than that of diesel at 100% load condition. The Brake thermal efficiency of diesel engine is lower due to the lower calorific value and higher viscosity of biodiesel. Higher viscosity of biodiesel fuel results poor fuel atomisation during the spray process which increasing the engine deposits and also requires more energy to pump the fuel which wears fuel pump elements and injectors [76].

The effect of injection pressures, injection timings and exhaust gas recirculation (EGR) on the performance of different vegetable oils in compression ignition (CI) engines has been reported by many investigators [77- 81]. Changes in injection timings change the position of the piston and cylinder pressure and temperature at the injection, retarded injection timings showed significant reduction in diesel NOx and biodiesel NOx [77, 79]. Cylinder pressures and temperatures gradually decrease when injection timings are retarded [81].

Advanced injection timing by 48 before top dead centre (BTDC) with waste cooking oil in direct injection diesel engine resulted in better efficiency with reduced CO and higher NO emissions [78]. Retarding the injection timing by 48 BTDC with honge biodiesel has resulted in better efficiency with reduced HC, CO and smoke emissions [82]. Performance tests on CI engine with vegetable oils at different compression ratios have been reported better performance, higher peak cylinder pressure and temperature were observed at an increased compression ratio [83, 84].

Since biodiesel fuel as an alternative fuel has many merits and is derived from a renewable and domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic compared to petroleum-based diesel fuel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide (CO), particulate matter (PM) and unburned hydrocarbons (HC). Carbon dioxide (CO₂) produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect [85, 86]. Biodiesel has a relatively high flash point (150°C), which makes it less volatile and safer to transport or handle than petroleum diesel [13]. It provides lubricating properties that can reduce engine wear and extend engine life [87].

II. MATERIALS AND METHODS

A. Vegetable oil (Crude oil)

The biodiesel production from vegetable oil or waste vegetable oil must be moisture free because every molecules of water destroy the molecules of catalyst which decrease its concentration and results poor conversion. The FFA content of oil should be less than 1%. It was found that lesser the FFA in oil, the better is the biodiesel conversions. Higher FFA oil can also be used but the biodiesel conversions will depend

upon the type of oil and amount of potassium hydroxide (KOH) or sodium hydroxide (NAOH) used.

B. Alcohol

Methanol (CH₃OH) or ethanol (C₂H₅OH) can be used as near to absolute as possible. As with oil, the amount of water content in alcohol affects the extent of conversion enough to prevent the separation of glycerol from the reaction mixture.

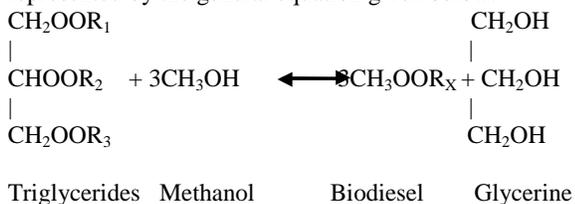
C. Catalyst

The catalyst Potassium hydroxide (KOH) or sodium hydroxide (NAOH) can be used for transesterification. The alkoxides also can be used as catalyst but it is prohibitively expensive. The best results are obtained if the catalyst is 85% potassium hydroxide (KOH). The best grades of potassium hydroxide (KOH) contain 14%-15% water which can not be removed. It should be low in carbonate, because carbonate is not an efficient catalyst and may cause cloudiness in the final ester. Since the quality of catalyst used is fairly less, a good-quality catalyst (in spite of high cost) can be used.

Most commonly method used for biodiesel production is known as transesterification process. Transesterification means alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process. It is just like to hydrolysis. This process has been commonly used to reduce the viscosity of triglycerides (Vegetable Oils). The transesterification reaction is represented by the general equation.



If methanol is used in the above reaction it is termed as methanolysis. The reaction of triglyceride with methanol is represented by the general equation given below.



Triglycerides are readily transesterified in the presence of an alkaline catalyst at atmospheric pressure and at a temperature of approximately 60-70°C with an excess of methanol. The mixture at the end of reaction is permitted to settle. The lower part of glycerol layer is drawn off while the upper part of methyl ester layer is water washed to remove entrained glycerol and is then processed further. The excess methanol is recovered by distillation and sent to a rectifying column for purification and recycling. The transesterification works well when the starting oil is of a high quality. However, quite often, low-quality oils are used as raw materials for biodiesel preparation. In cases when the FFA content of the oil is above 1% difficulties occur due to the soaps formation which promotes emulsification during the water washing and if the FFA content above 2%, the process becomes not viable.

III. VARIABLES AFFECTING THE TRANSESTERIFICATION REACTION

A. Temperature of oil

The temperature of oil which is heated before mixing with catalyst and methanol or ethanol affects the reaction. It was observed that an increase in oil temperature slightly increases the percentage oil to biodiesel production as well as the

biodiesel recovery. The higher temperatures of oil during mixing of methanol or ethanol in oil may result in methanol or ethanol loss in the batch process.

B. Temperature of reaction

The transesterification reaction is efficiently influenced by the reaction temperature. Usually, the reaction is conducted close to the boiling point of methanol (60°-70°) at atmospheric pressure. The maximum yield of ester occurs at temperature ranging from 60°-80° at a molar ratio (alcohol to oil) of 6:1. An increase in the temperature is reported to have an adverse effect on the biodiesel recovery. In the case of the alkaline catalyst many studies have indicated that sufficient time to transesterification can proceed satisfactorily at ambient temperatures. The biodiesel recovery was affected at very low temperatures but conversion was nearly unaffected.

C. Alcohol to oil ratio

It is the main important variable affecting the yield of ester is the molar ratio of alcohol to vegetable or waste frying oil. A molar ratio of alcohol to oil 6:1 is usually used in industrial processes to obtain methyl ester yields higher than 98% by weight. A higher molar ratio of alcohol to vegetable oil or waste frying oil interferes in the separation of glycerol. The lower molar ratios required more reaction time while the higher molar ratios, conversion increased but recovery reduced due to poor separation of glycerol. The most favorable molar ratios depend upon the type and quality of oil used.

D. Type of catalyst and its concentration

The most effective transesterification catalyst is the alkali metal alkoxides compared to the acidic catalyst. Sodium alkoxides are most efficient catalysts used for this purpose although potassium hydroxide (KOH) and sodium hydroxide (NAOH) can also be used. Transmethylations occur many folds faster in the presence of an alkaline catalyst than those catalyzed by the same amount of acidic catalyst. Alkaline catalysts are mostly used for commercial transesterification. The range of alkaline catalyst concentration is 0.5%-1% by weight yields 94%-99% conversion of vegetable oil into esters (biodiesel). If the catalyst concentration is increased it does not increase the conversion of biodiesel fuel. But it adds the extra costs because the removal of the catalyst at the end of the reaction increases the time consumption. High FFAs value in the oil needs higher amounts of sodium hydroxide (NAOH) catalyst. Otherwise higher amount of sodium hydroxide resulted in reduced recovery. Recently a catalyst-free method for biodiesel production has been developed by employing supercritical methanol [89].

E. Intensity of mixing

Intensity of mixing also affects the transesterification reaction. It is more important during the slow rate region of the transesterification reaction. As the single phase is established, mixing becomes unimportant. In the process scale-up and design the understanding of mixing effects on kinetics of transesterification reaction process is a precious. After adding methanol and catalyst to the oil stirring for 5-10 minutes help in higher rate of conversion and recovery.

F. Purity of reactants

Impurities of oil also affect the conversion levels into biodiesel.

At the same condition the conversion of crude vegetable oil into biodiesel is 67-84% while using refined oil the conversion into biodiesel (ester) is obtained ranges upto 94-97%. The amounts of FFAs (Free Fatty Acids) in the crude vegetable oil interfere with the catalyst. This problem can be overcome at the conditions of high pressure and high temperature. The production of biodiesel is equally good in comparison to refined oil. However the oil should be filtered. The quality of oil is very important for conversion into biodiesel. The oil settled at the bottom during storage give poor results in conversion into ester (biodiesel) due the accumulation of impurities similar to wax.

Various technologies are presently available for the industrial production of biodiesel which is sold under different trademarks, for example, the Italian process of novamont and the French IFP. A number of units are manufacturing biodiesel worldwide. These units are using sunflower oil, soybean oil, rapeseed oil, used-frying oil, jatropha oil, etc. as a source of triglycerides or crude oil.

IV. BIODIESEL CHARACTERISATION

At optimum condition biodiesel produces a clear yellow liquid. The conversion of ester (biodiesel) can be ensured by proton nuclear magnetic resonance ($^1\text{H-NMR}$). Gas chromatography or mass spectrometry is use to determine the fatty acid composition. The biodiesel produces from waste cooking palm oil exhibited more saturated fatty acids in comparison to unsaturated fatty acids [90]. The author tested the physical and chemical properties of WCO-ME / EE (Biodiesel) were compared with diesel and found that the kinematic viscosity of crude oil or WCO (Waste Cooking Oil) at 40°C was 19 times more than diesel at the same temperature. After the transesterification process of crude oil (WCO) into WCO-ME (Biodiesel) has eleven times less kinematic viscosity as compared to the WCO (crude oil). The calorific value (CV) of biodiesel obtained had 38.034 MJ/kg which is greater than that of WCO (35.82 MJ/kg) but less than the calorific value of diesel (42.11 MJ/kg). The reason of lower calorific value of WCO-ME/EE is responsible due to the presence of oxygen in the molecular structure of WCO-ME/EE (Biodiesel) which is proved by elemental analysis [90].

V. COMBUSTION, PERFORMANCE AND EMISSION OF CI ENGINE USING BIODIESEL & ITS BLENDS

A. Combustion

The blends of biodiesel (methyl esters) of soybean oil and diesel in a turbo-charged, four cylinders, DI (direct injection) CI (diesel) engine modified with bowl type piston and medium swirl type. The author found that the blends gave a smaller ignition delay and combustion characteristics were similar as diesel [91]. The use of methyl ester of tallowate as fuel in six-cylinder, direct injection (DI) 306 kW diesel engine at-cylinder pressure characteristics of a six-cylinder, direct injection, 306 kW diesel engine using esters of methyl tallowate as fuel. The author found that the blend of diesel methyl tallowate for the Peak rate of heat release to be lower than diesel [92].

An experiments conducting on a shock tube test rig with varying factors like equivalence ratio, ignition pressure and ignition temperature during the effect of ignition delay period of jojoba methyl ester, the author reported that the ignition delay period for jojoba methyl ester was lower while the

ignition pressure and ignition temperature were higher [93]. In a comparison of the effective pressure of used cooking oil biodiesel blended with glycerine and petroleum-based diesel in a direct injection diesel engine obtained that the effective pressure of these fuels yielded similar results for values up to 2000 rpm [94].

The combustion performance of ethyl ester of used palm oil relative to baseline diesel fuel in a water-cooled furnace was investigated and the combustion efficiency was tested over a wide range of air/fuel ratio ranging from very lean to very rich (10:1–20:1). The author found that at a lower energy rate, biodiesel burned more efficiently with higher combustion efficiency (66%) compared to 56% for the diesel fuel. At higher energy input of biodiesel combustion performance deteriorated because of its high density, viscosity and low volatility [95]. The methyl ester of waste olive oil used a DI diesel Perkins engine to study the effect on combustion efficiency. The results obtained that as oxygen concentration increased it provided more oxygen for combustion and the combustion efficiency did not drop during testing. It remained nearly constant using either methyl ester of waste olive oil or diesel fuel [96].

At a high-temperature and higher engine load inside the engine cylinder decreases the ignition delay. Biodiesel showed smaller ignition delay when it compared with diesel fuel for entire load range. The author observed that the minimum ignition delay period of 10.9°C which was 1.8°C shorter than petro-diesel at 100% load condition. This is primarily due to the higher cetane number of biodiesel [97, 98].

The ignition delay of the JTME and its blends are less as compared to that of petro-diesel fuel at the all loads conditions. Ignition delay can reduce with an increase in the quantity of JTME in the blend at all loads conditions. When the amount of JTME increases in the blend a large temperature drop is brought about owing to the absorption of heat resulting in the evaporation of fuel. This phenomenon might contribute to the increase in ignition delay however the amount of oxygen content in the JTME improves the ignitability and conquer the above-mentioned effect and may lead to the decrease of ignition delay [99].

B. Performance

The brake thermal efficiency of biodiesel (WCO-ME/EE) is lower than that of diesel at 100% load condition. Biodiesel showed higher BSEC (Brake Specific Energy Consumption) than that of diesel fuel for all loads conditions. This is due to the lower calorific value of biodiesel. The lower calorific value and higher viscosity of biodiesel lead to the lower brake thermal efficiency. The value of higher viscosity causes poor fuel atomization during the injection process that increases the engine deposits and increases more energy consumption to pump the fuel which wears fuel pump elements and injectors [76]. The brake power of biodiesel was almost the same as with petro-diesel, while the specific fuel consumption was higher than that of petrodiesel. The carbon deposits inside the engine were usual, with the exception of intake valve deposits. The performance of biodiesel fuels can improve by the additives in compression ignition (diesel) engines.

The use of rapeseed, sunflower, and safflower oils as liquid fuels was investigated and found that power output of engine is similar to that of diesel fuel. Due to carbonization long-term durability tests signifies strict problems in to the engine [100].

The use of rapeseed oil blends as fuel in an air-cooled, 300 cm³ indirect injection diesel engine and found that the output power was less for neat rapeseed oil in comparison to diesel and increased with increasing amount of rapeseed oil in the blend [101].

Brake thermal efficiencies of single cylinder diesel engine running on biodiesel from rubber seed oil and its blends with diesel were found lower for biodiesel blends compared to diesel. The lower heat release rates and higher combustion duration were recorded for biodiesel [102]. The performance of diesel engine using jatropha oil and its blends with diesel had investigated and found the significant enhancement in engine performance when compared to neat vegetable oil. Due to decrease in the viscosity of the vegetable oil the specific fuel consumption was minimized. The acceptable thermal efficiencies of the diesel engine had obtained with blends containing up to 50% of jatropha oil [103]. Engine performance test carried on a single-cylinder, four-stroke, naturally aspirated, direct injection (DI), and water-cooled diesel engine test rig. The test was conducted at different loads starting from no load condition to the rated full load using diesel, fresh oil biodiesel and WCO biodiesel. Results showed that the performance of the pure WCO biodiesel was only marginally lesser at part loads compared to diesel fuel performance. At higher loads the engine suffers from closely 1–1.5% brake thermal efficiency loss. However the thermal performance of WCO biodiesel closely bears a resemblance to the performance of fresh oil biodiesel [104]. The result of testing WCO biodiesel in a DI commercial diesel engine either pure or blends with diesel fuel was obtained the biodiesel concentration in the blend was increased, the BSFC increased. The efficiency of the engine remained unaffected at each tested operation mode [105]. In investigating the effect of the alcohol used in the production of WCO biodiesel on diesel engine performance obtained same results. The use of pure biodiesel fuels and their blends resulted in a small increase in fuel consumption while the brake thermal efficiencies were similar as compared to diesel fuel [106].

Figure (2) shows the variation in the brake specific fuel consumption (BSFC) for the various fuels with increasing load on the engine. For all the fuels, the specific fuel consumption decreases with an increase in load. The amount of JTME in the blend increases the specific fuel consumption due to the lower heating value of JTME as compared to the diesel fuel [107].

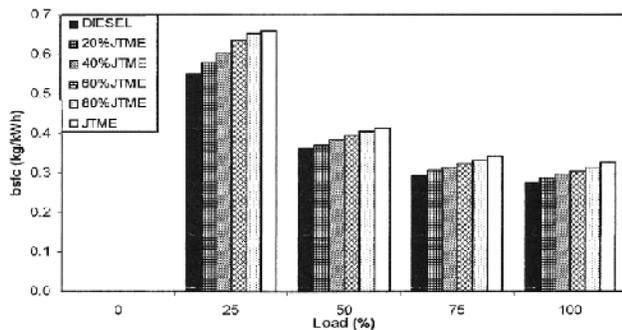


Fig. 2. Brake specific fuel consumption (BSFC).

Figure (3) shows the comparison of brake thermal efficiency of JTME, diesel oil and blended fuels at various loads. The brake thermal efficiency increases with increase in load for all the fuels. The brake thermal efficiency of JTME

blends with diesel decreases with an increase in amount of JTME in the blends. If an increment in amount of JTME blends the thermal efficiency decrease due to the earlier start of combustion than for diesel which increases the compression work. Since the engine operates under constant injection advance, the smaller ignition delay of JTME leads to initiation of combustion much before TDC. That increases the compression work as well as heat losses and thus the efficiency of the engine decreases. [107].

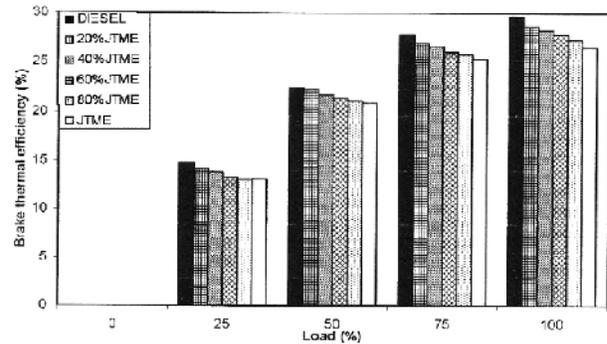


Fig. 3. Brake thermal efficiency.

C. Emissions

Biodiesel is nontoxic, biodegradable and it can significantly reduce toxic emissions and overall life cycle emission of carbon dioxide (CO₂) from the engine when used as a fuel [108, 109]. Biodiesel can be also used as a blended fuel in CI engines without any modification to the engines. An extensive review on the effect of biodiesel fuels on CI engine emissions found that in most of the investigations, HC, CO, smoke and particulate emissions are reduced. However, there is a slight increase in NO_x emission [106]. Biodiesel production from waste cooking oil (WCO) minimizes its cost and also advantages of decreasing waste oil disposal [110,111]. The percentage of carbon monoxide (CO), oxides of nitrogen (NO_x) and smoke emissions were slightly lower for soybean ester than diesel, whereas HC emission showed 50% reduction compared to diesel [112]. In the test of Karanja methyl ester (KME) and its blends with diesel from 20% to 80% by volume in a single cylinder direct injection (DI) diesel engine found that the carbon monoxide (CO), NO_x and smoke emissions were lower [113]. The emission characteristics of four stroke, four-cylinder, direct injection, unmodified, naturally aspirated diesel engine operating on neat rapeseed methyl ester (RPE) and its 5%, 10%, 20% and 35% blends with diesel fuel resulted carbon monoxide, hydrocarbon and visible emissions had decreased while an oxide of nitrogen emissions increased for methyl ester compared to diesel [114].

Biodiesel contains oxygen in structure which burns clearly that results the CO, CO₂ and UBHC emissions are reduced in bio-diesel and its blends. NO_x emissions are slightly increased in bio-diesel and its blends. This is due to the higher temperature in the combustion chamber using biodiesel [115, 116]. The exhaust gas recirculation can be used to give NO_x reduction up to 50% and reduce smoke emission by 15% by EGR [117, 118].

Single-cylinder engine tested at 2000 rpm and different loads with diesel fuel and three biodiesel fuels from used cooking oil. The biodiesel has different acid values from 0.33 to 0.90 mg KOH/g. As the acid value was increases the emissions of CO were also increases.

They measured small reduce in NO_x emissions at low loads but NO_x increases at high loads. The larger decreases in particulate matter (PM) emissions were observed at high load operation conditions [119]. A Perkins four-cylinder, four stroke diesel engine to investigate the exhaust emissions of WCO biodiesel produced by microwave irradiation. The slight increase in NO_x emissions decreases in CO, NO and NO₂ emissions as a result of firing biodiesel were found to be statistically important compared to the emissions of burning of petro-diesel fuel [120].

Fuel Properties of biodiesel and diesel fuel are mentioned in table 1. [98].

Table 1.

Sr. No.	Property	Diesel Fuel	Biodiesel	Procedure
1	Specific Gravity @15/15°C	0.8380	0.8830	ASTM D1298
2	Color	1.0	6.0	ASTM D1500
3	Cloud point °C	NA ^a	0.0	ASTM D2500
4	Pour Point °C	-3.0	0.0	ASTM D97
5	Flash Point °C	75.0	109	ASTM D93
6	Refractive Index	NA	1.45	-
7	Gross CV	4373	39305	ASTM D240
8	Kinematic Viscosity @ 20 °C (cst)	NA	15.09	ASTM D445
9	Conradson Carbon residue (wt %)	NA	0.30	ASTM D189
10	Total Sulfur Content	0.95	0.18	ASTM D1266

^aNA stands for not available. Source from [98].

The variation of carbon monoxide (CO) emission for different test fuels is shown in Figure 4. With increase of BMEP the emission of CO increases. The CO emission of biodiesel was lower than diesel fuel at all load conditions. The reduction of 43.3% in CO emission was observed using biodiesel when it compared to diesel at 100% load condition. It is due to higher cetane number and the higher oxygen content of the biodiesel [121].

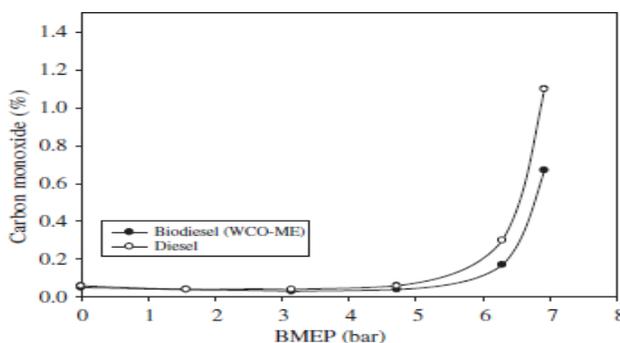


Fig. 4. Variation of CO emission with BMEP for test fuels.

The comparison between unburnt hydrocarbons (UHC) emissions for the test fuels is illustrated in Figure 5. UHC emission of biodiesel was lower than that of diesel for entire load range. At 100% load condition, UHC emission with biodiesel was 17 ppm which is 52.7% lower than that of diesel. The percentage of UHC reduction in emission using biodiesel is due to the higher cetane number and oxygen content of the biodiesel [121].

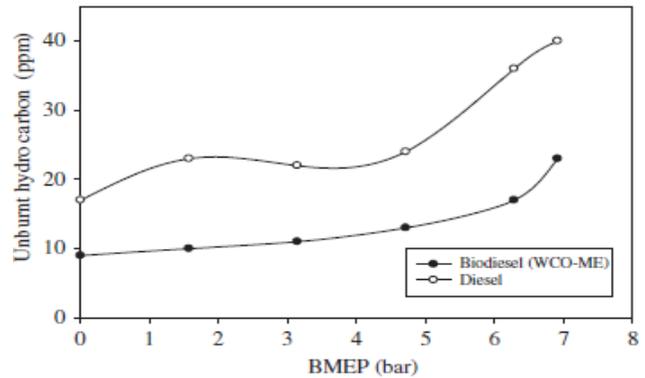


Fig. 5. Variation of UHC emission with BMEP for test fuels.

VI. CONCLUSIONS

The process of transesterification is a most commonly use to indicate the direct conversion of triacylglycerol lipids by the application of alcohols into alkyl esters without isolating the free fatty acids first. The purpose of the transesterification of vegetable oils to their methyl esters or ethyl ester (bio diesels) process is to lower the viscosity of the oil. Transesterification reactions can be catalyzed by acids, alkalis, or enzymes. The brake thermal efficiency of biodiesel (WCO-ME/EE) is lower than of diesel at 100% load condition. The brake power of biodiesel is approximately equal to diesel, while the specific fuel consumption is higher than that of diesel. The carbon deposits inside the engine as usual with the exception of intake valve deposits. The performance of biodiesel can be improved with the utilization of additives in compression ignition (CI) engines. Biodiesel has a high cetane number in comparison to petroleum diesel fuel. This results in higher combustion efficiency and smoother combustion.

Biodiesel has a comparatively high flash point (150°C) which makes it less volatile and safer to transport or handle than petroleum diesel fuel [13]. The properties of biodiesel provide lubrication that can decrease engine wear and increase engine life [90]. Biodiesel is biodegradable, non toxic, readily available has a high heat value and high oxygen content (10-11%). it does not contain sulphurs and aromatic compounds [17]. The properties of biodiesel diminish CO, SO_x, hydrocarbons and PM emissions. In addition, biodiesel does not contribute to global warming due to its carbon closed cycle [124].

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