2. LITERATURE REVIEW

2.1. INTRODUCTION

In the recent years, biodiesel has gained increased attention among scientists and researchers to use it as a substitute for fossil diesel in diesel engine applications. To understand the current scenario about biodiesel utility and its related issues, an extensive literature review has been carried out and reported in this chapter. The present review highlights the various issues related to biodiesel such as vegetable oil as fuel, biodiesel preparation methods, biodiesel production by transesterification process, optimisation of biodiesel production and use of biodiesel and its diesel blends as fuel in an unmodified diesel engines.

2.2. VEGETABLE OIL AS FUEL

“The use of vegetable oils for engine fuels may seem insignificant today, but such oils may in course of time be as important as petroleum and the coal tar products of the present time” said by Rudolph Diesel around 100 years ago when he has tested peanut oil in his CI engine. Rudolph Diesel made an attempt to use peanut oil directly as a fuel in diesel engine [9]. Being renewable in nature, vegetable oils are assuring feed stocks for biodiesel production.

There are many problems encountered during the direct usage of vegetable oils in diesel engines such as improper fuel atomization due to plugged orifices, gelling of lubrication oil, carbon deposits, and oil ring sticking etc.. All the above stated problems are due to the high viscosity and low volatilities of the vegetable oil and animal fats which cause improper vaporization, incomplete combustion and deposits in engines [10].

Large triglyceride molecule and higher molecular mass are the reasons for high viscosity of vegetable oils. An effective method of overcoming all the problems of direct use of vegetable oils as fuel in diesel engine is to convert
the oil into less viscous mono alkyl esters called biodiesel [11]. Biodiesel has higher cetane number than petroleum diesel, no aromatics, and contains 10-11% oxygen by weight thus facilitating complete combustion. These characteristics reduce the emissions of carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) in comparison with diesel [12].

Biodiesels possess attractive characteristics such as non-toxic, biodegradability, less pollutant to water and soil and contains very small amount of phosphorus and sulphur [13 & 14]. Monyem et al. (2001) pointed out the biodiesel suffers from lower calorific value, lower power output and increased NOx emission, despite having some advantages [15].

Sharma et al. (2008) recorded the latest aspects of development of biodiesel. It was reported that the yield of biodiesel was affected by molar ratio, moisture and water content, reaction temperature, stirring, specific gravity, etc.. The authors have critically reviewed the biodegradability, kinetics involved in the process of biodiesel production, and its stability. During the review, emissions and performance of biodiesel have also been reported. The authors felt that the edible oils are used extensively in developed nations such as USA and European nations but developing nations are not self-sufficient in the production of edible oils. It was concluded that the seeds of many plant species remain unutilized for the production of biodiesel [16].

2.3. BIODIESEL PREPARATION METHODS

Past research works revealed that high viscosity, density, iodine value and poor non volatality are the problems associated with the use of vegetable oils in diesel engines leading to problems in pumping, atomization and gumming, injector fouling, piston and ring sticking and contamination of lubricating oils in the long run operations [17-19]. Hence it is essential to reduce the viscosity of the vegetable oils by methods like preheating, thermal cracking and transesterification. Peterson et al. (1983) reiterated that the two major problems associated with the use of vegetable oils as fuels were oil deterioration and incomplete combustion [20].
Bagby (1987) reiterated that the high viscosity of vegetable oils leads to poor fuel atomization and inefficient mixing with air, which in turn contribute to incomplete combustion [21]. Even though vegetable oils can be successfully used in diesel engines, in long-term use, durability problems like nozzle coking, carbon deposition in different parts of the engine and lubricating oil dilution are encountered [22].

Considerable research has been carried out on vegetable oils as substitute to diesel fuel, which includes rubber seed oil, cottonseed oil, palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil, tung oil and others. Many researchers investigated the different methods to overcome the problems associated with the use of vegetable oils as diesel engine fuel i.e. conversion in to biodiesel [23].

Dennis et al. (2010) reviewed the different approaches of reducing free fatty acids in the raw oil and refinement of crude biodiesel that are adopted in the industry. The authors described other new processes of biodiesel production. It was concluded that with increasing concern over global warming, it is foreseeable that biodiesel usage would continue to grow at a fast pace which will trigger the development of more sophisticated methods of biodiesel production to cope with the increasing market demand [24].

Gerpen (2005) has discussed the processing and production of biodiesel. He observed that the reaction conditions involve a trade-off between reaction time and temperature and most of the process complexity originates from contaminants in the feedstock, such as water and free fatty acids, or impurities in the final product, such as methanol, free glycerol, and soap. The author has developed processes to produce biodiesel from high free fatty acid feedstock, such as recycled restaurant grease, animal fats, and soap stock. He has concluded that the biodiesel is an important new alternative transportation fuel which can be produced from many vegetable oil or animal fat feedstock [25].
(i) **Micro emulsions**

Pryde (1984) reported that micro emulsions could improve the spray characteristics of the vegetable oils by explosive vaporization of the low boiling constituents [26]. Ziejewski et al. (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol and 33.4% (vol) 1-butanol. This nonionic emulsion had a viscosity of 6.31 cSt at 40°C, a cetane number of 25 and an ash content of less than 0.01%. Lower viscosities, better spray patterns, no compromise in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscosity were also resulted [27]. Lin and Wang (2004) studied the effects of combustion improver on the engine performance and emission using three phase emulsions as fuel [28]. Schwab et al. (1987) studied the effect of micro emulsions with solvents such as methanol, ethanol and 1-butanol on the viscosity of vegetable oils for use in engines [29].

(ii) **Thermal cracking (pyrolysis)**

Pyrolysis is the process of conversion of one substance into another by means of heat or by heat with the aid of a catalyst. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum [30]. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules [31].

Chang and Wan (1947) reported a large-scale thermal cracking of tung oil calcium soaps. Tung oil was first saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene. 68 kg of the soap from the saponification of tung oil produced 50 liters of crude oil [32]. Soybean oil was thermally decomposed and distilled in air and nitrogen spared with a standard ASTM distillation apparatus [33 & 34]. Billaud et al. (1995) pyrolyzed rapeseed oil to
produce a mixture of methyl esters in a tubular reactor between 500 °C and 850 °C [35].

(iii) **Transesterification (Alcoholysis)**

Transesterification is the process of converting a fat or vegetable oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield [36]. Methanol, ethanol, propanol, butanol and amyl alcohol are some of the alcohols used in the transesterification process. Methanol and ethanol are the most commonly used in this chemical reaction. The reason is primarily due to its superior advantages of high solubility in oil, fast reaction rate with triglycerides, good physical and chemical properties, and low cost [37]. Zhang (1994) transesterified edible beef tallow with a free fatty acid content of 0.27% [38]. Ma et al. (1998, 1999) have also studied the transesterification process of beef tallow with methanol [39 & 40].

2.4. **BIO DIESEL PRODUCTION BY TRANSESTERIFICATION PROCESS**

Demirbas (2003) carried out a detailed review on the production and characterization of biodiesel and a review of various experimental works with biodiesel. In this work, it was reported that the transesterification of triglycerides by methanol, ethanol, propanol and butanol proved to be the most promising process for converting the vegetable oils into biodiesels [41].

Ghadge and Raheman (2005) developed a technique to produce biodiesel from mahua oil (Madhuca indica) with high free fatty acids (19% FFA). The high FFA level of mahua oil was reduced to less than 1% by a two-step pretreatment process. Each step was carried out with 0.30–0.35 v/v methanol to oil ratio in the presence of 1% v/v H2SO4 as an acid catalyst in 1-hour reaction at 60°C. After the reaction, the mixture was allowed to settle for an hour and methanol–water mixture that separated at the top was removed. The second step product at the bottom was transesterified using 0.25-v/v methanol and 0.7% w/v KOH as alkaline catalyst to produce biodiesel.
The fuel properties of mahua biodiesel were comparable to those of diesel and conforming to both the American and European standards [42].

Sanjib et al. (2005) prepared biodiesel from Pongamia Pinnata by transesterification of the crude oil with methanol and KOH as the catalyst and reported that properties such as viscosity, flash point compare well with accepted biodiesel standards [43].

Burnwal and Sharma (2005) reported two different methods for improvement in fuel properties (i) catalytic transesterification of triglycerides with alcohols to form mono alkyl esters of long chain fatty acids (ii) the supercritical method of producing biodiesel, which is quite similar to hydrocarbon based diesel fuels [44].

Bala (2005) strongly insisted that although there are many ways and procedure to convert vegetable oil into biodiesel, transesterification process was found to be the most viable oil modification process [45].

Sreeprasath et al. (2006) applied Fe-Zn double metal cyanide (DMC) complexes as solid acid catalysts in the preparation of fatty acid alkyl esters (biodiesel / biolubricants) from vegetable oils. It is reported that unlike other solid catalysts, the fe-zn DMC catalysts are highly active even for the simultaneous transesterification of triglycerides and esterification of the free fatty acids present in unrefined and waste cooking oils as well as non-edible oils [46].

Sahoo et al. (2006) prepared biodiesel (Polanga oil methyl ester) from polanga (calophyllum inophyllum) oil by triple stage transesterification process [47]. Richard et al. (2006) prepared biodiesel through transesterification process from beef tallow, a bi-product of meat production and processing system and investigated the resource availability, energetic efficiency, and economic feasibility of this biodiesel as a substitute to diesel [48].
He et al. (2007) prepared methyl esters (biodiesel) by the transesterification of cottonseed oil with methanol in the presence of solid acids as heterogeneous catalysts. The authors found that the methyl esters yielded over 90% under the conditions of 230°C, reaction time of 8 h and catalyst amount (catalyst/oil) of 2% (w) [49].

Demirbas (2008) conducted comparative studies on transesterification methods. It was found that diesel is obtained from a chemical reaction called transesterification (ester exchange) and the reaction converts esters from long chain fatty acids into mono alkyl esters. The authors observed that the vegetable oils can be transesterified by heating them with a large excess of anhydrous methanol and an acidic or basic reagent as catalyst. They also developed a non-catalytic biodiesel production route with supercritical methanol which gives high yield due to the transesterification of triglycerides and methyl esterification of fatty acids. The authors concluded that increasing the reaction temperature to supercritical conditions had a favorable influence on the yield of ester conversion [50].

Moser (2009) elaborated the process of biodiesel preparation, the types of catalysts used in biodiesel production, the influence of free fatty acids on biodiesel production and the use of different monohydric alcohols in the preparation of biodiesel [51].

Lin et al. (2009) proposed fermentation, transesterification and pyrolysis of biomass, industrial and domestic wastes as alternative solutions for the increasing energy demand. The authors carried out the production of biodiesel from RBO. Overall results from the study confirm that RBO may be used as a resource to obtain biodiesel by a series of experiments. One of the main conclusions derived from this study is that the high FFA level of crude rice bran oil can be reduced to less than 0.5% in a two-step pretreatment process of esterification using acid-catalyzed reaction with methanol [52].

Hanh (2009) studied the biodiesel production through transesterification of triolein with various alcohols such as methanol, ethanol,
propanol, butanol, hexanol, octanol and decanol. It was recorded that the rate of alkyl ester formation under the ultrasonic irradiation condition was higher than that under the stirring condition. The authors confirmed that the rate depended upon the kind of alcohols as the number of carbon in alcohol increased, the rate of the ester formation tended to decrease [53].

Oliviera et al. (2010) investigated the production of biodiesel by esterification with ethanol using waste oil generated in the refining of coconut oil. During the study, methanol was also evaluated as an esterification agent and conversions over 99 % mol were observed for both ethanol and methanol [54].

Vieitez et al. (2010) investigated and compared the reaction performance of soybean oil transesterification under supercritical methanol and ethanol, in a continuous catalyst-free process, as a cleaner alternative to conventional chemically catalyzed process. The authors performed reactions in a tubular reactor, at 20 MPa, with oil to alcohol ratio of 1:40. The authors concluded that both methanolysis and ethanolysis of refined soybean oil at different temperatures can be conveniently performed in order to maximize the alkyl ester content in the product and minimize the degradation of fatty acids [55].

Mthiyazhagan and Ganapathy (2011) reviewed the factors involved in transesterification reaction and recorded that biodiesel is a renewable alternate fuel to diesel engines which can partially or fully replace or reduce the use of petroleum diesel fuel and it can be produced from plant and animal fats through transesterification reaction [56].

Chandra Deka (2012) synthesised biodiesel from Pithecellobium monadelphum seed oil by transesterification with methanol and determined the composition of the biodiesel by employing various instrumental techniques. The chemical composition of biodiesel was determined by GC-MS analysis [57].
2.5. OPTIMIZATION OF BIODIESEL PRODUCTION

The process of transforming sunflower oil into biodiesel through transesterification process was optimized using Taguchi’s methodology. Three times of stoichiometric quantity of methanol, 0.28% w/w of potassium hydroxide, reaction temperature of 70 °C and two times washing process were identified as the optimum set of parameters with maximum conversion rate [58].

Prakash et al. (2006) optimized the transesterification parameters reaction temperature, quantity of alcohol, amount of catalyst and reaction time using Taguchi method. Methanol with KOH as base catalyst was used in the experiments. 1.5 g of KOH, 45 ml of methanol, 80 °C of reaction temperature and reaction time of 60 min were found to be the optimized data for 100 ml of Pongamia Pinnata seed oil. The maximum contribution of 59.5% on the yield was recorded for amount of methanol followed by the amount of catalyst with 32.66% [59].

Meher (2006), based on his investigation on optimization of alkali catalyst methanolysis of Pongamia Pinnata oil, he has recorded 97 – 98% of yield with 6:1 molar ratio of MeOH to oil, 65 °C temperature, and 360 rpm stirring speed within two hours [60].

Alok Kumar Tiwari et al. (2007) could reduce the FFA level of raw jatropha oil from 14% to less than 1% through pre-treatment with optimized parameter values of methanol (0.28 v/v), H₂SO₄ as catalyst (1.43% v/v) in 88-min reaction time at 60 °C temperature. In the second step transesterification, optimized parameter values of methanol (0.16 v/v) and 24 min of reaction time resulted in 99% yield [61].

Umer Rashid (2008) could achieve a biodiesel yield of 97.1% from sunflower oil using alkali catalyzed methanolysis with the optimized parameter values of 6:1 molar ratio of menthol to oil, reaction temperature of 60 °C and
1 wt % of catalyst amount. He has also concluded that among NaOH, KOH, NaOCH$_3$ and KOCH$_3$, NaOH is the suitable catalyst [62].

Eevera et al. (2009) have done an extensive study on optimizing process parameters such as amount of methanol, amount of sodium hydroxide, reaction time and reaction temperature for both edible and non-edible oils. Coconut oil, palm oil, groundnut oil, rice bran oil and gingelly oil are edible in nature and Pongamia, cotton seed oil and neem oil are non-edible oils considered for the study. Traditional optimization method was adapted in this study. The optimal value of each parameter was obtained by considering other parameters at constant level. After optimal value of each parameter was attained, those parameters were used for other parameter optimization. Out of five levels of each variables, 1.5 wt % of catalyst, 90 min of reaction time, 210 ml of alcohol and 50 ºC of reaction temperature were obtained as the optimal values for different oil types [63].

Kyong-Hwan Chung et al. (2009) recorded that the optimum parameter values of KOH 0.5% wt, 6:1 molar ratio of methanol to duck tallow and 3 hours of reaction time for the yield of 97% biodiesel from duck tallow, with no significant influence from reaction temperature [64]. Prafulla and Shuguang (2009) optimized the transesterification process parameters for some of the edible and non-edible vegetable oils and reported a biodiesel yield of about 90–95% for Jatropha, 80–85% for Pongamia, 80–95% for canola, and 85–96% for corn using potassium hydroxide (KOH) as catalyst [65].

Nakpong and Wootthikanokkhan (2010) used coconut oil with 12.8% free fatty acid (FFA) as a feedstock to produce biodiesel by a two-step process. The authors studied the effect of parameters related to these processes and optimized the parameters of methanol-to-oil ratio, catalyst concentration, reaction temperature, and reaction time. Methyl ester content of the coconut biodiesel was determined by GC to be 98.4% under the optimum condition. It was concluded that the viscosity of coconut biodiesel product was very close to that of Thai petroleum diesel and other measured properties met the Thai biodiesel (B100) specification [66].
The utility of non-edible moringa oleifera oil for biodiesel production was studied by Kafuku and Mbarawa (2010). The single step transesterification process using base catalyst was adopted for biodiesel production based on the acid value of oil which was found to be 0.6% (<2.5%). Five most influencing process parameters such as catalyst amount, methanol to oil ratio, reaction time, reaction temperature and agitation speed were considered for optimization process. Each parameter was varied with five levels. For identifying the effect of one parameter on end effect, other parameters were kept constant. At the end of the study, 1% (wt) of catalyst amount, methanol quantity of 30% (wt), 60 °C reaction temperature, 60 min of reaction time and 400 rpm of agitation speed were identified as the optimum results with 82% of conversion efficiency [67].

Sun Tae Kim et al. (2010) adopted Taguchi method for optimization of process parameters for Rapeseed methyl ester production. It was reported that, 96.7% yield of biodiesel was achieved using Potassium hydroxide as the catalyst, 1.5 Wt% catalyst concentration and 60 °C of reaction temperature as optimized parameters values [68].

Biodiesel production optimization from camelina seed oil using orthogonal experimental design has been carried out by Xuan Wu (2011). Methanol quantity, reaction time, reaction temperature and catalyst concentration were the four major parameters considered for optimization process. Catalyst concentration was identified as the most significant factor affecting the biodiesel yield followed by reaction time, reaction temperature and methanol to oil ratio. 95.8% of biodiesel yield was achieved under the optimum conditions of 8:1 methanol to oil ratio, 70 min reaction time, 50 °C of reaction temperature and 1% (wt) of catalyst [69].

Optimization of process parameters of two stage esterification process using design of experiments for high fatty acid rubber seed oil has been studied by Edwin Raj et al. (2011). The optimization problem was aimed at reducing the acid value in the first stage esterification process and maximizing the methyl ester yield in in second stage transesterification process. H₂SO₄
and NaOH were used as catalyst in first and second stage process respectively. Multi variant approach called response surface design was used in this study, as it took in to account of interaction effect between the variables. The minimum acid value at the end of the first stage esterification optimization was 3.8 mg KOH/g. Maximum methyl ester yield of 97.1% was attained with the following optimum set of variables: 0.2% (v/v) methanol to oil ratio, 0.5% (w/v) NaOH at 51.23 °C temperature and at 82.52 min time [70].

2.6. DIESEL ENGINE FUELED WITH BIODIESEL AND ITS DIESEL BLENDS

Dorado et al. (2003) analysed the exhaust emissions characteristics of a direct injection diesel engine fuelled with methyl ester of waste olive oil. The results revealed 58.9% reduction in CO emission, upto 8.6 % reduction in CO2 emission, upto 57.7% reduction in SOx with slight increase in brake specific fuel consumption and NOx emission [71].

Ramadhas et al. (2005) derived biodiesel from high free fatty acid Rubber seed oil, through two step transesterification and successfully used Rubber seed oil methyl ester as fuel in diesel engine with a notable increase in brake thermal efficiency and decrease in fuel consumption [72].

Sukumar Puhan et al. (2005) produced biodiesel from mahua oil by transesterification using sulfuric acid (H2SO4) as catalyst and ethanol as alcohol, conducted an experimental investigation on a 4-stroke direct injection natural aspirated diesel engine at a rated speed of 1500 rpm with different brake mean effective pressures and reported that Mahua oil ethyl ester produced, brake thermal efficiency at par with diesel and improved emissions in comparison with diesel [73].

Lin and Lin (2006) compared the performance, combustion and emission characteristics of a diesel engine fuelled with biodiesel from soybean oil, produced with and without peroxidation process. The results showed that the fuel consumption rate, brake thermal efficiency, equivalence ratio and
exhaust gas temperature were higher while emissions of CO\textsubscript{2}, CO and NO\textsubscript{x} were lower for fuel produced with peroxidation process [74].

Sahoo et al. (2007) prepared biodiesel from high free fatty acid (44 mg KOH/gm) polanga oil through three stage transesterification process and successfully tested an unmodified diesel engine fuelled with 100% polanga oil methyl ester with 0.1% improved thermal efficiency, 3.5% reduction in smoke emission and 4% reduction in NO\textsubscript{x} emission in comparison with diesel at full load [75].

Canakci (2007) compared the combustion characteristics of soybean biodiesel with two different petroleum diesels at steady state conditions in a four cylinder turbocharged diesel engine at full load with a rated speed of 1400 rpm. It was reported that use of biodiesel resulted in 11.2% increase in NO\textsubscript{x} with a significant reduction in PM, CO and UBHC emissions and with 11.8% increase in bsfc in comparison with petroleum diesel [76].

Karthikeyan and Mahalakshmi (2007) investigated the feasibility of use of a new bio-oil, turpentine derived from the resin of pine tree as a fuel in a dual fuel engine. The study ascertained the possibility of 60–65% replacement of diesel with turpentine within 75% load with better engine performance and better emissions except CO and UBHC [77].

Ejas (2008) through an extensive literature review made a general comment that 20% blending of biodiesel with diesel could be a better fuel for long run diesel engine applications without any engine modifications [78].

Srivastava and Madhumita (2008) tested methyl esters of Karanja oil in a direct injection diesel engine and recorded a small reduction in thermal efficiency with the corresponding increase in brake specific fuel consumption and increased emissions of CO, HC and NO\textsubscript{x} [79].

Sureshkumar et al. (2008) carried out an experimental investigation in an unmodified diesel engine fuelled with Pongamia Pinnata methyl ester
(PPME) and ascertained that, the blends of PPME with diesel up to 40% by volume (B40) provide better engine performance in terms of brake specific fuel consumption (BSFC) and brake specific energy consumption (BSEC) and improved emission characteristics [80].

Godiganur et al. (2009) carried out an experimental investigation on a Cummins 158 HP rated power, turbocharged heavy duty diesel engine fuelled with mahua oil methyl ester and its diesel blends and reported that 20% blending of mahua oil methyl ester with diesel could be suitable alternative fuel for heavy-duty engines with performance and emissions at par with diesel [81].

Baiju et al. (2009) produced methyl and ethyl esters from Pongamia Pinnata oil and tested in a compression ignition engine with several diesel blends. They had reported that methyl ester showed better performance and emission characteristics than that of ethyl ester of Pongamia oil and 10 – 25% increase in NOx emission was noted for both biodiesel in comparison with diesel at part loads [82].

Devan and Mahalakshmi (2009) used blends of paradise oil methyl ester and eucalyptus oil as a total replacement for diesel to run an unmodified CI engine and successfully reported that 49% reduction in smoke, 34.5% reduction in HC emission, 37% reduction in CO emission and 2.7% increase in NOx emission with 2.4% increase in brake thermal efficiency for 50% (v/v) blend of both oils at full load condition [83].

Nurun et al. (2009) used cotton seed oil methyl ester to run a CI engine and reiterated that 10% addition of the biodiesel with diesel resulted in 24% reduction in particulate matters and 14% reduction in smoke emissions as compared to diesel. They also experienced that 30% addition of biodiesel resulted in 24% reduction in CO emission and 10% increased NOx emission [84].

Sahoo et al. (2009) produced methyl esters from three different non edible oils namely Jatropha, Karanja and Polanga and tested them in a three
cylinder water cooled tractor engine. Nine different test fuels were produced with 20%, 50% and 100% blends of each biodiesel with diesel and the results were compared with diesel. It was reported that the maximum increase in power was observed for 50% jatropha biodiesel and diesel blend at the rated speed [85].

Purushothaman and Nagarajan (2009) examined the performance, emission and combustion characteristics of a single cylinder, constant speed, direct injection diesel engine fuelled with raw orange oil and compared the results with standard diesel. It was concluded that use of orange oil resulted in better performance and combustion characteristics with reduced CO and HC emissions and increased NO\textsubscript{x} emission as compared to diesel [86].

Haldar et al. (2009) had produced alternative fuels form three different non edible oils namely Putranjiva, Jatropha and Karanja through a new chemical process called degumming and conducted an experimental investigation on a diesel engine. The results confirmed the improved performance and emission characteristics produced by Jatropha oil in comparison with other fuels [87].

Aydin and Ilkilic (2010) studied the effect of ethanol as an additive to biodiesel for unmodified diesel engines applications. The results confirmed that 20% addition of ethanol with 80% biodiesel produced improved performance with reduced emissions in comparison with biodiesel diesel blend B20 [88].

Jindal et al. (2010) tested a diesel engine fuelled with 100% Jatropha methyl ester and concluded that a compression ratio of 18 and injection pressure of 250 bar were the optimum working conditions to run the engine without any compromise on engine performance and emission characteristics [89].

Panwar et al. (2010) confirmed the possibility of use of methyl esters of caster seed oil (derived through transesterification using KOH as catalyst) as
fuel in a diesel engine. The experimental investigation revealed that test fuels with lower biodiesel content produced improved brake thermal efficiency with reduced fuel consumption [90].

Rao (2011) investigated the combustion and NO$_x$ emission characteristics of Pongamia Pinnata methyl ester fuelled naturally aspirated, single cylinder, four-stroke, stationary, water cooled, rated speed, direct injection diesel engine and also studied the effect of preheating of the biodiesel and compared the results with diesel. It was recorded that the peak pressure and net heat release were slightly high for biodiesel against diesel and preheated biodiesel. Decreased peak cylinder pressure for preheated methyl ester was noted due to late injection and faster evaporation of the fuel. The emission of NO$_x$ at full load for Pongamia Pinnata methyl ester was increased by 6% and a significant reduction was noted for preheated biodiesel [91].

Jinlin Xue et al. (2011) concluded through the extensive literature review that a slight power loss, increase in fuel consumption and increase in NO$_x$ emission along with a significant reduction in PM, HC and CO emissions were recorded for biodiesel and diesel blends in CI engine. It was ascertained that use of biodiesel in an unmodified diesel engine applications favours engine durability through reduced carbon deposits on key engine parts and blending of biodiesel with diesel in smaller proportions could be a solution for air pollution and diesel scarcity [92].

Breda (2011) through numerical and experimental investigations on a Rape seed oil methyl ester fuelled diesel engine, reported an advancement in injection timing and increase in injection pressure, due to high density, high viscosity and high bulk modulus of the biodiesel. Also a slight increase in NO$_x$ emission with substantial reduction in smoke and CO emission, due to higher injection pressure and higher oxygen content were noted [93].

Muralidharan and Vasudevan (2009) investigated the effect of variation of compression ratio on fuel consumption, combustion pressures and exhaust gas emissions of an unmodified diesel engine fuelled with the methyl esters of
waste cooking oil and compared with diesel. The result revealed that, at high compression ratio, the waste cooking oil methyl ester recorded the maximum rate of pressure rise, longer ignition delay, higher mass fraction burnt and lower heat release rate in comparison with diesel [94].

2.7. COMMENTS ON EARLIER WORKS

An exhaustive literature review has been carried out with the following conclusions.

- Biodiesel has been derived from many different vegetable oils and so far no body across the world has tried to extract it from Manilkara zapota seed oil. MZO based biodiesel research has not been reported in any literature so far.
- Transesterification is the most suitable process to convert the vegetable oils in to biodiesel.
- Taguchi method is the most widely used one for the optimization of transesterification process parameters influencing the biodiesel yield.
- Biodiesel derived from all vegetable oils and their blends with petrodiesel could be successfully used as fuel to run CI engine without any modification.

2.8. PRESENT WORK

The objective of the present work is to study the suitability of a new third generation biodiesel resource Manilkara zapota seed oil, optimization of biodiesel production from that resource and studies on its diesel engine application. In order to accomplish the above objective, this investigation has been divided into three major parts.

- In the first part, the Manilkara zapota seed oil is completely characterized and its suitability for biodiesel production based on its fatty acid profile and physicochemical properties was studied.
In the second part, the optimization of key transesterification process parameters for maximum biodiesel yield has been done using Taguchi experimental design.

In the third part the combustion, performance and emission characteristics of an unmodified diesel engine fuelled with new biodiesel and its diesel blends have been studied.