STUDY ON BIODIESEL PRODUCED FROM INEDIBLE AND WASTE FEEDSTOCK IN A DIESEL ENGINE

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A THESIS SUBMITTED

FOR THE DEGREE OF DOCTOR OF

PHILOSOPHY

DEPARTMENT OF MECHANICAL ENGINEERING

NATIONAL UNIVERSITY OF SINGAPORE

2014

DECLARATION

I hereby declare that the thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

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Vedharaj Sivasankaralingam
9 January 2014

ACKNOWLEDGEMENTS

First and foremost, I wish to supplicate my reverence and obeisance to the living GODS - my parents, for showering all praises on me to accomplish my Ph.D. work. Undeniably, their support and motivation have helped me to perform better in my research and though I travelled in un-trodden path, I managed to achieve much because of their encouragement and affection. Professionally, I wish to thank my main supervisor, Prof. S.K. Chou, who gave his support and encouragement in this research work. As a matter of significance, he inculcated in me the habit to work independently and from his esteemed research career; I got to learn a lot. I would always remain grateful for his moral support and guidance throughout the course of my Ph.D. work. In the same note, I also thank my co-supervisor, Dr. Chua Kian Jon, Ernest, who provided his assistance to complete my Ph.D. work. Significantly, I was also under the auspice of Dr. Yang Wenming, who is an expert in the field of IC engines, biofuels and combustion and therefore, I would like to convey my profound sense of gratitude to him. Being an eminent person in the field of my research, he has offered much technical guidance related to my work and assisted to help shape my research direction. My alliance with him during the time of data analysis and manuscript preparation has helped me. Dr. Yang Wenming opened the gates of knowledge through which I managed to climb the ladder of success. Throughout my life, I would remain obliged to him for his help on various aspects of my research work. Finally, I also wish to thank the other members of my group Dr. Lee Poh Seng, Dr. An Hui, Mr. Balaji Mohan, Mr. Tan Tiong Thiam, Mr. Amin Maghbouli and Mr. Mohammad Fahd Ebna Alam for their cooperation and support in realizing my work.

As a part of my Ph.D. work, I had an opportunity to carry out some experiments in India under the guidance of Prof. V.Ganesan, Professor-Emeritus, Department of Mechanical Engineering, IIT Madras and Dr. C.G. Saravanan, Professor, Department of Mechanical Engineering, Annamalai University. At the time, when I sought their help regarding my research work, they were extremely generous and magnanimous to extend their helping hand. Based on their recommendations and technical help on the lines of my research work, I was able to develop my research plans. In addition to being supportive, they were amicable and inspired me to rationally think through the relevant areas of my experimental works carried out during my tenure in India. My Ph.D. work, devoid of their mentoring and guidance could not have progressed well and they literally molded me as an ambitious research scholar. No words could appropriately describe their help and support and I wish to submit my heartfelt thanks and respect to them. In addition, I also feel grateful to my friends and other well-wishers, who steered me in the correct path and extended their support. Finally, I would like to express by immense gratitude and thanks to my friend and colleague, Dr. Vallinayagam Raman, who ably supported me in all aspects of my research endeavors. Much to my support and growth, he instigated and motivated me right from the beginning to the end so as to accomplish this research work successfully.

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SUMMARY

This research work has been undertaken to utilize low cost, inedible and waste feedstock as raw materials for biodiesel production and utilization in a diesel engine. As such, we have proposed two inedible and waste feedstock, namely, kapok oil and CNSL (cashew nut shell liquid), to be synthesized into biodiesel. Significantly, kapok oil has not been considered as an alternate fuel for diesel engine thus far despite being an indispensable renewable source, while CNSL is at the beginning stage of development. As a different approach, steam treatment process followed by mechanical crushing has been employed to extract bulk quantities of oil from kapok seeds as well as cashew nut outer shell. Subsequently, kapok biodiesel was produced from kapok oil through alkaline trans-esterification process, while CNSL biodiesel was synthesized through double stage trans-esterification process due to the higher FFA content of CNSL. Notably, the estimated thermal and physical properties of biodiesel were found to be conducive for their use in a diesel engine.

After the synthesis of the required biodiesel, the operation of them in a diesel engine was studied through various fuel and engine modification strategies. As such, in the first phase, the operation of kapok biodiesel was optimized and to incept with, conventional testing of kapok biodiesel in blends with diesel was done. From the experimental investigation, B25 (25% biodiesel and 75% diesel) was found to be the optimum blend. To reduce the emissions for B25, in our next attempt, we modified the properties of the blend by adding 1,4-Dioxane, a multipurpose fuel additive. Furthermore, we attempted to adapt higher blends of kapok biodiesel in a diesel engine by coating the engine components using insulating material and varying the combustion chamber geometry. As an outcome of these studies, B50 (50% biodiesel and 50% diesel) was found to be the optimum blend. In addition, NO_X (nitrogen oxide) emission from a coated diesel engine was mitigated by implementing SNCR (Selective non catalytic reduction) in the tail pipe. In the second phase of this study, CNSL biodiesel was investigated in a diesel engine and by varying the fuel injection pressure, B25 was shown to have better engine characteristics than diesel. To further improve the engine performance, B25 was tested in a coated diesel engine and finite element analysis was performed to understand the effect of coating on engine performance. Finally, to harness the renewability of 100% CNSL biodiesel, it was operated in diesel engine after preheating it, and, additionally, an economic analysis was performed to verify its economic feasibility.

In the last phase of this research study, combustion and emission modeling for kapok biodiesel were performed through a 3D CFD code, KIVA4. Accordingly, the fuel library of KIVA4 was updated with the properties of kapok biodiesel and appropriate reaction mechanisms for combustion and emission of kapok biodiesel were chosen. In the end, simulations were performed and the results such as in-cylinder pressure, CO, HC and NO_X emissions were validated with the experimental data.

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Journal Papers:

1. **Vedharaj S**, Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Experimental investigation of kapok (Ceiba pentandra) oil biodiesel as an alternate fuel for diesel engine. Energy Conversion and Management. 2013;75:773-9.
2. **Vedharaj S**, Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Experimental and finite element analysis of a coated diesel engine fueled by cashew nut shell liquid biodiesel. Experimental and thermal fluid science.2014;53:259-268.
3. **Vedharaj S**, Vallinayagam R, Yang WM, Saravanan CG, Chou SK, Chua KJE, Lee PS. Reduction of harmful emissions from diesel engine fueled by kapok methyl ester by combined coating and SNCR technology. Energy Conversion and Management.2014:79:581-589.
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5. **Vedharaj S**, Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Performance emission and economic analysis of preheated CNSLME as alternate fuel for a diesel engine. International Journal of Green Energy.2013 (Accepted)
6. **Vedharaj S**, Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Cashew nut shell liquid (CNSL) biodiesel - An alternate fuel for diesel engine. Renewable energy (under review)
7. **Vedharaj S**, Vallinayagam R, Yang WM, Saravanan CG, Lee PS. Optimization of combustion chamber geometry for the operation of kapok biodiesel in a diesel engine. Fuel (under review)
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1. **Vedharaj S,** Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Influence of additive (1,4-Dioxane) on the performance and emission characteristics of kapok oil biodiesel. In proceeding of: International Conference on Applied Energy (ICAE) 2013, Pretoria, South Africa.
2. **Vedharaj S,** Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Experimental study on thermal barrier coating of a diesel engine powered by kapok biodiesel. In proceeding of: 12th International Conference on Sustainable Energy technologies (SET-2013) 2013, Hong Kong.

LIST OF ABBREVIATIONS

ATDC – After top dead centre

ASTM – American Society for Testing and Materials

B25 – 25% Biodiesel + 75% Diesel

B50 – 50% Biodiesel + 50% Diesel

B75 – 75% Biodiesel + 25% Diesel

B100 – 100% Biodiesel

BP – Brake power

BSFC – Brake specific fuel consumption

BTDC – Before top dead centre

BTE – Brake thermal efficiency

CA – Crank angle

CC – Combusiton chamber

CD – Combustion duration

CFD – Computational fluid dynamics

CHRR – Cumulative heat release rate

CI – Compression ignition

CNSL – Cashew nut shell liquid

CNSLME – Cashew nut shell liquid methyl ester

CO – Carbon monoxide

CO_2 – Carbon dioxide

EGR – Exhaust gas recirculation

EGT – Exhaust gas temperature

FEA – Finite element analysis

GMV – General mesh viewer

HC – Hydrocarbon

HCC	– Hemispherical combustion chamber
HCCI	– Homogeneous charge compression ignition
HSU	– Hatridge smoke unit
IC	– Internal combustion
ID	– Ignition delay
KME	– Kapok methyl ester
NDIR	– Non dispersive infrared
NO_X	– Oxides of nitrogen
O_2	–Oxygen
PHRR	– Peak heat release rate
PM	– Particulate matter
PPM	– Part per million
PSZ	– Partially stabilized zirconia
SCR	– Selective catalytic reduction
SNCR	– Selective non catalytic reduction
SFC	– Specific fuel consumption
SI	– Spark ignition
SOC	– Start of combustion
TBC	– Thermal barrier coating
TDC	– Top dead center
TCC	– Toroidal combustion chamber
TRCC	– Trapezoidal combustion chamber

CHAPTER 1

1. Introduction

1.1. Renewable sources of energy for power production

With the onset of globalization, the world has been witnessing a rapid growth and development in almost all possible spheres, especially science and technology has been immensely fostered. In wake of the upsurge in development and increase in world population, the gap between electricity demand and supply has been increased. In a forecast, US Department of Energy has predicted an increase in demand for electricity by 28%, from 3,839 billion kWh in 2011 to 4,930 billion kWh in 2040, necessitating for capacity addition to meet the demand [1]. Since the majority of electricity production emanates from coal and natural gas fired power plants, these energy sources are getting depleted with the each passing day and the world's energy system is being pushed to the breaking point. In addition to this, burning of these sources of energy also contributes to the emission of hazardous gases and soot emission into the atmosphere, paving way for climate change. Obviously, the effect caused by climate change is no less ominous and in current form, the world is on track for warming of 6 Celsius – a level that would create devastation, wiping out agriculture in many areas and rendering swathes of the globe uninhabitable.

Scientists and research community are aware of the above mentioned consequences and they are attempting to advocate few solutions to overcome the rampant issues with energy demand and climate change. More often than not, sustainability and renewability are two quintessential affordable solutions that could help avert these problems. Significantly, the world has already committed to some contemporary renewable sources of energy like wind, solar and hydro to meet the energy demands. Generally, these are touted to be clean energy technologies as natural sources were used for producing power, enabling greener environment. Reportedly, solar, wind, hydro power and biomass does contribute to renewable energy generation from 524 billion kWh in 2011 to 858 billion kWh in 2040, growing by an average of 1.7 percent per year [1], as statistically depicted in Figure 1.1. However, there are three important factors which have to be considered in deciding the suitability of these renewable sources over the conventional coal technologies such as 1) Availability of the source 2) cost competitiveness with fossil fuel technology 3) Long term viability and geographical conditions. In the beginning of 21st century, spurred by the growth of these renewable energy technologies, the electricity demand has been offset from 9.8% to 0.7% [1]. If this scenario is likely to improve with the deployment of more renewable technologies, a restraint on energy deprivation and environmental devastation can be brought to prominence in the near future

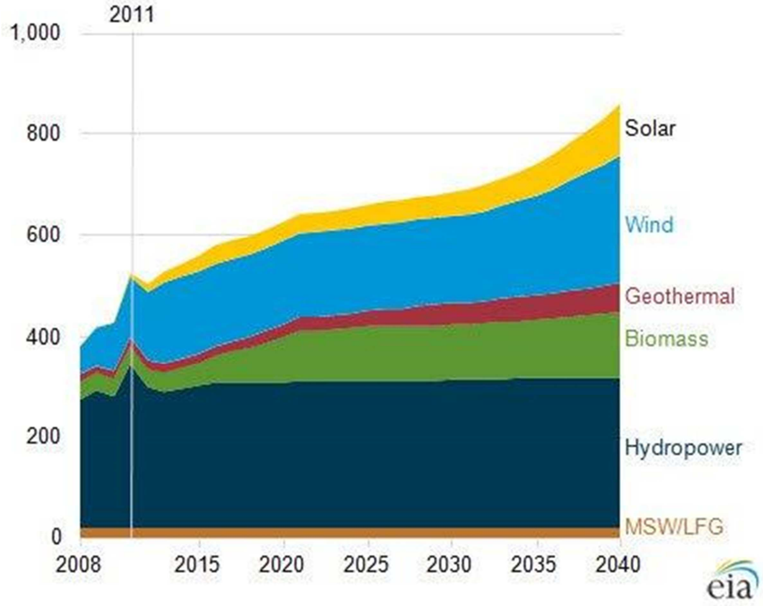


Figure 1.1 Prediction of renewable electricity generation by EIA

1.2. Liquid biofuels and its application in power generation

In addition to the power generation in large scale through renewable source of energy, domestic electricity has also been produced from certain prime movers, driven by fossil petroleum fuel [2]. One common type of prime mover being used for generating electricity is a diesel engine, which has been designed to operate in stationary mode. Appreciably, this prime mover offers better efficiency than gasoline engines due to lean burning of the fuel, with the additional advantage of reduced HC and CO emissions. In the application point of view, they are used in buses, trucks, cars, compressors, generators and pumps, which could be broadly classified under transport, industrial, marine and agricultural applications. It is noteworthy to mention that stationary diesel engine (generators) is being used in many industries and domestic applications to generate power and electricity while for transport application; the engine being used is different. Characteristically, though these generators are rationally conceived to meet the emergency power demands, they also find application in agricultural and marine fields. Also, since they are deemed to operate at a constant engine speed, design perspective of the engine is simple. In addition, this kind of diesel engine also finds use in marine applications, in which, huge capacity engine are designed to produce a power output of 90,000kW, running at a precisely slower speed of 100rpm. On contrary, in agricultural sector, relatively small capacity stationary diesel engines are used in tractors, irrigation pumps and threshing machines.

Basically, diesel engines are powered by fossil diesel and all its operational characteristics are standardized for the use of diesel, ever since the age of engine invention and development. However, our dependence on petroleum based fuel grows stronger each year and in light of this, the price of the crude oil is escalated to greater heights, which has become the potential threat to the developing and developed countries [3]. If this current scenario is likely to prevail for next couple of decades, the world would be at the risk of severe depletion of petroleum based fuels. Environmentally, the emission of greenhouse gases through the burning of petroleum fuels has caused havoc with no end in sight. Moreover, the other emissions such as CO, NO_X and smoke could cause ruinous effect on atmosphere if not precisely contained. These pitfalls of fossil fuel shortage and environmental degradation could be overcome by supplementing biomass based fuels, which are reported to effectively mitigate the emissions in addition to replacing the petroleum based fuels [4, 5]. Statistically, biomass based fuels are the third largest source for renewable energy generation and has contributed phenomenally to the generation of electricity, from 37 billion kWh in 2011 to 102 billion kWh in 2021. On the whole, there have been prediction about these biomass based fuels contributing to one half of the energy demand by 2050 and both the developed and developing countries are thriving to see this happen in the near future.

In respect of several benefits in the utilization of biomass based fuels against the use of conventional fossil fuels, considerable attention has been paid on the development of them all over the world, with particular focus on biofuels that possess advantages of being renewable and biodegradable [6]. Notably, liquid biofuels, produced from plants and biological raw materials have grabbed the attention of many researchers as viable substitute for diesel in a diesel engine. From the production point of view, these biofuels are pointed out to be synthesized from the parts of plants such as seeds, crops and other naturally available renewable materials. Distinctly, these biofuels contains essential hydrocarbons and unlike diesel, it possesses inherent oxygen that makes it distinct and advantageous in respect of fuel oxidation and combustion process. Moreover, though the properties of these liquid biofuels are different due to their chemically different molecular structure and composition, they could be made conducive for their operation in diesel engine, which makes them more attractive. Systematic classification of these liquid biofuels delineates to vegetable oils, alcohols, biodiesel or esters, carbonates and ethers, which has been shown in Figure 1.2. In a broader classification, biofuels can be categorized into first and second generation biofuels, depending on the source from which it is produced. Characteristically, the biofuels produced from vegetable sources such as edible oil, starch and cellulose are termed as first generation biofuels, while second generation biofuels are synthesized from inedible sources such as lingo cellulosic biomass and agricultural wastes. From the production point of view, these biofuels are synthesized from different sources through biological or chemical treatment methods. In the present trend, according to an international energy agency, replacement of 6% of petroleum fuels by biofuels in USA and Europe appears to have been possible and for other nations, depending upon the availability and policies, this is likely to vary. In all prognosis, many biofuel refineries are believed to prosper in the near future and the economy will grow in the 21st century.

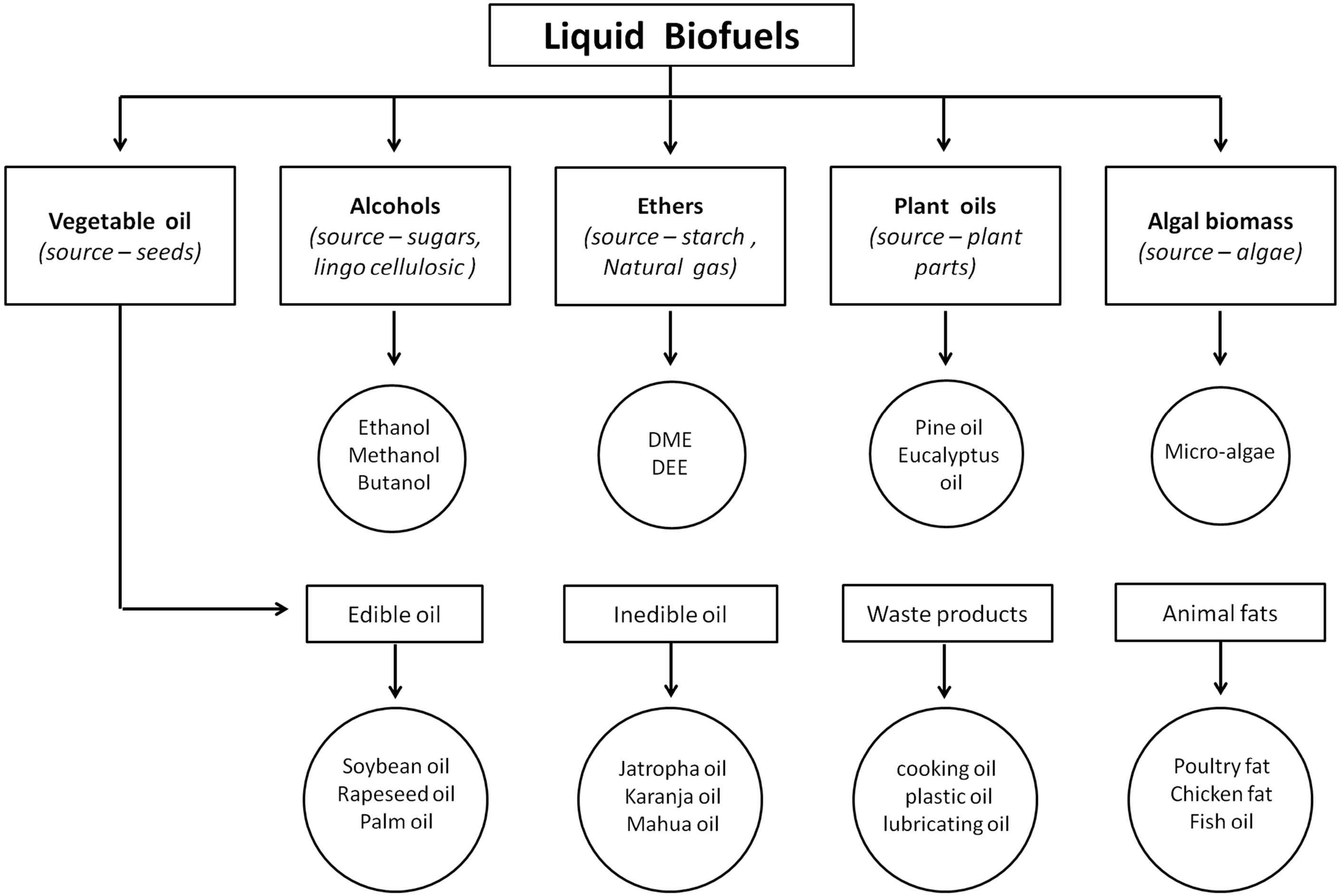


Figure 1.2 Classification of liquid biofuels

1.2.1. Vegetable oil as source of fuel for diesel engine

From the classification of biofuels, vegetable oils from both edible and in-edible sources seems to be arguably one of the best alternate fuels for diesel engine, while alcohols are suited for operation in gasoline engine. The use of vegetable oils directly in diesel engine had been commemorated early since 1900, when Rudolf diesel tested peanut oil in a diesel engine [7, 8]. Though the cost of vegetable is higher compared to diesel fuel, it was used at times when there arose an imminent threat of petroleum fuel deprivation. In particular, during the World War II, between 1930 and 1940, vegetable oils were used as a potential substitute for diesel. Normally, the source for these vegetable oils is from oil seeds, which are either cultivated or collected from scattered locations. Subsequently, oil is extracted from the seeds by means of mechanical, solvent or enzymatic extraction techniques, after preprocessing the seeds by drying it in an oven or sun. In the mechanical extraction technique, either manual or screw driven press has been employed, which contributes to around 60% to 65% and 68% to 80% extraction of oil, respectively [9]. Nonetheless, this method of oil extraction is not suitable for all kind of seeds and hence in the event of seeds not appropriate for mechanical extraction, solvent extraction technique can be adopted. For solvent extraction technique, it has been pointed out that a highly soluble less viscous solvent is needed to extract oil from powdered seeds [10]. In-order for this to be realized, the particle size and temperature of the medium seems to have a crucial role and besides this, the mixture has to be agitated well to increase the oil yield. In addition to the above two methodologies, there prevails an environmental friendly mode of oil extraction, known as enzymatic extraction method [11], which refrains from producing any volatile organic compounds thereby, preventing environmental pollution.

Chemically speaking, vegetable oils are water insoluble hydrophobic substance composed of fatty esters of glycerol with higher molecular weight [12, 13]. However, the fatty acid composition of different types of vegetable oil varies, due to the distinction of being extracted from different sources. Besides the presence of free fatty acids, vegetable oil also does have sterols, phospholipids, water, odorants and other contaminants, which obligate for refining of the oil to get purified [14]. However, when compared to fossil diesel, vegetable oils are bound to more oxidation when stored for a prolonged duration, especially for fuels with more unsaturated hydrocarbons. Eventually, when used in a diesel engine, the formed peroxide then polymerizes into insoluble compound, which could block the fuel filter and injector nozzle holes.

Vegetable oil could be directly used in diesel engine because of its better burning properties and it is reported to have reduced the emission of deleterious greenhouse gas, CO_2, and carbon foot prints [15, 16]. Moreover, the cetane number of it is higher and approximately, the calorific value of it is 90% of diesel, equipping as a pertinent substitute for diesel in a diesel engine. Nevertheless, the use of neat vegetable oil directly in diesel engine is not advocated as its viscosity is higher, affecting the engine performance and combustion, and prolonged use of them in diesel engine would pave way for problems such as injector clogging, carbon deposits and lubrication oil contamination [3, 17-19]. Notably, the possible ways to reduce the viscosity are 1) Dilution or blending 2) micro-emulsification 3) pyrolysis and 4) trans-esterification. Dilution of vegetable oil pertains to blending it with conventional diesel in various proportions wherein, mixed properties of vegetable oil and diesel could be subtly balanced. Importantly, there have been observations about the reduction in viscosity, when the proportion of diesel with the vegetable oil is increased and this has shown to improve the engine performance and emission [20, 21]. The other possible attempt to reduce the viscosity of the vegetable oil amounts to micro-emulsification wherein, water particles are infused into the oil and the homogeneity of the resultant mixture is ensured by a surfactant. Technically, the emulsified vegetable oil comprises of three phases namely, oil, aqueous and surfactant phases, and during evaporation and combustion of fuel, the low boiling fraction water evaporates and help improve the fuel spray characteristics [22, 23]. Besides these two approaches, chemical treatment of vegetable oils has earned the interest of many researchers and in light of this, processes like pyrolysis or trans-esterification has been considered to reduce its viscosity. Characteristically, pyrolysis involves breaking down of higher molecules of vegetable oil into smaller molecules, after subjecting it to decomposition in the absence of catalyst [24, 25]. On the other hand, trans-esterification is a chemical reaction in which the vegetable oil reacts with an alcohol to form smaller compounds, esters and glycerol. Subsequently, glycerol is drained out and the formed ester is termed as biodiesel, a potential renewable source of fuel.

1.2.2. Biodiesel and its development

Biodiesel is a fuel made up of mono alky ester of fatty acids, derived from animal fat or vegetable oil by trans-esterification process [26]. Significantly, biodiesel synthesized from vegetable oils has many advantages such as renewability, higher combustion efficiency, lower sulfur and aromatic content [26, 27]. Furthermore, the presence of inherent oxygen within it enhances its biodegradability [28] and the fact that biodiesel is enriched with free fatty acids improves its lubricity [29]. Besides these inherent merits of biodiesel, literature review on biodiesel claims that it has a potential to reduce the economic dependency on foreign oil import, supported by its authoritative domestic origin.

In the aftermath of the extensive revelation about the composition and properties of biodiesel, many experimental studies on the performance, emission and combustion characteristics of a diesel engine fueled by it came to fore. From the engine experiments, it was reported that ignition delay reduces as the mixing ratio of biodiesel increases, because the cetane number of biodiesel is greater than that of conventional diesel [30]. Also, biodiesel produced from various vegetable oils emits lower exhaust emissions such as smoke, HC and CO [31]. Over and all, from the extensive studies conducted using blends of biodiesel in a diesel engine, 20% blend of it with diesel has been recommended as an optimum one, considering the engine performance and emission. Accordingly, this has provided an impetus for many researchers to find a viable biodiesel from several vegetable oil sources. It is worthwhile to mention that in the process of selecting suitable oil for biodiesel production, there are several considerations such as availability, cost, stability and manufacturing method. In recent times, researchers have forfeited using edible vegetable oil as source for biodiesel production and rather they have set their sight on inedible oils as the demand for edible vegetable oil has been increased and there are concerns such as high cost and impact on food chain [32]. In this regard, inedible oils such as Jatropha (*Jatropha carcus*), Karanja (*Pongamia pinnata*), Nagchampa (*Callophyllum inophyllum*), Rubber seed (*Hevca brasiliensis*), Neem (*Azadirachta indica*), Mahua (*Madhucha indica*), Jojoba (*Simmondsia chinensis*), and Microalgae are being used as prominent sources for biodiesel production as they are readily available and are economical [33]. Moreover, inedible plants can be grown in waste lands, which further benefits as green cover to waste land.

Besides the edible and inedible oils, waste products such as waste cooking oil and animal fats have also been given attention by many researchers as a viable candidate for producing biodiesel. Considerably, harnessing the renewable source of energy from the waste products would help combat the land availability issue for growing crops. In all likelihood, biodiesel produced from these inedible oils as well as waste products, when being used as alternate fuel in a diesel engine, would replace a fraction of petroleum based fuels and other conventional fuels in the near future, and will supposedly generate green energy to help prevent adverse effect on atmosphere. However, there are still several constraints associated with the use of biodiesel such as higher viscosity, lower energy content, higher cloud and pour point and increased NO_X emission [28]. On account of its higher FFA content, the long term use of biodiesel in a diesel engine is likely to pose durability problems and soot depositions on the engine parts, especially the fuel injection equipment’s. After weighing the pros and cons of biodiesel derived from various vegetable oil, researchers have proposed several strategies to compensate the limitations with the thermal and physical properties of biodiesel. These techniques relate to modifying the engine design and operating parameters or altering the properties of the fuel by adding additives or other chemical treatment methods. Notably, these strategies would not only improve engine performance and emission but also enables adaptation of higher blends of biodiesel.

1.3. Motivation and Outline of the thesis

Over the years, though different species of biodiesel have been capitalized as substitute for diesel, its cost and availability are the two factors, forbidding the commercialization of these fuels holistically. Further, it has been duly noted that the cost of biodiesel, which is still higher than the conventional diesel, is dependent on the feedstock cost and therefore, exploration of low cost feedstock is the need for the current ongoing research. In the wake of all contemporary issues pertaining to the choice of suitable feedstock for biodiesel production, various studies on the characterization of biodiesel form inedible oils have been investigated by many researchers [33-35], given inedible oils are cheaper and can be grown in abundant. Further, the selection of inedible feedstock could also help avert the dispute between food and fuel, and might provide a chance to establish well defined agricultural policies for rural development. In further introspection, it was noticed that even with the inedible food crops, the availability of land for cultivating crops is of concern. Therefore, besides exploring an inedible feedstock for biodiesel production, focus on utilizing waste product as suitable raw material for producing biodiesel is beneficial. In the final consensus for the development of biodiesel, the feedstock should be both in-edible and a waste product as these considerations would not only reduce the cost of biodiesel but would also help encounter the land availability and problems associated with food chain. In this regard, we have set an objective to a select feedstock, which is in-edible, waste and economical for biodiesel production and utilization in a diesel engine. Further, to make the produced biodiesel more amenable for diesel engine, we have aimed to optimize the use of them by adopting various strategies.

With the above stated objectives, an extensive literature review on the list of vegetable oils available so far was made and the performance, emission and combustion characteristics of few inedible biodiesel have been summarized. Further, to get insights on the optimization of biodiesel in a diesel engine, review of fuel modification strategies have been made and distinctly, a summary on design modification strategies for optimizing biodiesel in a diesel engine, which has not been accomplished before has been made. The review work is made in line with the objectives proposed and has been described in Chapter 2. After an extensive search, we have chosen kapok oil, in our study, to synthesize biodiesel and operate them in a diesel engine. As a matter of fact, the oil extracted from kapok seeds are being underutilized, despite having the potential to qualify as a viable substitute for diesel. Previously, kapok oil was extracted only in small quantities by Soxlet extraction technique, with the intent to produce and optimize biodiesel. However, it is reliably learnt from the literature study that testing of kapok biodiesel in diesel engine has not come to light so far, which would demand production of large quantity of biodiesel. In this scenario, as a different attempt, this study has adopted steam treatment process followed by mechanical crushing technique, which extracts larger proportion of oil conveniently. Further, this study has focused on preparing biodiesel from extracted kapok oil by trans-esterification process and the properties of it, as determined by ASTM standard methods, were found to be in agreement with international biodiesel standards. All details pertaining to the extraction of kapok oil from its seeds, biodiesel production and the evaluation of fuel properties have been explained in Chapter 3. Further, the engine used for the experimentation and other information regarding the experimental methodology with engine have been explained in this chapter.

After ensuring the feasibility of using KME (kapok biodiesel) in diesel engine, various blends of KME with diesel were prepared and the performance, combustion and emission characteristics of a diesel engine powered by KME – diesel blends are investigated for the first time. Followed by this, we decided to choose an optimum blend and improve the engine characteristics for the reported blend by adding a fuel additive. After scrutinizing several additives and their role on engine performance and emission, it was identified that 1,4-Dixoane, despite its multipurpose benefits, has not been used as an additive with biodiesel. Therefore, 1,4-Dixoane was added with the optimum blend of KME in a measure to improve the blend fuel properties and achieve better engine characteristics.

Followed by the experimental investigation of kapok biodiesel in diesel engine without any modifications, we carried out optimization studies by making certain engine design modifications so as to adopt higher blends of KME in diesel engine. Notably, in this study, considering the advantage of design modification strategy over optimization of engine operating parameters, the former has been chosen to operate KME – diesel blends. From the literature review, we identified two probable design modification techniques known as thermal barrier coating of engine components and optimization of combustion chamber geometry. Initially, the engine components were coated by insulating material, partially stabilized zirconia, so that the heat losses to the cooling water and exhaust were reduced to improve the thermal efficiency. The coating was achieved through plasma spray technique and various blends of KME with diesel were prepared and tested in a coated engine. Further, the contentious issue of increased NO_X emission from coated engine was identified, which has not been addressed so far by many researchers when testing any of the biodiesel in a coated engine, and measures were taken to mitigate it. After the experimental investigation, the optimum blend with better engine performance and emission was identified. In our next study, the design of the combustion chamber geometry was altered when testing KME – diesel blends in a diesel engine and finally, the best combustion chamber design was zeroed in. In this attempt, three different combustion chambers such as toroidal, trapezoidal and hemispherical chambers were selected to test kapok biodiesel. The optimization of kapok biodiesel in a diesel engine through design and fuel modification strategies has been elucidated in Chapter 4.

This research study is not only limited to identifying KME as viable alternate fuel for diesel engine but has also targeted to propose one more potential feedstock for biodiesel production and utilization in a diesel engine. As such, in the second phase of this study, a low cost feedstock, cashew nut shell liquid, which is at the beginning stage of development, was considered for our study. From the literature study, it is certain that despite the economic viability of CNSL, not much attention has been paid to harness the renewable source of energy from it due to difficulties encountered in fuel processing and characterization. Since the sole objective of this research study is to choose low cost and waste feedstock for biodiesel synthesis, we have shed some light on using CNSL in a diesel engine. Further, as a different attempt, CNSL was extracted from the cashew nut shell through steam treatment process, which has not been considered by previous researchers. To enhance the recovery of maximum proportion of CNSL, the shells are further crushed in a mechanical expeller. Subsequently, CNSL biodiesel was produced by double stage trans-esterification. The extraction of CNSL from cashew shell, biodiesel synthesis and fuel characterization have been explained in Chapter 3, alongside the fuel characterization of kapok biodiesel.

After the synthesis of CNSL biodiesel, experimental investigation was carried out in a diesel engine using various blends of CNSLME with diesel. Based on the outcome of this study, the optimum blend of CNSLME was identified and the use of it in diesel engine was optimized by increasing the fuel injection pressure. Further, the effect of thermal barrier coating on the engine performance and emission using the optimum blend of CNSLME was realized. However, herein, in-order to understand the improvement in thermal efficiency by coating and understand the physical mechanism behind this, a finite element analysis was performed. In this regard, a 3D model of the key component of the engine, piston, was created using SOLIDWORKS and a coupled field thermal-stress analysis for the conventional and coated engine piston was carried out using ANSYS workbench. Finally, the results of the simulation work such as thermal stress, heat flux and temperature were examined and effect of coating on engine performance was analyzed. At last, apart from the design change, the fuel property i.e. viscosity was reduced for CNSL biodiesel and has been used as neat fuel by preheating the fuel before supplying to the engine. Notably, this measure offered the benefit of exclusive use of 100% renewable fuel in a diesel engine. Interestingly, among the various vegetable oils, CNSL appears to have lower cost and hence an economic analysis was conducted to justify this claim. The experimental investigation of CNSLME and the design as well as the fuel modification strategies followed to optimize it has been described in Chapter 5. Thus, for both the proposed biodiesel, KME and CNSLME, design and fuel modification strategies were employed so as to optimize the use of them in a diesel engine.

In the last phase of this research work, numerical investigation on the modeling of biodiesel combustion and emission was performed using a computational three dimensional CFD code, KIVA4. It is worthwhile to note that KIVA4 cannot handle complex chemistry and hence to accommodate the chemical kinetic reaction mechanisms for biodiesel and model combustion, CHEMKIN solver was used and results of it were coupled with KIVA4. In this work, the numerical study was carried out for both conventional diesel and kapok biodiesel. Based on the surrogate component for diesel and KME, appropriate reaction mechanisms were chosen from literature and they were coupled with KIVA4. Followed by this, the critical properties and other advanced properties of KME were evaluated based on the composition of it through property prediction models and were included in KIVA4 fuel library. Finally, engine simulations were carried out and the obtained combustion as well as emission results are compared with the experimental data. The model description, simulation procedure and analysis of results for diesel and KME are detailed in Chapter 6. Finally, the summary and future recommendations are elucidated in Chapter 7.

CHAPTER 2

2. Literature review

Since this research work focuses on the selection of low cost feedstock for biodiesel production, a comprehensive literature review on the production and characterization of biodiesel produced from inedible vegetable oil and waste products has been made. Further, the most prominent inedible and waste feedstock's were chosen and the engine characteristics such as performance, combustion and emission when fueled by the reported fuels were elucidated. Though lower proportion of biodiesel could be blended with diesel and operated in a diesel engine without any modification, to envisage better engine characteristics and realize the use of biodiesel in higher proportions, engine operating and design parameters have to be optimized. However, when compared to the review work on optimization of operating parameters of a diesel engine, no efforts were up taken to summarize the design modification strategies of a diesel engine when fueled by biodiesel. Therefore, this review work would furnish a comprehensive review on the possible design modification strategies for biodiesel operation in a diesel engine. In addition, certain fuel modification strategies adopted to improve the performance and emission of a diesel engine, when fueled by biodiesel, have also been summarized in this work. Significantly, the literature review is made in line with the objective of the current study, focusing on inedible and waste feedstock and their optimization in a diesel engine through design and fuel modification strategies.

2.1. Inedible sources for biodiesel production

Thus far, more than 350 oil bearing crops have been identified to produce biodiesel, encompassing edible and inedible feedstock [36]. In a survey, Botanical Garden of Indian Republic (BGIR) has found a plethora of oil yielding crops and classified their family name, habit and uses, besides identifying the prospects of using them as fuels [37]. From the survey, it is evident that a growing interest has been shown to cultivate inedible crops, considering that they are cheap and grow without affecting the food chain. In addition to these inedible sources, waste products such as animal fats, waste lubricating oil and waste cooking oil have garnered much attention as a renewable fuel for diesel engine, predominantly because of their cheaper price [38-41]. In this backdrop, researchers have figured out many pertinent inedible feedstock's for biodiesel production so as to use them as alternate fuel in a diesel engine. These days, since many species have been cultivated and evolved, review work on categorizing the inedible feedstock based on properties, production method and engine characteristics have been brought to fore. Notably, Mohibbe Azam et al [42] studied the properties and fatty acid composition of 75 species of vegetable oil in India and gave a good account on the possibility of using them as alternate fuels. From their study, 26 species of crops, encompassing some inedible oil crop species such as *Azadirachta indica*, *Calophyllum inophyllum*, *Jatropha curcas* and *Pongamia pinnata,* have been declared as appropriate substitutes for diesel in the near future.

Demirbas [36], in his review on progress and recent trends in biodiesel, recognized some inedible plant species such as Jatropha (*Jatropha curcas*), Karanja or Honge (*Pongamia pinnata*), Nagchampa (*Calophyllum inophyllum*), Rubber seed (*Hevca brasiliensis*), Neem (*Azadirachta indica*), Mahua (*Madhuca indica* and *Madhuca longifolia*), Silk cotton (*Ceiba pentandra*), Jojoba (*Simmondsia chinensis*), Babassu, *Euphorbia tirucalli*, and microalgae for biodiesel production. Besides categorizing the properties and fatty acid composition of these inedible sources for biodiesel production, the review work of Demirbas [36] asserted that these inedible oils are cheap when compared to edible oils in India. In another review work on characterization and production of biodiesel from different sources, Singh et al [43] identified few inedible sources such as Babassu, Brassica carinata, B. napus, Camelina, Cumaru, Cynara cardunculus, Jatropha curcas, Jatropha nana, Jojoba oil, Pongamia glabra, Laurel, Lesquerella fendleri, Mahua, Piqui, Palm, Karang, Tobacco seed, Rubber plant, Rice bran, Sesame and salmon oil. The performance of these alternate sources of fuel, properties, composition, constraints and their economic viability were addressed in this review work, besides focusing on the future prospect of biodiesel utilization and production.

No et al [44], emphasized the need to tap the renewable source of energy from inedible sources of vegetable oil and its derivatives to encounter the present energy crisis, and also to produce biodiesel at cheaper prices. Notably, in his review, different vegetable oils in the likes of Jatropha, Karanja, Mahua, Linseed, Rubber seed, Cotton seed and Neem oil were zeroed in and distinction in respect of fuel properties, engine performance and emissions were summarized. Based on the extensive collection of data on these reported aspects, Jatropha oil was identified to be the better candidate for diesel engine and it was shown to be operated through engine modification techniques like preheating, dual fueling and fuel modification strategies like blending with diesel, biodiesel and degumming. Considering the energy scenario of India, Kumar et al [45] reiterated the need to utilize inedible feedstock for biodiesel production to attain energy sustainability and underscored the need to search for dedicated inedible seeds and examine the possibilities of producing biodiesel from the extracted oil. Few species, noted in their study were *J. curcas, P. pinnata, R. communis, A. Mexicana, C. odollam, P. roxburghii, S. mukorossi, H. brasiliensis, C. inophyllum, M. azedarach, S. chinensis, M. indica, S. triguga, T. peruviana* and *A. indica*.

Apart from these inedible sources of vegetable oils, micro algae biomass has been widely contemplated by many researchers, highlighting that the oil productivity of it is higher than oil yielding crops [46, 47]. Characteristically, the cultivation of microalgae depends on the natural sources such as sun, CO_2 and water. Once cultivated, the microorganisms convert them into sugar, which is then converted into tri-glycerides. In addition, significant focus has also been made to harness energy from waste products such as waste cooking oil, animal fats, discarded engine lubricating oil or waste plastic oil [48-51].

2.2. Properties of biodiesel and vegetable oils

Internationally, there exists a legitimate standard to authenticate the properties of biodiesel and every newly emerging biodiesel has to comply with this standard. Categorically, the American system of standards can be termed as ASTM, which has postulated a unique standard for the operation of B20 or

20% of biodiesel with diesel in a diesel engine. In the same note, the other popular standards emerged in the recent past are European standard - EN, United Kingdom – BS, German – DIN and to name a few. The international standard for the properties of biodiesel have been depicted in Table 2.1 and despite this, each country has set its own norms and standards as per the location, climate factors and so on.

Table 2.1 Standard for the properties of Biodiesel

Ester content	>96.5% (m/m)
Viscosity at 40ºC	<6.0
Flash point ºC	>100
Sulphur content	>15 ppm
Cetane number	>47 (747-751)
Water content	<500 ppm
CU strip corrosion	3 Max
Acid value	>0.8
Iodine value	<140

Characteristically, when the vegetable oil undergoes trans-esterification process, some of its properties change and therefore, it is essential to compare the properties of vegetable oil and biodiesel. Foremost, viscosity, which determines the flow and atomization properties of the fuel, is noticed to be higher for vegetable oil and after the trans-esterification process; it is reduced by one of eighth of the original value due to the breaking of heavier compound to smaller one. Generally, the energy density of biodiesel and vegetable oil are lower than diesel due to the presence of chemically bound oxygen in it [41]. Comparatively, after trans-esterification process, the calorific value drops from 38.20 MJ/kg to 37.2 MJ/kg and 37.5 MJ/kg to 36.5 MJ/kg for Jatropha and Rubber oil methyl ester, while it was noticed to be increased from 34.0 MJ/kg to 36.0 MJ/kg and 35.6 MJ/kg to 36.8 MJ/kg for Karanja and Mahua oil methyl esters [44]. In another comparison, the cetane number of the vegetable oil, which defines the ignition quality, is noted to be lower for vegetable oil when compared to its biodiesel. For example, an increase in cetane number from 37.9 to 45.7 and 37.6 to 51, respectively, was noted in the transition from soybean and rapeseed oil to their respective biodiesel. It is worth mentioning that the length of the hydrocarbon chain is directly correlated to cetane number and since the carbon chain length of biodiesel is greater, the cetane number of it is generally higher. Further, with the notion that there prevails an opposite effect between ignition and cold flow properties, biodiesel reports poor cold flow properties such as cloud point (CP), pour point (PP) and cold filter plugging point (CFPP). In general, the CP is defined as the temperature at which the fuel appears cloudy, PP is the temperature at which the fuel stops to flow and CFPP is the temperature at which the fuel blocks the filter due to crystallization. The cold temperature properties are dependent on the amount of saturation and length of the carbon chain and by this token, the increase in degree of saturation of biodiesel is believed to increase the CP, PP and CFPP. Illustratively, coconut oil was reported to possess higher saturated fatty acids and therefore, the ester of it has higher cloud point of 5ºC, while safflower oil relatively has higher unsaturated hydrocarbons and hence it was observed to show lower cloud point of -6ºC. Finally, from the environmental aspects, biodiesel contains lower sulfur and phosphorous content, minimizing the toxicity and making the environment greener. Thus, most of the fuel properties of biodiesel are dependent on its chemical composition and structure and therefore, the distinction in properties of biodiesel obtained from different source is reasonable.

2.3. Engine characteristics for inedible oil and its derivatives

With the assurance that biodiesel produced from inedible feedstock hold promise in reducing the overall production cost, their characteristics in a diesel engine, with and without chemical treatment, have to be analyzed. Undeniably, each feedstock exhibit a different scenario of engine characteristics as their properties are bound to vary depending on the geographic and climatic conditions. To ascertain this, few inedible as well as waste feedstock's were chosen in the current study and the performance, combustion and emission characteristics of them and their derivatives were discussed. The notable feedstock selected in this review work are Jatropha, Polanga, Karanja, Mahua, Castor, Rubber seed, waste cooking oil, animal fats, plastic oil and engine lubrication oil.

The most prominent feedstock, Jatropha, is widely distributed in tropical and subtropical region such as Africa, India and Southeast Asia. Statistically, the oil yielding capacity of the jatropha seed ranges from 30 to 50%, with linoleic or oleic acid as its major constituent. The experimental investigation of Jatropha oil in blends with diesel in a diesel engine was carried out by Pramanik et al [52], after analyzing its properties. From the study, 50% addition of Jatropha oil with diesel was regarded as an optimum blend for which the engine showed decreased BSFC and EGT, with an increased BTE than diesel. Conclusively, considering the long term durability of the engine, the authors have recommended for modification of fuel properties. In the wake of this, Chauhan et al [53] attempted to reduce the viscosity of Jatropha oil by preheating it, before being supplied to the engine. In this regard, a shell and tube heat exchanger was used to recover the heat from the engine exhaust gases so as to increase the fuel inlet temperature. Subsequently, the experimental study revealed an increase in BTE of the engine and decrease in emissions such as HC, CO and smoke with the increase in fuel inlet temperature. As an outcome of this study, 80ºC was regarded as an ideal preheat temperature for Jatropha oil with respect to engine performance and emission. In another study, Senthil kumar et al [54] perceived effective improvement in fuel properties by blending Jatropha oil with less viscous methanol. However, since the ignition delay of the resultant blends were noticed to be longer, the authors went for dual fuel operation by injecting methanol in the inlet manifold and biodiesel through the main fuel injection system. In this regard, the ignition of methanol was supported by the auto-ignition of biodiesel and the experimental investigation revealed decreased NO_X emission, with increased HC and CO emissions. In another measure to reduce the viscosity, Rao et al [55] subjected Jatropha oil to trans-esterification process to produce biodiesel and subsequently, the prepared biodiesel was used in blends with diesel. From the experimental study, reduction in ignition delay and pressure rise rate was reported and the emissions such as HC, CO and smoke were reduced for Jatropha biodiesel blends. Similarly, many experimental studies on the operation of Jatropha biodiesel blends were up taken in the past decade and over and all, 20% addition of it with diesel was regarded as the suitable blend based on the engine characteristics [56-58].

Polanga oil, also called as poon or tamanu oil, commonly referred by the name of *calophyllum inophyllum,* is now being considered as a potential source for producing biodiesel. The seeds of the tree possess about 50 - 60% oil content and typically, the oil was reported to have 29.7% saturated fatty acid and 62.3% unsaturated fatty acid [59]. Devan et al [59] made a comparative study on the engine characteristics of poon oil and poon oil methyl ester blends with diesel. Based on their experimental results, reduction in smoke, CO and HC emissions were observed for poon oil methyl ester and its blends, whereas these emissions were reported to be higher for poon oil and its blends. These discrepancies are due to the distinction in their properties; especially the viscosity of poon oil is very much higher than poon oil methyl ester. In another study, Sahoo et al [60], considering the higher viscosity and acid value of Polanga seed oil, produced biodiesel from it through triple stage trans-esterification process. In the first stage, the organic matters and other impurities were removed by them using a reagent and subsequently, acid trans-esterification followed by alkaline trans-esterification were carried out to synthesize the required biodiesel. From their engine experimental investigation, higher BTE and lower BSFC were obtained for neat Polanga biodiesel at 100% load, with lower HC and smoke emissions than diesel.

The oil extracted from the seeds of *pongamia pinnata*, formally called as Karanja or honge oil, is an inedible source for producing biodiesel and is native to countries like India, Malaysia, Indonesia, Taiwan, Bangladesh, Sri Lanka and Myanmar [61]. The oil content in the seeds ranges from 25 to 40% and the fatty acid composition of the extracted oil from the seeds reveals the presence of 51.8% oleic acid, 17.7% linoleic acid, 10.2% palmitic acid, 7% stearic acid and 3.6% linolenic acid [62, 63]. In a recent study, Agarwal et al [64] blended Karanja oil with mineral diesel and carried out an experimental load test in a diesel engine, with and without preheating the oil. For preheating, hot exhaust gases from the tail pipe of the engine were recovered and utilized in a specifically designed heat exchanger. From the results obtained, 50% mix of Karanja oil with mineral diesel was declared to be the suitable blend for both with and without preheating. In another study, instead of preheating the oil, Raheman et al [65] trans-esterified it to synthesize Karanja methyl ester, using their own developed trans-esterification system and by this the viscosity was reduced by 2.9 times than that of Karanja oil. Based on the engine experimental results, emissions such as CO and smoke were reduced by 80% and 50%, respectively, for Karanja biodiesel blends than diesel. However, the engine power reduced for blends with biodiesel proportion beyond 40% and thus B40 was chosen as an optimum blend.

Another important inedible oil of Indian origin that has gained popularity as renewable source of fuel for diesel engine is Mahua oil, recognized by the botanical name, *Maducha Indica*. Reportedly, the oil yielding capacity of the seeds was found to be 50% [66] and the extracted mahua oil from the seeds contain both saturated and unsaturated fatty acid; however, the presence of saturated fatty acid is predominant in this oil, affecting its cold flow properties [67]. To help authenticate the adaptability of Mahua oil for diesel engine, Agarwal et al [68] conducted an experimental investigation in a single cylinder stationary diesel engine. As an outcome of their study, blends up to 30% of Mahua oil with diesel was proved to be efficient, showing increased BTE and reduced BFSC at lower load while at higher load, the BSFC was found to be akin with diesel. However, the smoke density was noticed to be higher for the reported blend and it was shown to increase further with the increase in proportion of Mahua oil with diesel. In the same study, an economic analysis was conducted and the authors documented reports of price of Mahua oil to be slightly higher than conventional diesel fuel. In further development, Puhan et al [69] trans-esterified Mahua oil using NaOH and methanol, and the properties of the produced biodiesel were found to be conducive for its operation in a diesel engine. The single cylinder diesel engine showed a slight loss in engine power and increase in fuel consumption when testing biodiesel. However, in terms of emission, reduction in CO and smoke emissions were noted for Mahua oil methyl ester. In another study, Raheman et al [70] pretreated Mahua oil and then subjected it to trans-esterification process to synthesize the required biodiesel. The prepared biodiesel was then experimentally investigated in a diesel engine in blends with diesel and it was concluded that 20% addition of Mahua biodiesel with diesel is recommended as the reported blend did not significantly affect the engine performance and emission.

Castor tree (botanical name – *Riccinus Communis*), popularly grown as drought resistance plant crop, is widely grown in tropical and subtropical countries like India, China, Brazil and Thailand. In addition to the domestic use, castor oil produced in many countries are being imported, and India top the market, importing about 80% of the produced castor oil [71]. Notably, the estimated properties of it showed an increased viscosity and boiling point due to higher colligative properties of it, while the melting point and solidification point are observed to be lower. Due to its higher viscosity and hygroscopic nature, direct use of castor oil in a diesel engine is not recommended, while ester of castor oil is found to be suitable for its operation in a diesel engine. In a recent study, Panwar et al [72] converted castor oil into its methyl ester by trans-esterification process and the test carried out in a constant speed diesel engine showed increased BTE and lower BSFC for lower blends of castor oil methyl ester.

Rubber seed oil, a unique vegetable oil obtained from the seed of the tree, has 17% free fatty acid content. After analyzing the composition of the oil, it was noted to be highly unsaturated, with 39.6% linoleic acid, 24.6% oleic acid and 16.3% linolenic acid [73]. Ramadhas et al [74] examined the prospects of using inedible rubber seed oil as an alternate fuel for diesel engine. As such, they prepared suitable blends of rubber seed oil with diesel and evaluated their physical and thermal properties by ASTM standard methods. From their investigation, the blend proportion of 50% to 80% rubber seed oil with diesel was found to be the optimum blend. Subsequently, to ensure the durability of the engine for the operation of this optimum blend, it was operated in a long run and consequently, high carbon deposits were found on the fuel injection equipment, mandating frequent change of fuel pump, filter and combustion chamber. Therefore, in their next study, to encounter the higher viscosity of rubber seed oil and long term durability problems, Ramadhas et al [75], endeavored to trans-esterify it to synthesis biodiesel. Due to the higher FFA content of rubber seed oil, double stage trans-esterification was employed to improve the yield of biodiesel. Their experimental investigation in a diesel engine asserted an improvement in BTE for lower blends of biodiesel whereas, the engine emissions were pointed out to be decreased with the increase in proportion of biodiesel.

In addition to the above described inedible vegetable oils, waste cooking oil has grabbed the attention of many researchers, as it subtly reduces the cost of the fuel. Despite their economic benefits, used cooking oils are reported to have higher viscosity, while all other properties are shown to be comparable with other vegetable oils. Significantly, in few cases, the quality of the used cooking oil is deteriorated due to the oil decomposition and therefore, it requires proper treatment before being used in a diesel engine. The possible strategies to pre-treat used cooking oil are steam injection, column chromatography, neutralization, film vacuum evaporation and vacuum filtration [40]. In a study, Yu et al [76] experimentally investigated waste cooking oil in a diesel engine and pointed out a decrease in ignition delay, with the SOC being noted to be in advance than diesel by 2.7^{o} CA. Followed by this, to mitigate the emissions and improve the performance, Pugazhvadivu et al [77] preheated waste frying oil and showed improvement in engine performance and reduction in CO and smoke emission. Subsequently, many researchers opted for trans-esterification of used cooking oil so as to reduce its viscosity and make it amenable for its use in a diesel engine. In this connection, Utlu et al [78] designed a reactor to produce biodiesel from waste frying oil and found the physical and chemical properties of it to concur with the general biodiesel standards. Further, the experimentation conducted in a turbocharged four cylinder diesel engine revealed a reduction in CO, CO_2, NO_X and smoke emission, while the engine torque, power output and specific fuel consumption were found to be in par with diesel. As opposed to this, when Valante et al [50] operated a stationary engine using waste cooking oil biodiesel in blends with diesel, the emissions such as CO, HC, NO_X and opacity were observed to increase with the increase in biodiesel concentration. Notably, 50% blend of biodiesel showed 20.1%, 23.5% and 4.8% increase in

CO, HC and smoke emission, respectively. The discrepancies with the results of emission between various studies could be attributed to the difference between the nature of the engine and the properties of the produced biodiesel, which are deemed to be vital for the operation of any biodiesel.

Now-a-days, plastics have become inevitable and since it is being non-degradable, it inflicts severe environmental concerns. In this juncture, Mani et al [48] engineered the use of plastic oil, which are disposed of as waste, in a diesel engine as a substitute for diesel. The properties of the waste plastic oil were noticed to be similar to diesel, qualifying it as essential alternate fuel in a diesel engine. With this token, the plastic oil was tested in a diesel engine and the results evinced a comparable BTE with diesel, with an increase in CO and HC emission. Further, the engine emitted more NO_X emission and to counteract this, Mani et al [79], in their next study, implemented cold EGR with the engine. As a notable mention, in their study, EGR level was estimated to be 20% was found to be effective in the reduction of NO_X emission without compromising the engine performance. In another study, to improve the engine performance and emission, Mani et al [80] varied the fuel injection timing, when using waste plastic oil. Among the various fuel injection timing considered, retarded injection timing of 14° CA BTDC showed reduced NO_X, CO and HC emission, with an increase in BTE.

Arpa et al [39] identified that the engine lubrication oil is being discarded as waste and thus, initiated an attempt to utilize it as a fuel for diesel engine. In this regard, the contaminants present in the lubricating oil were filtered and a diesel like fuel (DLF) was produced by pyrolyitic distillation method. Further, oxidative desulfurization method was adopted to remove toxic sulfur from 3500 to 420 ppm at a temperature of 50°C. After ensuring the physical and thermal properties of the low sulfur diesel like fuel (LSDLF), it was operated in a diesel engine. From their analysis, the engine torque, brake mean effective pressure and BTE were found to be increased, while the emissions such as SO_2, CO and NO_X were noticed to be decreased than ordinary diesel. Many experimental investigation on using blends of waste lubricating oil with diesel have been reckoned in the past [81, 82] so as to equip it as an additional sources of alternate fuel.

The use of animal fats as source for producing biodiesel has been considered in the recent times by many researchers, as these are normally abandoned as restaurant waste. In this connection, Wyatt et al [51] produced biodiesel from lard, beef tallow and animal fat and measured the properties and composition of the fatty acid methyl ester. Distinctly, the produced biodiesel showed better oxidative stability and lubricity, however, the cold flow properties of it were noticed to be inferior to conventional soy based biodiesel. In another study, Oner et al [83] performed an experimental investigation in a diesel engine using inedible animal tallow biodiesel. From their study using biodiesel – diesel blends, decrease in effective efficiency and increase in fuel consumption were noticed with the increase in biodiesel concentration, much because of its lower calorific value. However, emissions such as CO, NO_X, SO_2 and smoke were observed to be lower for 100% tallow methyl ester when compared to diesel. When illustrating the production and utilization of biodiesel from animal fats, it is noteworthy to cast some attention on using fish oil, obtained the discarded waste parts of fish, as source for producing biodiesel, which is a triglyceride containing essential fatty acids. The notable fatty acids present in the fish oil are 24.8% stearic, 23.6% palmitic, 9.84% myristic, and 6.56% octadecatetraenoic acids. In a recent study, Godiganur et al[84] noted that the higher viscosity of fish oil as main obstacle for using it directly in a diesel engine, as it would affect the pumping, atomization and the ensuing combustion process. To counteract the above problem, they trans-esterified the fish oil and the produced methyl ester was found to have properties closer to diesel. With this token, blends of fish oil methyl ester was tested in a single cylinder stationary diesel engine and from the engine test results, the BSFC of B20 was noticed to lower than diesel, while the engine showed maximum BTE of 31.74% for B20. Notably, the CO and HC emissions were noted to be decreased with the increase in proportion of fish oil methyl ester in the blend, while the NO_X emission was reported to be increased due to the presence of oxygen within the biodiesel itself and high in-cylinder temperature.

The above discussion on the properties, production and engine characterization of biodiesel produced from in-edible oil and other waste feedstock's confides them as potential substitute for diesel in the near future. In addition, the main highlight of the discussion is the ability of them to reduce the overall biodiesel production cost, as they are cheap, readily available and sustainable. Therefore, looking towards the future, more research work should evolve on the synthesis of in-edible and waste product feedstock as source for producing biodiesel and utilize them in a diesel engine. Finally, though production of algal biodiesel has grabbed attention, it has not been extensively tested in a diesel engine like other contemporary biodiesel. Therefore, considering the large production capacity from algae and other benefits, researchers should also operate algal biodiesel in diesel engine.

2.4. Engine design modification strategies

The above discussion on the characteristics of a diesel engine with inedible vegetable oils and its derivatives, waste product and animal fats throws some insights on the pervasive trend likely to follow when using fuels other than diesel in a diesel engine. Comparatively, biodiesel and its blend are agreeable for its use in a diesel engine than vegetable oil itself in respect of their fuel properties and engine characteristics. However, there prevails a restraint on the maximum quantity of biodiesel to be blended with diesel and significantly, most of the researchers, if not all, have contended to blend only 20% biodiesel with diesel for achieving fairly better engine characteristics [85, 86]. In this outset, researchers have contrived strategies to modify the engine so as to realize the use of higher blends of biodiesel in a diesel engine. Typically, modifications of engine operating and design conditions have been regarded as the two strategies to optimize the use of biodiesel in diesel engine. In such a backdrop, it is noteworthy to perceive the proposals that have been dealt with in the past to change the engine operating and design conditions. Noticeably, researchers have pointed out variation of operating parameters such as fuel injection timing, injection pressure, injection pulse and duration to optimize biodiesel in a diesel engine [87-90]. Similarly, for changing the engine design, researchers have opined to alter the engine compression ratio, insulate the engine components and change the geometry of the combustion chamber [91-93].

With the advent of different varieties of biodiesel and the experimentation of them as viable alternate sources of fuel happening around the corner, researchers have judiciously summarized the study on biodiesel. Initially, much to the betterment of growing researchers, many review work have been specifically set to demonstrate the ensemble list of feedstock available for synthesizing biodiesel and various strategies that goes into the production of biodiesel from these indigenous feedstock's [94-98]. Subsequently, many other review works established the life cycle, policy issues and economic analysis of biodiesel, given the production cost of biodiesel is crucial in its commercialization [99-103]. Ecologically, depending on the geography, each country has their own protocol in the production of biodiesel and consequently, this has led to the development of different varieties of biodiesel at different regions. For instance, countries such as India, USA, Europe, Malaysia, Indonesia, Iran, and Pakistan have identified their own feedstock for biodiesel production and the prospects of these biodiesel as sustainable energy solutions have been documented as separate review works [104-111]. In addition, the behavior of these biodiesel in a diesel engine have been reported as review work [112-115] and most of these work delineate the characteristics of a diesel engine, powered by different variants of biodiesel.

With umpteen number of review work on characterization of biodiesel production and experimentation flourishing, only meager of works have contemplated on summarizing the optimization methods, pertaining to engine operating and design conditions. Recently, Mohan et al [87], consolidated the various injection strategies such as optimization of fuel injection timing, pressure and rate shaping for the operation of biodiesel in a diesel engine that has happened in the past few decades. Apart from this, no studies have attempted to summarize the design modification strategies, aimed to optimize the use of biodiesel, as a review work. With such motivation, in the current review work, we have summarized three major engine modification techniques such as variation of engine compression ratio, insulation of engine components and modification of combustion chamber design, when using biodiesel as an alternate fuel. The intricacies that go into the task of design change, impact of the design modifications on engine characteristics and other advantages as well as the limitation of it have been duly addressed in the current review work.

2.4.1. Thermal barrier coating of engine components

The historical perspectives of engine coating studies date back to two decades when the ceramic coatings acquired much prominence as an efficient insulating material for variety of applications [116-119]. At a time, when there was an adjuration to improve the engine performance, many researchers adopted coating technique to accomplish it. The objective with the realization of coating is to increase the surface temperature of the engine components and thereby, the temperature difference between cylinder and wall could be minimized to prevent heat transfer. Conceptually, the notion of decreased temperature gradient or otherwise reduction in heat loss, aids in the conversion of trapped heat into useful piston work, improving the engine power output and efficiency. Significantly, thermal barrier coating of engine components has several advantages such as improved performance, high power density, prevention of metal components from thermal stress and decreasing the cooling requirements [120].

As a matter of fact, it is noteworthy to lay an emphasis on the selection of suitable material for the intended coating process, as the material properties plays a crucial role in ascertaining the impact of coating on engine characteristics [121]. Normally, materials with poor thermal conductivity are chosen as it seldom allows heat to percolate into the material under investigation. As such, materials such as ceramics and zirconates, both of which are reported to have good mechanical properties, are contended by modern researchers as pertinent coating materials [122, 123]. In addition to the thermal conductivity, another important property that presides over the durability of the coating material is CET (coefficient of thermal expansion). Undesirably, the CET of insulating materials are lower, while for the metal substrate it is observed to be higher; when the difference between the CET of coating and substrate material increases, delamination of coated surface from the substrate takes place, affecting the durability of the coated engine [124]. Therefore, in consideration, it is advisable to maintain the difference in CET between the metal and coated surface as low as possible.

The motive to improve the efficiency by TBC has been accomplished in the past studies by applying ceramic coating using various methods [125-127]. Regardless of the wide range of methods available for insulating the engine components, plasma spray coating is the common method employed to apply suitable coating for diesel engine application, as it creates a spat structure with 10-20% volume fraction of voids and cracks [128]. There are several factors which govern the application of coating on the engine components and in the past few years, many researchers have investigated and studied the effect of thermal barrier coating on engine performance. In this connection, Morel et al [129] showed that the heat transfer was ably prevented by applying thermal barrier coating. Also, the same study pointed out the prevalence of high temperature, supporting better combustion so as to improve the thermal efficiency. Lawrence et al [130] investigated the performance and emission characteristics of LHR diesel engine with ethanol as fuel and emphasized the benefit of coating the engine components with PSZ. This study reported an increase in BTE of up to 1.64% for ethanol with coating and a significant reduction in BSFC. However, in contrary, there are also few research works which had reported no improvement in efficiency even after coating the engine components, presumably due to some defects in coating [131, 132]. Considerably, Mendera et al [133], who examined the effect of plasma sprayed coating on engine heat release, conceded that the PSZ coating in diesel engine application didn’t help to improve the efficiency as expected, given that PSZ coatings were transparent to heat radiation and the ceramic materials were translucent, affecting the heat barrier properties. Further, Cheng et al [131] compared the performance of insulated and non-insulated diesel engine and it was noticed that insulated engine barely showed an improvement in efficiency. All the endeavors being made in the context of TBC brings into light an importance of optimum balance between decrease in heat rejection rate and thickness of applied coating. A recent report added that an increased intensity of coating would reduce volumetric efficiency and increase pumping power [134]. Therefore, failing to strike an optimum balance would yield contradictory results of improving the fuel efficiency in some cases while decreasing it in other cases. Besides fuel savings, the high temperature encountered with TBC could reduce emissions like CO and HC, with slight reduction or increase in NO_X [125]

2.4.1.1. Effect of coating on biodiesel combustion and emission

Stationary diesel engines are widely being used in agricultural and marine applications and suffers less operational difficulties, as they are bound to be operated at fixed load and operating conditions for a long time. Despite their flexibility in handling and operating alternate fuels like biodiesel and alcohols, the prevailing concerns of energy insecurity and sustainability mandate for some energy efficiency measures [135]. Adding further, due to the lower calorific value of biodiesel, fuel consumption and brake power of the engine were reported to have been increased and decreased, respectively. In this connection, engine developers are trying to find a promising solution in utilizing the energy efficiently when using biodiesel. Apparently, thermal barrier coating of engine components, an attempt to minimize the energy losses has conquered the interest of many researchers when fueling a diesel engine by biodiesel. Besides the implementation of thermal barrier coating in a diesel engine for the operation of conventional diesel fuel, this strategy has also been extended to a diesel engine powered by biodiesel, which are summarized below.

Prasad et al [136], to combat its poor viscosity and volatility of Jatropha oil, emphasized the need to supply additional heat for the burning of Jatropha vegetable oil by conceiving LHR engines. In this regard, a separate piston crown was made of superini-90, a material with lower thermal conductivity, and screwed in between the crown and body of the piston with an air gap of 3mm. In consequence of their experimental study, the engine performance was noticed to be improved, with the combustion parameters in par with diesel. These results are reported to be justifiable as the heat lost to the engine coolant has been reduced, declaring inedible Jatropha oil as substitute for diesel in the developed LHR engine.

Though preheating of vegetable oil esters is one promising solution to reduce its viscosity so as to improve the combustion process, the concept of LHR engine offered much more benefits, as noted by Hasimoglu et al [126].

Therefore, in their study, they insulated the engine components using yttria stabilized zirconia ($Y_2O_3ZrO_2$) with a thickness of 0.35mm over 0.15mm thickness of NiCrAl bond coat. From their study, the BSFC of the engine was reduced by 4%, which in turn had a positive impact of improved engine efficiency. Further, the authors also conceded the increase in in-cylinder temperature as reason for the reported decrease in fuel consumption and improvement in BTE. In summary, the above study had hinted the thermal barrier coating of engine components as an alternate idea to preheating the fuel, while the former prevents the heat loss to improve the efficiency whereas, the latter technique reduces the fuel viscosity to improve the combustion and performance.

Significantly, Hazzar et al [137], foresaw the higher viscosity and lower calorific value of cotton methyl ester (CME) as major obstacles for better combustion and therefore, they decided to test CME in an engine coated by molybdenum (Mo). Notably, the coating thickness of about 300 microns is maintained and care is taken to ensure that the compression ratio of both the coated and uncoated engine is same. As a result, BTE of the engine was increased up to 2.2 to 2.3%, with the reduction in BSFC of up to 3.5 to 5.6%. In wake of this reported increase in combustion efficiency, the emissions such as CO and smoke were observed to be reduced by 17 to 22% and 5.2 to 10%, respectively. Significantly, the authors highlighted the remarkable advantage of effective burning of the fuel due to the injection of biodiesel into the combustion chamber after it is heated. However, as a negative consequence, NO_X emission was noticed to be increased for coated engine due to more active combustion and the subsequent increase in in-cylinder temperature.

In another study, Hazar et al [138] employed two different coating materials in the form of $MgO\text{-}ZrO_2$ to be applied on cylinder head and valves for a thickness of about 0.35mm and, ZrO_2 to be applied on the engine piston with a thickness of 0.15mm. For this study, canola methyl ester was used as renewable source of fuel. The reported study conceded a decrease in heat transfer from the engine and because of this; engine power output and specific fuel consumption were increased and decreased, respectively, for canola methyl ester. Though CO and smoke emissions were noted to be reduced, the

NO_X emission was increased due to the increased in-cylinder temperature and the inherent presence of oxygen within the biodiesel. The significant highlight of the above study was effective utilization of 100% canola methyl ester, enabling complete replacement of fossil fuel, in a coated diesel engine.

In a different attempt, MohamedMusthafa et al [139] compared the performance and emission characteristics of a coated diesel engine, fueled by rice bran and pongamia methyl ester. Distinctly, fly ash, a thermal power plant waste, had been used as coating material to be applied on piston crown, cylinder head, cylinder liner and valves and the thickness of the coating is set to be 200 microns. Comparatively, the BSFC of the coated engine was decreased by 6.6% for rice bran methyl ester and 3.2% for pongamia methyl ester, due to the positive effect of improvement in combustion, than uncoated engine. On the other hand, the gaseous emissions such as CO and smoke were reduced more for rice bran methyl ester than pongamia methyl ester. Invariably, with the coated engine, 100% use of these renewable methyl esters was appreciable with the assured token of enhanced performance and reduced emissions. Having studied the effect of TBC on diesel engine characteristics with biodiesel, Iscan et al [140] explored the feasibility of fueling straight vegetable oils in a coated engine, instead of biodiesel. With the reported advantage of the coating process, waste corn oil was chosen as the requisite vegetable oil and ZrO_2 was chosen as the pertinent insulating material to be applied on piston combustion chamber and valves. As an outcome of their experimental attempts, interesting facts were transcribed with the engine components showing no abnormalities after 100h of operation and so does are the other insulated components. Apart from these positive results on durability of the coating, the engine also showed improved performance, with a reduction in fuel consumption and increase in torque. Followed by this, Aydin et al [141] extended the concept of LHR engine to other vegetable oils such as cotton and sunflower oil. Ironically, the same coating material, ZrO_2, was used and the authors ascertained the utilization of pure vegetable oil, without subjecting it to pyrolysis, crackling or trans-esterification process, in a coated engine. From the experimental investigation, the performance of the engine was enhanced and simultaneously, HC and CO emissions were decreased, with a compromise of increased NO_X emission.

Realizing the importance of LHR engine and motivated by the uncertain demand in petroleum fuels, Prasath et al [142] targeted to combine the benefits of coated engine and renewable biodiesel fuel in their study. In addition, a detailed analysis of the combustion, heat release rate and heat transfer rate from the engine was accomplished through a simulation technique and the predicted results were validated over the engine experimental data. For the experimental part, Jatropha oil methyl ester was used as a renewable fuel and the engine components were coated using NicrAl through plasma spray coating technique at a thickness of 0.5mm. Notably, the combustion results duly pointed out an increase in in-cylinder pressure for both diesel and Jatropha biodiesel in a coated engine in view of more amount of fuel being burnt in the premixed combustion phase. Followed by this, cumulative heat release calculations were performed by them and numerical heat release rate was found to be in par with diesel. The heat transfer and NO_X model predicted a reduction in heat rejection and increase in NO_X emission, representing a highly useful tool to predict the heat transfer for different fuels in different engine configuration.

2.4.1.2. Summary and future recommendations

With coating studies on diesel engine proving to be vital in improving the engine performance and combustion, there has been a growing inclination in the adoption of this design modification technique by many researchers. Instead of making changes with the properties of biodiesel by preheating, it is rather rational to go for coating of diesel engine components as this is more practical, reliable and effective in improving the engine characteristics. Conceptually, the increase in available energy by preventing the heat transfer improves the combustion characteristics such as shortening of ignition delay, increase in combustion duration and higher accumulated heat release. In consequence, the trapped heat is ably converted into piston work, increasing the engine torque, power and efficiency. Thus far, the studies which report the use of biodiesel or vegetable oil in a coated diesel engine, as summarized in

Table 2.2 Summary of research work on coated diesel engine fueled by vegetable oil/ methyl esters

Year	Research group	Type of fuel	Coating material	Performance	Emission
2008	Hasimoglu et al	Sunflower oil methyl ester	Y_2O_3 ZrO_2 – 0.35mm NiCrAl – 0.15mm	BTE – ↑ BSFC – ↓	-
2009	Hazar et al	Canola oil methyl ester	Cylinder head, valves - MgO ZrO_2 Piston - ZrO_2	BP – ↑ SFC – ↓	CO – ↓ Smoke – ↓ NO_X – ↑
2010	Hazar et al	Cotton seed oil methyl ester	Molybdenum – 0.25mm NiAl – 0.05mm	BTE – ↑	CO – ↓ Smoke – ↓ NO_X – ↑
2011	Musthafa et al	Methyl ester of Pongamia and Rice bran oil	Fly ash	BSFC – ↓ BP – ↑ BTE – ↑	Smoke – ↓ HC – ↓ NO_X – ↑
2012	Iscan et al	Waste corn oil	ZrO_2	BP – ↑ Torque – ↑ BSFC – ↓	CO – ↓ Smoke – ↓ HC – ↓ NO_X – ↑
2013	Aydin	Pure Cotton seed oil and Sunflower oil	ZrO_2	BSFC – ↓ BP – ↑ BTE – ↑	Smoke – ↓ CO – ↓ HC – ↓ NO_X – ↑

↑ – increased, ↓– decreased when compared to uncoated engine

Table 2.2, has acceded to increase in BTE, reduction in BSFC, decrease in CO, smoke and HC emissions. However, due to the higher in-cylinder temperature, the NO_X emissions was reported to be higher and as of now, no studies have resorted to control NO_X emission from a coated diesel engine. Therefore, in the right earnest, researchers could try developing a coated diesel engine with effective after treatment techniques like SCR or EGR to reduce the NO_X emission. Otherwise, the NO_X reduction additives could be added with biodiesel or vegetable oil, when testing in a coated diesel engine, to avoid the complexity of more arduous engine modifications with SCR and EGR.

2.4.2. Variation of compression ratio

The basic laws of thermodynamics assert that there is a factor by which the pressure inside the combustion chamber could be surged past or reduced below the optimum pressure. Significantly, this factor is called the compression ratio, which is defined as the ratio of total cylinder volume to the clearance volume.

$$CR = \frac{Vs + Vc}{Vc}$$

Where V_S- Swept volume; V_C – Clearance volume

The change in clearance volume, which entails the change in distance between the cylinder head and top of the piston (squish region), affects the compression ratio, and depending on the requirement, it could be set to a prescribed value. Typical values of compression ratio are 12 to 24 for compression ignition engine, while for SI engines it ranges from 8 to 12. Understandably, there are two eminent ways by which the compression ratio of a DI diesel engine can be altered. One pragmatic approach is to change the thickness of cylinder gasket so as to decrease or increase the clearance volume. On the other hand, there exists another enviable approach to alter the compression ratio of engine, which delineates to changing the geometry of piston bowl so that the clearance volume can be either increased or decreased [143]. However, a great deal of efforts has to be paid to accomplish this, though there are additional benefits like increase in airflow and turbulence in the combustion chamber, and hence normally not preferred for changing the compression ratio.

In addition to the above two strategies, with the advancement in technology and development, engine developers have also devised some other approaches to change the compression ratio without stopping the engine and altering the combustion chamber geometry. Conceptually, engine cylinder block was made to be tilted to change the clearance volume and this methodology is applicable for both stationary and variable speed engine [144]. In further advancement, few engine developers have made provisions in the engine like diesel injection point or spark advancement so as to enable engine operation at lower compression ratios. At any particular speed and loading condition, either the injection of fuel or ignition through spark point can be enabled, facilitating the realization of engine operation from lower compression ratio of 8 up to the maximum permissible value of 22.

It is worthwhile to reprise the fact that compression ratio of an engine is directly proportional to cycle efficiency. With the increase in compression ratio, the output power of the engine increases and so does is the engine torque, and therefore, the BTE of the engine is deemed to increase. Further, the combustion parameters such as in-cylinder pressure and temperature increases with the increase in compression ratio, which could be positively correlated with the improvement in efficiency [145]. On the emissions front, NO_X emission increases with the increase in compression ratio due to high in-cylinder temperature, however, the other gaseous emission were reported to be lower [143]. These assertions on engine characteristics with the change in compression ratio unanimously applies for all VCR engine fueled by diesel and this scenario is likely to prevail over for biodiesel too, given that the principle is applicable for all fuels.

2.4.2.1. Effect of compression ratio on biodiesel combustion and emission

Most of the research work reports the use of lower blends of biodiesel with diesel in a diesel engine without any modifications and therefore, a design change is required to adapt higher blends of biodiesel. Notably, many researchers have emphasized the need for engine modifications to help adapt biodiesel in face off its distinct properties [146, 147] and therefore, suggested increasing the compression ratio of the engine as a viable approach. Typically, the lower calorific value and higher viscosity of biodiesel appears to have affected the combustion process and with the increase in compression ratio, these shortcomings are limited to some extent. The excerpt of the work on the modification of compression ratio with biodiesel as fuel for a diesel engine has been summarized in this subsequent section, to get better insight on it

Jindal et al [146] diligently identified the need to bring about some modification in engine design, when biodiesel is being used in a diesel engine. With this consideration, they set about a research study to change the compression ratio of the engine to increase the brake power and compensate for the setback of lower calorific value of biodiesel. Synonymous with their objective, the BSFC was decreased with the increase in compression ratio, when using Jatropha methyl ester as renewable fuel. Further, to help improvise the atomization of biodiesel, the fuel injection pressure was optimized and with the increase in injection pressure, there was a noticeable improvement in engine performance. After several combination of compression ratio and injection pressure value, the engine was found to show reduced fuel consumption at an injection pressure of 250bar and a compression ratio of 18, which happens to be 10% lower than standard setting (CR-17.5 and IP-220bar). Regarding the emissions, CO and smoke emission were noticed to be decreased with the increase in compression ratio due to the persistence of higher in-cylinder temperature, caused by more complete combustion. However, interesting observation of increase in HC emission was reported with the increase in compression ratio due to the dilution by residual gases, whereas at lower compression ratio, the longer ignition delay has prompted to reduce the HC emission. On the other hand, NO_X emission was reported to increase with the increase in compression ratio. In the final consensus, though some increase in emissions were reported with the increase of compression ratio, the fact that they were still lower than diesel was conceded to be appropriate, with a notable advantage of utilizing 100% Jatropha methyl ester.

Gumus [148], to study the combined effect of modifying the engine operating and design parameters on the characteristics of a diesel engine powered by biodiesel, initiated a research work by varying compression ratio, injection pressure and timing. In his work, Hazel nut kernel oil methyl ester was used as the renewable fuel and the combustion characteristics were investigated at different operating and design conditions. It was noticed from his study that increase in compression ratio resulted in shortening of ignition delay and increase in in-cylinder pressure, rate of heat release rate and cumulative heat release, when using hazel nut kernel biodiesel and its blends in diesel engine. Further, as the compression ratio was increased, BSFC was pointed out to be decreased, while the BTE was increased. Conclusively, the increased injection pressure, compression ratio and injection timing were demonstrated to be crucial in the improvement of engine combustion and emission characteristics.

Haik et al [149], have shed some light on using algae biodiesel in a variable compression ratio diesel engine, emphasizing the importance of algae oil over other vegetable oils. As such, algae oil methyl ester was prepared by trans-esterification process and suitable blends of it with diesel were investigated in a diesel engine. With the experimental testing at a default compression ratio of 22, the engine was reported to show higher heat release rate and noise for algae oil methyl ester, though the torque output produced for it lower than diesel. To avert engine noise, the compression ratio of the engine was reduced to 18 and in light of this, the experimentation showed no sign of engine knocking or noise. Reportedly, this was attributed to the reduction in in-cylinder pressure as well as temperature at the time of fuel injection. By this token, the maximum pressure rise rate was reduced so as to control the degree of smoothness of operation of the engine.

Raheman and Ghadege [85] identified the need to optimize the engine operating and design parameters such as injection timing, injection pressure and compression ratio, when fueled by biodiesel, to improve the engine performance and emission. In this light, Mahua oil biodiesel was chosen as renewable source of fuel and from the engine study, it was identified that biodiesel showed a remarkable improvement in engine performance when the compression ratio was increased, whereas for diesel, the improvement in performance at higher compression ratio was not highly appreciable. After the root cause analysis of the reported occurrence with biodiesel and diesel, the lower volatility and higher viscosity of biodiesel was adjudged as potential reasons. Though the results confirmed the utilization of 20% Mahua biodiesel in blend with diesel at any compression ratio for getting fairly comparable performance with diesel, higher compression ratio of 20 was recommended for pure Mahua biodiesel operation. In an another study, Sayin et al [150], when using biodiesel - diesel blends in a variable compression ratio engine, procured a suitable biodiesel from the external source, as biodiesel was commercialized and readily available in markets these days. Notably, the authors reported that increase in compression ratio resulted in improvement in BSFC, BTE and BSEC due to faster combustion at higher compression ratio. On the other hand, HC and CO emissions were reported to be lower when the compression ratio was increased due to the increase in in-cylinder temperature during the expansion stroke. However, these benefits were achieved only at the expense of higher NO_X emission.

Selvan et al [91], as a different attempt, conducted an engine testing using diesel – biodiesel – ethanol blends at compression ratio of 15, 17 and 19. The renewable biodiesel used in their study was Jatropha biodiesel and all the physical and thermal properties of it were ensured to be within general biodiesel standard. Noticeably, despite the lower cetane number of ethanol present in the blend, the in-cylinder pressure was observed to higher at higher compression ratio due to complete combustion. In the same note, the peak heat release rate for the blend fuels were noted to be higher at a compression ratio of 19 and the total combustion duration decreased with the increase in compression ratio. In another study, Mohanraj et al [151], tilted the cylinder block of the engine to vary the engine compression ratio form 14 to 18, and investigated tamanu oil biodiesel in a diesel engine. The results of their experimental study confirmed that the performance of the engine is a function of compression ratio and the engine emissions such as HC, CO and smoke were drastically reduced with the increase of compression ratio.

Amarnath et al [144], in their experimental study to compare the performance of engine fueled by Jatropha and Karanja methyl esters, acceded to the decrease in BSFC with increase in compression ratio. As such, BTE of the engine was perceived to be 5.31% and 6.34% higher for Jatropha and Karanja methyl esters, respectively, when the compression ratio was increased from 14 to 18. Further, HC and CO emission were observed to be decreased as the compression ratio is increased on account of higher heat of the compressed air. As expected, NO_X emission was shown to be increased for both the biodiesel when the compression ratio was increased due to higher in-cylinder temperature and availability of surplus oxygen within the biodiesel. In another study, Amarnath et al [152] optimized both the compression ratio and injection pressure of a diesel engine fueled by Karanja biodiesel using genetic algorithm. While the increase in compression ratio resulted in shortening of ignition delay and increased the peak in-cylinder pressure, the increase of injection pressure enhanced the atomization and air/fuel mixing process. Accordingly, at higher injection pressure and compression ratio, BTE of the engine was increased, and emissions such as HC, CO and smoke were reduced at a negative consequence of higher NO_X emission. As a final disposition of the optimization study, the authors disclosed 220bar injection pressure and compression ratio of 18 as optimum value.

Recently, Kassaby et al [153] employed waste cooking oil biodiesel as a renewable fuel for diesel engine and examined the engine characteristics under varying compression ratio of 14, 16 and 18. As expected, the BSFC of the engine decreased not only with the increase in proportion of biodiesel with the blend, but also with the increase in compression ratio. According to their study, on an average, BTE of the engine was increased by 18.39%, 27.48%, 18.5%, and 19.82% for B10, B20, B30 and B50, respectively, when the compression ratio is increased from 14 to 18. Similarly, HC and CO emission were decreased by 52% and 37.5%, respectively, while NO_X emission was increased by 36.84%. These benefits were ascribed to the promotion in combustion with the increase in engine compression ratio, wherein the combustion delay was reported to be decreased by 13.95% than diesel.

2.4.2.2. Summary and future recommendations

In summary, the increase of compression ratio resulted in increase of in-cylinder pressure and shortening of ignition delay, while BTE of the engine was increased and emissions such as HC, CO and smoke were reduced.

However, increased in-cylinder pressure and maximum pressure rise rate could lead to engine knocking at high load and hence the extent to which the compression ratio can be increased has to be refrained. In addition, the enhanced combustion was asserted to have increased the in-cylinder temperature, thereby increasing the NO_X emission. However, many researchers have enunciated optimization of operating parameters along with variation of compression ratio to control the NO_X emission. In a general perspective, though retardation of injection timing in an engine with higher compression ratio could reduce the NO_X emission, it would compensate for engine performance and therefore, effect of increase in compression cannot be realized. As a suggestion, suitable after treatment technique of SCR or addition of NO_X reduction additives with the fuel blend can be adopted in the near future to mitigate the NO_X emission, without compromising on the engine performance.

2.4.3. Modification of combustion bowl geometry

In the history of engine development, engine manufacturers are conspicuous of design of the combustion chamber meticulously as it is the key component, determining the degree of combustion and engine performance. Usually, the combustion chamber is a bowl in piston type, with the swirl being generated in the angular direction to control the air/fuel mixing and speed of combustion. Typically, different combustion chamber design will have different effect on air/fuel mixing process and improved air/fuel mixing will help achieve enhanced fuel burning rate [154]. In conception, when the piston moves toward TDC (at the end of compression stoke), the gas is pushed into the piston bowl and shape of the combustion bowl determines swirl motion and air/fuel mixing process. On the other hand, the impingement of fuel spray into the combustion chamber has to be properly designated as it controls the fuel vaporization. For example, in conventional diesel engine, part of fuel impingement is on the combustion chamber surface and the mixture distribution is highly non-uniform, leading to incomplete combustion [155]. Therefore, in the design process, care should be taken to develop a proper combustion chamber, which could enhance the air/fuel mixing and the subsequent combustion process. With these considerations, in the past, researchers have been nursing several options to decide on the shape of the combustion chamber and figure out an optimal design. Right from the development of simple design of open combustion chamber, there is a phenomenal change in design to re-entrant type, swirl combustion chambers, pre-combustion chambers and so on.

In the primitive stages of engine development, owing to the complexity and strenuous efforts to be paid in optimizing the combustion chamber geometry experimentally, many numerical studies were conducted. However, with the age of development, few experimental studies were also thoroughly accomplished using conventional diesel fuel with different combustion geometries like hemispherical, open cup, toroidal, shallow depth and re-entrant combustion chamber. The air flow and the associated flow fields in the bowl and squish region are interconnected, and for different shapes of combustion chambers, the engine performance, combustion and emission characteristics are different. In order to study the effect of combustion chamber geometry on engine performance and emission, Saito et al [156] opted for re-entrant type instead of conventional hemispherical type combustion chamber and showed an improved performance and combustion. As a significant measure of their study, the heat transfer calculations manifested an increase in temperature of the combustion chamber wall, which ably prevented the ignition lag. Further improvement in combustion and engine performance, were justified by increase in in-cylinder velocity and the accompanied higher turbulence. In the experimental investigation by Kidoguchi et al [157], a high squish combustion chamber with a squish lip was recommended to reduce the NO_X and soot emissions simultaneously. However, the authors insisted on the need to retard the injection timing when using the reported combustion chamber so as to avoid the rapid pressure rise and engine knocking.

2.4.3.1. Effect of combustion chamber geometry on biodiesel combustion and emission

In the past, there have been many revelations about the engine characteristics when using different combustion chamber for diesel [158-160]. Nevertheless, with some general trend obtained for diesel, the effect of combustion chamber geometry when using biodiesel is worth of an investigation and in wake of this, few researchers have recently changed the combustion chamber design for using biodiesel. Since the properties of the biodiesel are distinct, a design modification in respect of change in geometry of the combustion chamber is quintessential to enhance the fuel/air mixing process and the combustion process. The following is the excerpt on the effect of various piston bowl geometry on the performance, combustion and emission characteristics of the engine when fueled by biodiesel.

Jaichandar et al [161] carried out engine experimental testing with three types of combustion chamber geometries in the form of hemispherical, toroidal and shallow combustion chamber without altering the compression ratio of the engine. As a notable mention, the authors emphasized the necessity to go for engine modifications, in particular the combustion chamber shape, when using B20 blends of Pongamia biodiesel as alternate fuel, so as to improve the air/fuel mixing process. From their investigation, among the three combustion chambers, toroidal combustion chamber was observed to evince better performance and emission, due to its geometric consideration. Significantly, both the squish and swirl motions for toroidal combustion chamber was noted to be superior, enabling better vaporization and mixing of the blend fuel. Further, due to the improvement in combustion process and presence of oxygen with in biodiesel, the gaseous emissions such as CO, HC and smoke were reduced, with an increase in NO_X emission. However, regardless of the type of combustion chamber, a perceptible increase in diffusion combustion phase and decrease in premixed combustion phase were reported for B20 due to the shortening of ignition delay. However, the authors remarked that the likelihood of the results to comply for various biodiesel, produced from different feedstock was noted to be impossible as the fuels properties of biodiesel are prone to variations.

In-order to study the effect of re-entrant combustion chamber design over the hemispherical, toroidal and shallow combustion chamber design, Jaichander et al [162], in another study, conducted an experimental study in a diesel engine using the same B20 blend of Pongamia biodiesel. As a notable mention, in re-entrant combustion chamber, the lip of the combustion chamber protrudes beyond the wall surface of bowl and this was reportedly facilitated to increase the engine performance and emission on account of better air/fuel mixing process. Further, with re-entrant combustion chamber, the surfaces were reported to be hotter and this enabled to prevent the ignition lag and provide better fuel economy. From the experimental results, toroidal combustion chamber discerned higher BTE than re-entrant combustion chamber and interestingly, the BTE of the re-entrant combustion chamber was found to be flanked between toroidal and hemispherical combustion chamber. Due to better mixture formation and the subsequent hot combustion environment, HC, CO and smoke emission were divulged to be lower for toroidal as well as re-entrant combustion chamber than conventional hemispherical combustion chamber, while NO_X emission was reported to be higher.

As a follow up to the modification of combustion chamber geometry for achieving better performance and emission, when using Pongamia methyl ester, Jaichandar et al [163] coupled the effect of varying the combustion chamber design and operating parameters in their next study to realize more effective engine characteristics. From their previous studies, as explained above, toroidal combustion chamber was chosen as an optimum design along with the conventional hemispherical combustion chamber in the current study. In addition to the design change, the fuel injection pressure was increased so as to enhance the atomization of the Pongamia biodiesel blends and the holistic effect of these changes on engine characteristics was recorded. Previously, when compared to hemispherical combustion chamber, the toroidal combustion chamber showed lower BSFC and with the increase of fuel injection pressure, BSFC was further reduced. As remarked by them, the fuel was atomized finer due to higher injection pressure and this coupled with higher swirl ratio of toroidal combustion chamber has supported better fuel/air mixing process, improving the performance of the engine. As a reflection of complete combustion, BTE of the engine was increased and notably, for toroidal combustion chamber, the BTE was increased to 34.31% from 33.07% when the injection pressure was increased up to 230bar. Further, the HC emission for toroidal combustion chamber was pointed out to be 30% lower than that for hemispherical combustion chamber at full load condition and it was further decreased when the injection pressure was increased. Similarly, there was a reduction in CO and smoke emission by 44.5% and 28%, respectively, for toroidal combustion chamber, when compared to hemispherical combustion chamber at higher injection pressure of 230bar. With the observation of increased NO_X emission with toroidal combustion chamber, due to the increase in in-cylinder temperature inflicted by the enhanced combustion, Jaichandar et al [164] attempted to retard the injection timing to control NO_X emission. As a case in point, the injection timing was retarded form 23º CA to 20º CA in steps of 1º CA. With the retardation of fuel injection timing, the fuel mixing time was reduced and hence the burning rate of the fuel was abated to decrease the in-cylinder temperature and NO_X emission, with a marginal increase in HC, CO and smoke emission.

2.4.3.2. Summary and future recommendations

The degree to which the swirl motion of the air and turbulence within the confines of the combustion chamber are amplified is dependent on the geometry of the bowl in piston. The better air movement offers the benefit of improved performance and emission. Though basic implication of combustion chamber geometry can be learnt though simulation studies, a myriad of experimental data is needed to make this comprehensive. However, extensive revelations on the modification of combustion bowl geometry have not been considered for the experimental testing of biodiesel in a diesel engine. Owing to the availability of different categories of biodiesel, each being produced from different renewable source, the experimental investigation of certain species of biodiesel in a diesel engine with different combustion geometry is alone not adequate. Therefore, there exactly props a paucity of experimental data on different species of biodiesel been tested in a diesel engine with different combustion geometry.

2.5. Fuel modification strategies

The use of neat vegetable oil in diesel engine already exists in literature [135], while the initiative to use them as fuel incepted way back in 1900 when Rudolf diesel used peanut oil to fuel diesel engine [165, 166].

Vegetable oils could be directly used in diesel engine because of its good burning properties and it was reported to have reduced the deleterious greenhouse gas CO_2 (carbon dioxide) and carbon foot prints [15, 16]. Nevertheless, the use of neat vegetable oil directly in diesel engine without reliability issues hasn't been realized thus far, as its viscosity is significantly higher than diesel affecting the engine performance and combustion. Further, prolonged use of them in diesel engine would pave way for long term problems such as injector clogging, carbon deposits and lubrication oil contamination [3, 19, 167]. Therefore, in order to reduce its viscosity, several studies have focused on using preheated vegetable oil in a diesel engine to enhance the fuel atomization such that the fuel is effectively mixed with air to favor combustion process [53, 77, 168].

In a recent study on preheating of fuel inlet temperature, Chauhan et al used preheated jatropha oil for fueling diesel engine and found that such an option could increase BTE (brake thermal efficiency) and decrease BSFC (brake specific fuel consumption) [53]. Furthermore, it is also learnt from their study that preheated jatropha oil gave less emission of HC (hydrocarbon), CO (carbon monoxide) and smoke with slight increase in NO_X (oxides of nitrogen) than unheated jatropha oil. Similarly, many other research studies have shown an improvement in engine performance and reduction in emission when using preheated vegetable oil than unheated oil [135, 169]. Literature analysis gave ample evidence of decrease in viscosity by preheating the vegetable oil and subsequent improvement in performance and emission when tested in a diesel engine. Though the idea of preheating would wriggle out the difficulties encountered in trans-esterification process and minimizes the production cost, the viscosity hasn't been considerably reduced. Therefore, researchers have entrusted on producing biodiesel by trans-esterification process as it is an efficient method to reduce the viscosity to amenable levels [170, 171].

The addition of fuel additives is gaining popularity, as this can be done with ease when compared to engine modification techniques. Significantly, additives play a crucial role in changing the molecular structure of the fuel and its enhanced chemical reactivity benefits in attaining better performance [172].

Fuel additives can be classified into four categories as cetane number improvers, fuel injection deposit cleaning detergents, combustion promoters and oxygenates. The general classification of fuel additives that are intended to be added with biodiesel are shown in Figure 2.1.

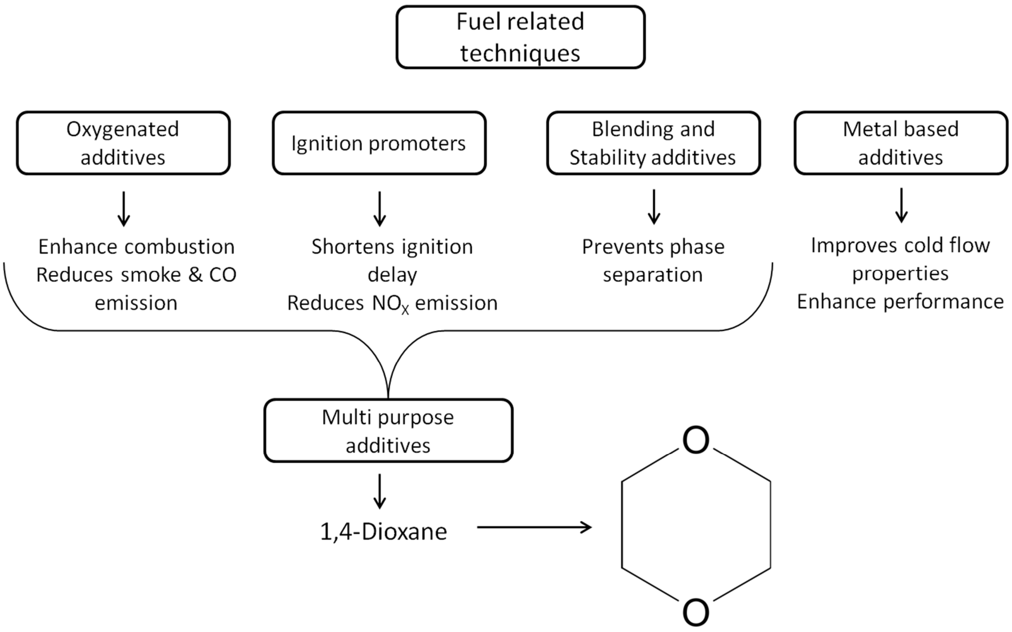


Figure 2.1 Different types of fuel additives

To begin with, cetane number improvers are either peroxide group or nitrate group members that are deemed to control both NO_X and smoke emission simultaneously [173, 174]. Prolonged use of injector without proper cleaning is at high risk of clogging, because of deposits blocking the injector, and these deposits could be evaded away by the cleaning detergents [175]. The combustion promoters are concocted to accelerate the pace of combustion and soot oxidation process, reducing the combustion duration on the whole [176, 177]. In addition to this, oxygenated additives like di-ethyl ether, di-methyl ether and carbonates have the tendency to promote oxidation of fuel to support better combustion [178-181]. Nowadays, contrary to regular additives, metallic fuel additives have also been considered to improve the performance and emission characteristics of a diesel engine, when fueled by diesel as well as biodiesel. In this connection, a recent investigation, conducted by Keskin et al [182], on the effect of metallic particle additives such as Mg (Magnesium) and MgO (Magnesium oxide) brought into light an improvement in BSFC (brake specific fuel consumption) by 6%, when the engine is driven by tall oil biodiesel mixed with suitable metallic particles. On the similar lines, the fuel borne catalyst, $FeCl_3$ (ferric chloride), have been added to biodiesel to improve the engine performance [183].

Besides the prevalence of many fuel additives, there exists an ether based oxygenated additive, 1,4-Dioxane, known to improve engine performance and emissions. A recent study on the use of ethanol – diesel blend in diesel engine reveals that 1,4-Dioxane allows splash blending of ethanol with diesel in a clear solution, reporting improved performance and emissions [184]. Moreover, 1,4-Dioxane acts as a cetane improver, besides generating stable blends and promoting fuel oxidation [172], so as to improve the ignition attributes of the fuel. It is surprising to note that diethyl ether is rather insoluble in water, whereas 1,4-Dioxane, ether based additive, is miscible and hygroscopic. Since it is being an oxygenated additive, the aromatic intermediates are reduced [185] and thus, 1,4-Dioxane, unlike other fuel additives, materialize as an dual purpose additive, serving to improve the combustion as well as the ignition of the fuel.

2.6. Conclusions

A comprehensive literature review on the characterization and optimization of biodiesel produced from inedible and waste feedstock in a diesel engine has been made. The properties and engine characteristics of selected biodiesel were elucidated and the prospect of lowering the biodiesel production cost when utilizing inedible and waste feedstock has been emphasized. With regards to the adaption of biodiesel, engine and fuel modification strategies were proposed and past experimental investigations pertaining to these have been documented. The design modification techniques such as thermal barrier coating, variation of compression ratio and modification of combustion chamber geometry, employed to operate biodiesel has been summarized. Interestingly, such a review on design modification strategies has not been accomplished before and hence in the pursuit of this research work, this review work has been up taken to the benefit of researchers. Finally, in the fuel modification strategies, the impact of adding certain additives with biodiesel on engine characteristics was summarized.

CHAPTER 3

3. Materials and experimental methodology

3.1. Kapok biodiesel

3.1.1. History of kapok seeds

Kapok tree is grown in India, Malaysia and other parts of Asia and has greater economic importance for domestic and industrial use in Nigeria. The pods of the tree contain seeds surrounded by a fluffy, yellowish fiber that is a mix of lignin and cellulose and about 120–175 seeds could be found inside each pod. In hindsight, kapok tree is mainly grown for its cotton and fiber, while the seeds are normally disposed of as waste material. Historically, the identification of kapok seeds dates back to 1931, when Dr. C.L.Alsberg, happen to collect some kapok seeds, during his visit to Java, and examine the fatty acid composition of the small quantity of oil extracted from the seeds [186]. Reportedly, from his study, the oil was found to contain 17.15% of saturated fatty acid and 76.32% of unsaturated fatty acid. Later, from 1964 to 1974, various studies disclosed the presence of more unsaturated fatty acid than saturated fatty acids in kapok oil with variable proportions of cyclo-propenoid fatty acids [187].

At present, the kapok oil has only limited application and the natural production of seeds remain underutilized. However, very recently, the oil extracted from the seed is being considered as an indispensable source of biodiesel and researchers are deliberating to harness benefits from it. As a significant contribution, a recent study on the production of biodiesel from inedible kapok (C. Pentandra) oil has reported the use of soxhlet extractor and n-hexane as a solvent to extract oil from the dried and powdered kapok seeds [188]. Subsequently, they optimized the biodiesel production, presenting the results of reaction time, reaction constant and activation energies, during the conversion of raw oil in to methyl ester. Another research work in connection with production of biodiesel from kapok oil has adopted the same approach to extract oil and have reported higher oxidative stability of kapok methyl ester than the standard values [189]. In the above works, only the chemistry part for the biodiesel production was discussed in detail, targeting the kinetics of biodiesel production form kapok oil. However, no study has attempted to experimentally investigate it as an alternate fuel in a diesel engine.

3.1.2. Extraction of oil from kapok seeds

In the current research work, kapok pods, entailing a large number of black color kapok seeds surrounded by silky fiber, were collected from a village in India. Thus far, kapok oil is reported to have been extracted by Soxhlet extraction method using n-heptane as solvent [190, 191]; however, this study has attributed to extract kapok oil by steam treatment process followed by mechanical crushing. The outline of the steam treatment process followed by crushing of the hot seeds in an expeller has been depicted in Figure 3.1.

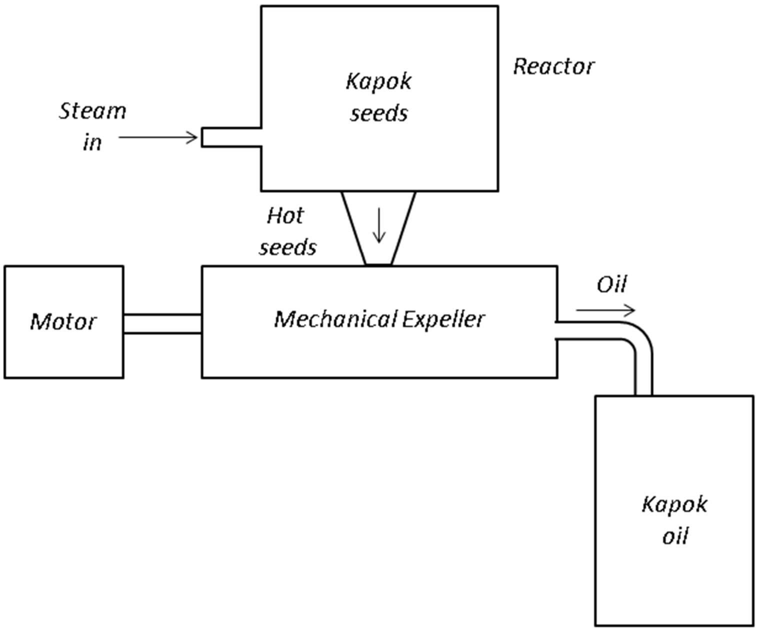


Figure 3.1 Outline of the oil extraction process from kapok seeds

Firstly, the seeds separated from the fibers were noted to be in good physical condition and therefore, without subjecting it to any pretreatment process, these seeds were fed into a reactor of large capacity to hold bulk volume of kapok seeds. After which, steam from a separate line is allowed to be passed into the reactor so as to soak the seeds with hot steam and help extract small fraction of raw oil. Subsequently, the left out oil in the seeds is recovered by crushing the hot seeds in a mechanical expeller and the total quantity of oil, as collected through these steps, is channelized into a separate tank as shown in Figure 3.1. The extracted oil is then purified through a filter so as to remove any sediments or contaminants left out in it. After the extraction process, the total oil yield, which was calculated to be 21%, was ensured from the weight of seeds used and weight of total oil extracted using the following formula,

$$Total\ yield\ (\%\ weight) = \frac{Weight\ of\ oil\ extracted}{Weight\ of\ seeds}$$

For application like diesel engine, this method of oil extraction is reasonable, as it admits bulk extraction of oil in a single trail and makes the method economical. Further, this method is believed to enhance the recovery of oil than normal mechanical expulsion technique and would help improve the properties of the extracted oil. This is because, hot treatment of seeds by steam recovers some proportion of oil and this coupled by a mechanical expeller would help enhance maximum recovery of oil. Distinctly, the process of steam treatment followed by mechanical crushing has not been attempted by many researchers when compared to other oil extraction techniques such as mechanical, solvent and enzymatic extraction methods [192]. The physical and thermal properties of the extracted kapok oil, as evaluated by ASTM standard methods, have been shown in Table 3.1. The estimated fuel properties of kapok oil reveal that it has higher viscosity and boiling point, which does not support its direct use in a diesel engine. Therefore, it is essential to trans-esterify the extracted kapok oil to reduce its viscosity and make it feasible for its use in a diesel engine.

3.1.3. Trans-esterification of kapok oil

The process of trans-esterification to synthesize biodiesel entails an alcohol and catalyst wherein, the tri-glycerides with larger molecules are broken into smaller compounds, esters. As such, in the sample preparation of biodiesel, one litre of kapok oil is heated in a magnetic stirrer apparatus, containing a hot plate and stirrer. Subsequently, the oil is heated up to 65°C and in parallel, KOH pellets were dissolved in methanol in a separate vessel to form potassium methoxide solution. The formed potassium methoxide solution is then poured into the heated oil and stirred well. When the reaction completes, methyl ester and glycerol gets separated and glycerol is drained out. After repeated washing using distilled water, biodiesel is separated out and heated up to 100ºC to remove the last traces of water molecules from it. The physical and thermal properties of the produced biodiesel are imperative before using it in a diesel engine and hence, they were evaluated by ASTM standard methods, as shown in Table 3.1. It is worthwhile to note that, after the trans-esterification process, all the properties of KME were found to be in compliance with biodiesel standard.

Table 3.1 Physical and thermal properties of raw kapok oil and KME

Property	Measurement standards	kapok oil	KME	Diesel
Density (kg/m^3)	ASTM D1298	923.2	875	822
Kinematic viscosity (m^2/s)	ASTM D445	$31.2 * 10^{-6}$	$5.4 * 10^{-6}$	$3.6* 10^{-6}$
Flash point (°C)	ASTM D92	170	156	74
Pour point (°C)	ASTM D97	-10	-8	-23
Gross calorific value (kJ/kg)	ASTM D240	39086	36292	42700
Sulphur content (%)	ASTM D5453	Less than 0.005	Less than 0.05	-
Calculated cetane index	ASTM D976	38	54	50
Copper strip corrosion @100°C for 3 hours	ASTM D130	Not worse than no 1	Not worse than no 1	Not worse than no 1

3.1.4. Composition of KME

It is a well-known fact that biodiesel are methyl esters of fatty acids and therefore, typical composition of a biodiesel, synthesized from vegetable oils, ought to possess long chain methyl esters. The composition of KME was estimated by conducting a gas chromatography – mass spectrometry (GC-MS) analysis. Notably, the column of the GC-MS was initially heated up to 50ºC and subsequently, at the ramp rate of 2°C/min, the temperature was raised up to 200ºC with the split ratio of 80:1. Further, helium, with a purity of 99.99%, was used as a carrier gas at the flow rate of 2µl/min. From the spectrum (Figure 3.2), the major constituents of KME were identified to be methyl esters of linoleic acid, oleic acid and palmitic acid. This is done after comparing the retention time of various compounds with standard database and finally, arriving at the exact constituent. The typical composition of KME in % volume is shown in Table 3.2 and after analyzing the fatty acid composition, the presence of both saturated and unsaturated hydrocarbons with oxygen in their structure is perceivable, as shown in Figure 3.2.

Table 3.2 Composition of KME

Fatty acid methyl ester	Composition (%)
Palmitic acid (C16:0)	21.2
Stearic acid (C18:0)	4.14
Oleic acid (C18:1)	23.55
Linoleic acid (C18:2)	37.4
Linolenic acid (C18:3)	1.5

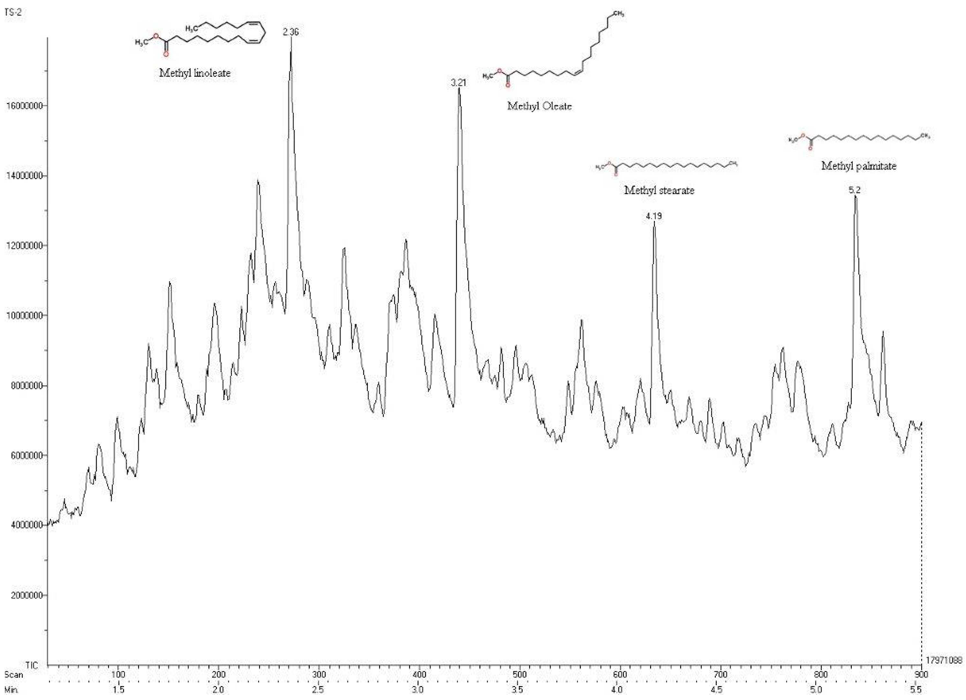


Figure 3.2 GC-MS spectrum of kapok methyl ester

3.2. Cashew nut shell liquid biodiesel

3.2.1. Cashew tree and cashew nut production

The cashew tree is evergreen, growing up 10-12m with a short irregularly shaped trunk. The tree is most prevalent in Asia and other south East Asian countries. The main commercial product of the cashew tree is the nut and from the production statistics of food and agriculture organization, it has been found that India is the second largest producer of cashew nuts among the top ten producers listed in Table 3.3 [193]. The total cultivation area of cashew in India amounts to 0.7 million hectares and 0.4 million tons of cashew were reported to have been produced [194].

The cashew fruit obtained from cashew tree has a kidney-shaped nut, consisting of coriaceous epicarp, spongy mesocarp and stony endocarp. The cashew nut shell is the outer covering of the cashew nut, which is normally peeled off during the processing of cashew nuts. The cashew nut shell is about 0.3 cm thick, having a soft feathery outer skin and a thin hard inner skin. Between these skins is the honeycomb structure, containing the phenolic material known as CNSL. In ancient times, the outer shell of cashew was usually discarded as waste and later, researchers have documented the presence of useful oil in cashew nut shells through their scientific studies.

Table 3.3 Top ten cashew nut (with shell) producers

Country	Production (metric tons)	Yield (MT/hectares)
Nigeria	650,000	1.97
India	613,000	0.66
Ivory coast	380,000	0.44
Vietnam	289,842	0.85
Indonesia	145,082	0.25
Philippines	134,681	4.79
Brazil	104,342	0.14
Guinea-Bissau	91,100	0.38
Tanzania	80,000	1.0
Benin	69,700	0.29
World Total	2,757,598	0.58

3.2.2. Prospects of CNSL as an alternate fuel – An overview

CNSL may be generated from cashew shells by various processes such as hot bath process, cold solvent extraction techniques and roasting process. The general roasting of the cashew shell in a furnace produces a dark brown liquid with higher FFA content. However, in hot bath process, oil is extracted from cashew shell by immersing it in hot bath at 185-190°C, while cold solvent extraction process has also been adopted to extract CNSL. The hot extraction produces a different CNSL when compared to that obtained by cold extraction process [195]. CNSL obtained either by hot or cold extraction process consists of anacordic acid, cardol and cardanol [196], but their typical composition varies depending upon their process. Initially, the extracted CNSL is being used to treat wood and is believed to prevent termite attack. Composite Technical Services (Kettering, Ohio, USA) have investigated the use of CNSL as a resin for carbon composite products [197]. It is extensively used in the manufacture of superior type of paints, insulating varnishes in the electrical industry, special types of adhesive cement, brake linings, phenolic resins and also in petrochemical industry [196]. In addition to its commercial use, as stated above, since it is a biodegradable source of energy; it is worthwhile to replenish the erstwhile degrading petroleum reserves by harnessing it as a renewable fuel. Therefore, nowadays, it is also being viewed as one of the probable source for producing biodiesel as it is economically viable and available in abundance.

Past studies, which focused on utilizing the unattended CNSL as an alternate fuel, have resorted to use it after subjecting it to some pre-treatment processes. When compared to other contemporary vegetable oils, CNSL is reported to have higher viscosity and FFA content. Consequently, it is an arduous task to trans-esterify CNSL and only limited focus has been paid so far to adopt this method. Considering these factors, few researchers have attempted to use CNSL in a diesel engine without trans-esterifying it or reducing its viscosity to desired levels. In this connection, Kasiraman et al [198] have tried using CNSL directly in diesel engine, however, they blended CNSL with camphor oil to enhance the evaporation rate of the blend fuel. In another study, Loganathan et al [196] used pyrolyzed CNSL as blends with diesel to investigate the characteristics of a single cylinder diesel engine. Notably, pyrolysis increased the calorific value of the fuel, however, the viscosity was still observed to be higher, affecting the fuel atomization and combustion process [199]. A recent study also pointed out subjecting CNSL to second stage distillation process, after the initial distillation of cashew shells, to remove the waste polymeric materials from CNSL and use them as a bio-oil with diesel [200, 201]. Until now, only one research study has attempted to trans-esterify CNSL, obtained by hot extraction followed by distillation process, [202]. Despite the higher viscosity of CNSL, this study has resorted alkaline trans-esterification process, which is not recommended for oils with higher FFA as it would lead to soap or sludge formation.

3.2.3. Cost comparison of CNSL with various vegetable oils

The exuberent price of the vegetable oil is a major concern, which contributes to around 80% of the total biodiesel production cost, increasing the total cost of biodiesel [3]. Therefore, it is highly required to find a pertinent feedstock for biodiesel production that would sustain the economy of biodiesel in the international market. In order to comprehend the current cost scenario, an extensive cost comparative study of different vegetable oils has been performed and is shown in Table 3.4. After getting to analyze the cost of various vegetable oils, it is envisaged that CNSL is the cheapest among the list of vegetable oils considered and hence it could be proclaimed as the low cost feedstock ever available for biodiesel production.

Table 3.4 Cost details of various vegetable oils

Type of oil	Price/ Litre in USD
Palm oil	0.98
Rice bran oil	1.39
Jatropha oil	1.07
Pongamia oil	0.98
Karanja oil	1.15
Castor oil	1.97
Mahua oil	1.48
Neem oil	1.97
Cashew nut shell liquid (CNSL)	0.33

3.2.4. Extraction of CNSL from cashew shell

In this study, a different approach to synthesize CNSL from cashew nut shell has been employed as shown in Figure 3.3. Large quantities of cashew shell are placed in a huge steel container and from the bottom; steam is fed into the container to initiate the steam treatment process. Subsequently, the shells are further crushed in a mechanical expeller and by which, maximum quantity of CNSL have been extracted. The steam treatment process followed by mechanical crushing was selected over other contemporary techniques like roasting and hot bath process, as it is convenient and believed to enhance the recovery of CNSL from the shells. The major composition of CNSL was noted to be anacordic acid, cardanol and cardol. Further, the physical and thermal properties of raw CNSL were determined by ASTM standard methods and it could be well comprehended that it possesses higher viscosity, flash point and boiling point when compared to conventional diesel. In the past, a research study has reported the properties of raw CNSL [203] wherein, the viscosity of it was perceived to be $53 * 10^{-6}$ m^2/s at 38°C. In our case, the physical and thermal properties of raw CNSL were different from the past reported study and this difference in properties could be attributed to difference in method of CNSL extraction.

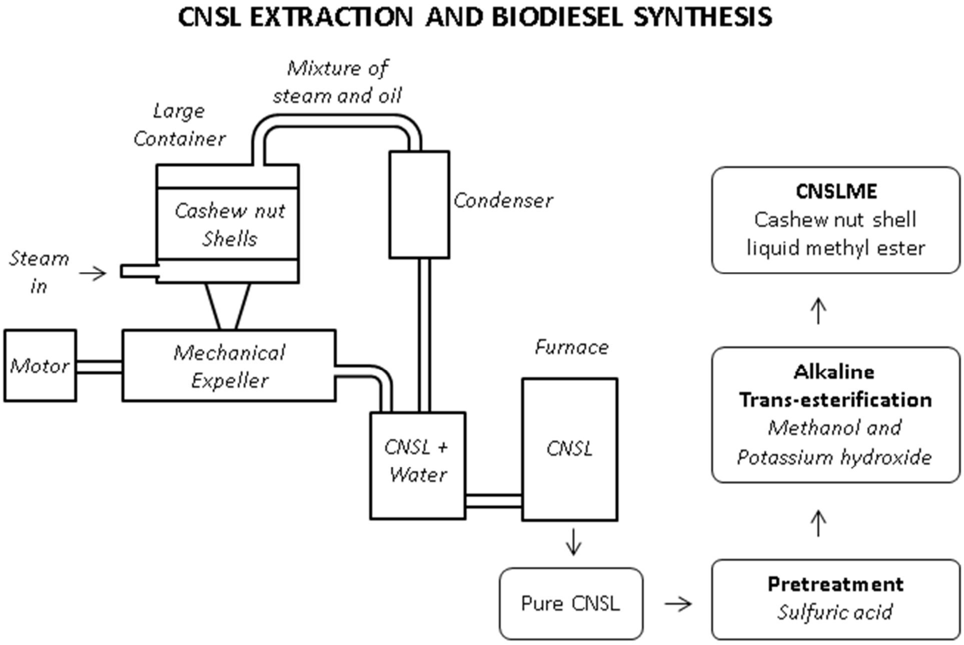


Figure 3.3 CNSL extraction and biodiesel production

3.2.5. Synthesis of CNSL biodiesel

Attempts on trans-esterifying CNSL by single stage alkaline trans-esterification process proved futile. This is because, CNSL with higher acidity and viscosity, when subjected to alkaline trans-esterification, decreased the yield of biodiesel and was liable to soap formation. In light of this, as a different attempt to counter the difficulties with trans-esterification process, CNSL was trans-esterified in two stages. In the first stage, an acid catalyst, sulfuric acid and an alcohol, methanol were used to minimize the higher viscosity and acidity of CNSL and then in the second stage, methanol and an alkali catalyst, i.e. potassium hydroxide, were used to produce CNSL biodiesel. The glycerol, produced during the trans-esterification, was drained and sufficient washing was done to get the required CNSLME. Finally, the cleaned biodiesel is heated to about 100°C so as to remove last traces of tiny water particles. The basic fuel properties of CNSLME such as specific gravity, kinematic viscosity, calorific value, flash and pour point were determined by ASTM standard methods and are shown in Table 3.5.

Table 3.5 Thermal and physical properties of CNSL and CNSLME

Property	CNSL	CNSLME
Density (kg/m^3)	956.4	909.3
Kinematic viscosity (m^2/s)	$43.1 * 10^{-6}$	$10.3 * 10^{-6}$
Ash (%)	0.08	0.16
Carbon residue (%)	6.74	1.29
Flash point (°C)	226	170
Pour point (°C)	-12	-1
cloud point (°C)	-7	-5
Copper strip corrosion @100°C for 3 hours	Not worse than NO 1	Not worse than NO 1
Gross calorific value (kJ/kg)	38681	34300
Sulphur content (%)	Less than 0.005	Less than 0.05
Calculated cetane index	33	48

3.2.6. Composition of CNSLME

Having identified the key constituents of the raw CNSL as anacardic acid and cardonol, the composition of biodiesel synthesized from it was determined in a gas chromatography – mass spectrometry (GCMS), with the column specification; 200°C operating temperature, 2°C/min ramp rate, 2µl/min flow rate and 80:1 split ratio. The GC-MS spectrum, as shown in Figure 3.4, identifies methyl esters of linoleic acid and palmitic acid as two major constituents of CNSLME. The individual esters were determined from the retention time, noted above the peak of each compounds, with the standard library of database. Deeper scrutiny of their structure reveals that both are unsaturated hydrocarbon, perhaps with longer hydrocarbon chain length and inherent oxygen in their structure, in the likes of other contemporary biodiesel.

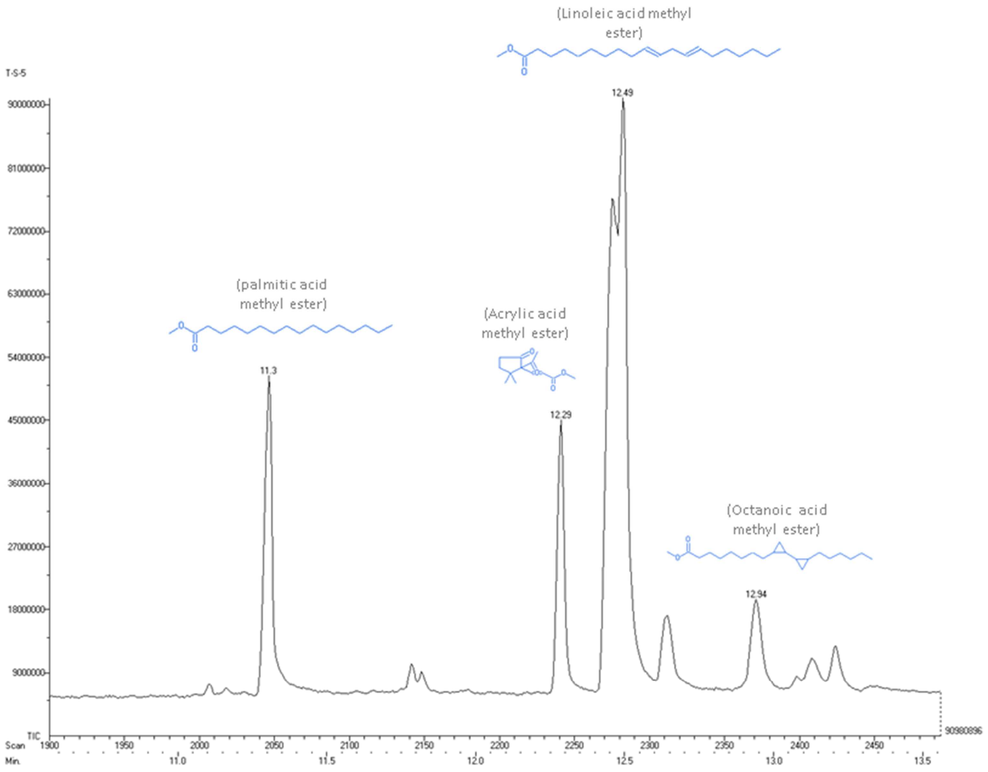


Figure 3.4 GC-MS spectrum for CNSL biodiesel

3.3. Diesel engine and experimentation

Typically, generator sets are available in different assortments such as small, medium and high power requirements and depending up on the application, preferred specification can be chosen. These days, for research studies, there is a growing interest in the adoption of this single cylinder diesel engine generator for testing alternate renewable fuels like alcohols, vegetable oils and biodiesel, owing to the flexibility in handling as well as the ability to operate at desired operating and loading conditions for long hours. Therefore, in the current research study, to experimentally investigate kapok and CNSL biodiesel, this single cylinder constant speed diesel engine (genset), enabling variation of operating and design parameters, has been used. The engine, which is a naturally aspirated one, is configured to operate at a default compression ratio of 17.5, with a capacity to produce a maximum power of 5.2kW. Further, combustion chamber is a hemispherical bowl in piston type and the other detailed specification of the reported diesel engine has been discerned in Table 3.6.

Table 3.6 Engine specification

Type	Four stroke, Kirloskar make, direct injection, constant speed ,vertical, water cooled
No of cylinders	one
Bore	87.5 mm
Stroke	110 mm
Compression Ratio	17.5:1
Rated Power	5.2 kW
Rated Speed	1500 rev/min
Dynamometer	Eddy current
Start of injection	23° BTDC
Injection pressure	220 bar
Type of injection	Mechanical pump-nozzle injection
No of nozzle holes	3

Conventionally, the air flow rate of the stationary diesel engine is maintained constant and this is ensured by the pressure drop measured in the u-tube manometer, attached to orifice meter in the inlet manifold. The air, which has been filtered through an air filter, is inducted into the cylinder, while the fuel is injected directly into the cylinder. The fuel injection equipment, which necessarily comprises of a fuel pump, injector and fuel flow lines are of mechanical type and therefore, fuel delivery and operational characteristics are regulated manually. Typically, the fuel injection pump is an inline pump with plunger, barrel, and associated components. The plunger is actuated by the camshaft and the fuel delivery is governed by shape of the plunger as well as the profile of the cam. Based on the speed and load requirements, the delivery is changed, though the stroke of the plunger is fixed. For instance, when the load is increased, the fuel pump rack rotates the plunger and controls the required quantity of fuel to be sent to the engine. Notably, the start of fuel injection is fixed at 23º CA BTDC and this can be either retarded or advanced by changing the thickness of the shim with the fuel pump. The schematic diagram of the engine experimental setup and the associated equipment’s has been shown in Figure 3.5

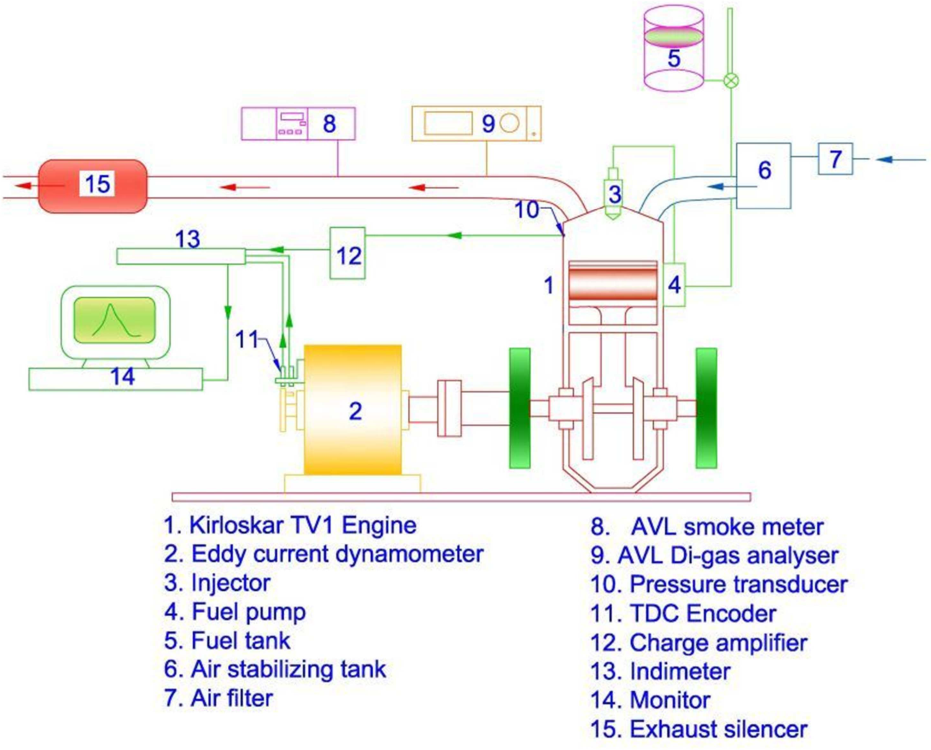


Figure 3.5 Schematic diagram of the engine experimental setup

3.3.1. Eddy current dynamometer and power measurement

The engine is loaded by water cooled eddy current dynamometer, which works on the faraday’s law of electromagnetic principle. When the load applied to the engine has to be varied, the current supplied to the dynamometer is varied and depending upon the magnitude of the current supplied, required load is applied. The force (F) exerted by the applied load on the dynamometer is measured by the strain gauge, fitted in its housing, and the measured force signals are converted to torque (T) as noted below,

$$Torque\ (T) = Force\ exerted\ (F) * R$$

Where R is the distance measured from center point of the shaft to the pivot point of the stain gauge.

From the estimated torque values, the respective power output of the engine are calculated as follows,

$$Brake\ power\ (BP) = Torque\ (T) * N$$

Where N is the speed of the engine is rpm.

3.3.2. Engine measurements

The quantity of fuel consumed by the engine, for each and every loading condition, is measured manually by a burette and stopwatch. In this regard, the time taken for the consumption of 10cc of fuel is noted down, for three times, and finally the average of the time taken is used in the calculation of total fuel consumption. If ρ is the density of the fuel, then the fuel consumption can be written as follows,

$$\text{Total fuel consumption} = \frac{Density\ (\rho) * volume}{time}$$

Significantly, the two important parameters that define the performance of the engine are BSFC and BTE, both of which have been accounted in the present study for the performance evaluation of both kapok and CNSL biodiesel. BSFC of the engine, quantifying the amount of fuel consumed for producing 1kW of power output, can be estimated from the total fuel consumption using the below formulation,

$$BSFC = \frac{TFC}{BP}$$

BTE of the engine, which defines the effectiveness with which the engine converts the chemical energy, after burning the fuel, into useful power, can be figured out from TFC, BP and amount of heat supplied to the engine.

Technically, it manifests how efficient the combustion process has been, which can be manipulated as follows,

$$BTE = \frac{BP}{Heat\ supplied\ to\ the\ engine}$$

Where, the heat supplied to the engine is given by,

$$Heat\ supplied\ to\ the\ engine = TFC * Calorific\ value$$

The major gaseous emissions measured in the current study are HC, CO, CO_2, O_2 and NO_X. Arguably, the reason for the occurrence of these emissions are general and depends up on the type of fuel being used, engine operating and design condition, engine loading condition, fuel injection system employed and other factors. Notably, these reported emissions were measured using AVL 444 di gas analyzer, which detects the constituent of the exhaust gases by non-dispersive infrared (NDIR) principle. According to this principle, when infrared radiation of different wavelength and frequency is being sent by the analyzer into the sample exhaust gases, each and every gas will absorb the radiations at a particular frequency and emits are different frequency. Depending up on the absorption potential of individual gases, the individual compounds are identified through the respective peaks of the infra-red graph. Prior to the measurement of exhaust emissions, the exhaust sample to be evaluated was passed through a cold trap and filter element to prevent water vapor and particulates from entering into the analyzer. HC and NO_X emission were measured in ppm and CO and O_2 emission were measured in terms of percentage volume.

In addition to these gaseous emissions, the other product of incomplete combustion being contended is the smoke emission. An AVL 437C smoke meter has been employed to measure the smoke density in terms of smoke opacity, which is the number of smoke particles per unit volume of gas. The smoke meter works on the principle of light extinction principle, wherein, the percentage of light transmitted through the source is prevented by the smoke particles from reaching the detector and percentage reduction is quantified in terms of HSU. Apart from the emission, temperature of exhaust gases is also an important consideration to ascertain the combustion process and in our study, a K-type thermocouple is employed in the exhaust pipe to measure the exhaust gas temperature.

Besides evaluating the engine performance and emission, the combustion characteristics were also examined in the current work and this has been realized by measuring the in-cylinder pressure. The in-cylinder pressure is measured by AVL pressure transducer, which is installed on the top of cylinder head. Further a crank angle encoder, installed at the engine crank shaft, clarifies the crank angle at which the in-cylinder pressure is being measured. The pressure transducer, which is subjected to water cooling, produces charge output proportional to the pressure inside the cylinder. In turn, this charge output of the pressure transducer is amplified in the Indi meter hardware, and the amplified analog signals are converted into digital signal using analog to digital convertor. Further, the converted pressure signal are analyzed in the indiwin software, which calculates the associated combustion parameters such as heat release rate and pressure rise rate using the standard formulations. Characteristically, the software records the pressure signal for 100 consecutive cycles and the average value of the in-cylinder pressure has been considered. Finally, the measured and calculated combustion data, stored as a separate ASCII file, are collected from the PC interface and plot of the requisite combustion parameters such as in-cylinder pressure, heat release rate and cumulative heat release rate are drawn to analyze the combustion results.

CHAPTER 4

4. Operation of kapok biodiesel in a diesel engine

4.1. Experimental investigation of kapok (Ceiba pentandra) oil biodiesel as an alternate fuel for diesel engine

4.1.1. Background

It is reliably learnt from the literature study that testing of kapok biodiesel in a diesel engine hasn’t come to light so far and only the production of it has been optimized. Therefore, in this study, attempts were taken to experimentally investigate KME in a diesel engine for the first time. It is noteworthy to point out that the extraction of kapok oil in large quantities for producing KME is a new attempt with this study. Since the extraction of kapok oil, production of KME and analysis of its properties has been discussed in the previous chapter, it has not been dealt separately here.

4.1.2. Methodology

Initially, the engine is made to run with diesel for 30 minutes to attain warm up condition which is ensured by the cooling water and lubrication oil temperature. Subsequently, the engine is tested using different blends of KME such as B25, B50, B75 and B100 without any modifications. Before testing the engine with respective fuel blends, the previously used fuel was completely drained from the fuel lines, filters, pumps, injector and other associated equipment’s. During the engine testing, BP is varied by changing the engine load through an eddy current dynamometer in steps of 20% from 20% to 100% load. Each time, the speed and required power output are maintained constant by adjusting the fuel pump rack position. The engine parameters such as BSFC, TFC, BTE, heat release rate and emissions parameters such as CO, smoke and NO_X were recorded then. Variation of all these parameters with respect to brake power for different blends of KME was examined at standard engine operating and design conditions. All the reported measurement with regards to engine and emission parameters, which were realized at ambient condition, was noted for three times to improve the accuracy of the measured readings. In order to figure out the total uncertainty of the intended experiment using KME in the diesel engine associated with various instrumentation, an error analysis was conducted in the right earnest. The accuracy and uncertainty of the equipment's and measured parameters are listed in Table 4.1. From the uncertainty of the individual parameters, the total uncertainty of the experiment was computed by the method of propagation of errors, as described in Holman [204], and was noted to be ±2.0%

Table 4.1 List of measurement uncertainties

Measurement	Accuracy	% uncertainty
Load	±10N	±0.2
Speed	±10rpm	±0.1
Burette fuel measurement	±0.1cc	±1
Time	±0.1s	±0.2
Manometer	±1mm	±1
CO	±0.02%	±0.2
NO_X	±12ppm	±0.2
Smoke	±1HSU	±1
EGT indicator	±1°C	±0.15
Pressure pickup	±0.1 kg	±0.1
Crank angle encoder	±1°	±0.2

Total experimental uncertainty = Square root of {(uncertainty of TFC)^2 + (uncertainty of BP)^2 + (uncertainty of BSFC)^2 + (uncertainty of BTE)^2 + (uncertainty of CO)^2 + (uncertainty of smoke)^2 + (uncertainty of NO_X)^2 + (uncertainty of EGT indicator)^2 + (uncertainty of pressure pick up)^2}.

= Square root of {$(1)^2 + (0.2)^2 + (1)^2 + (1)^2 + (0.2)^2 + (1)^2 + (0.2)^2 + (0.15)^2 + (0.1)^2$}.

= 2.0 %

4.1.3. Results and discussion

4.1.3.1. Brake specific fuel consumption

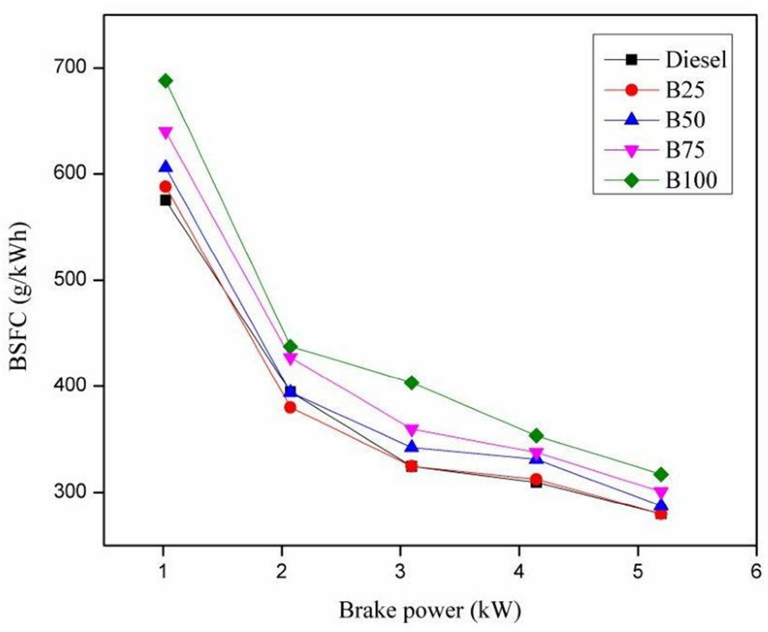


Figure 4.1 Variation of BSFC with respect to brake power

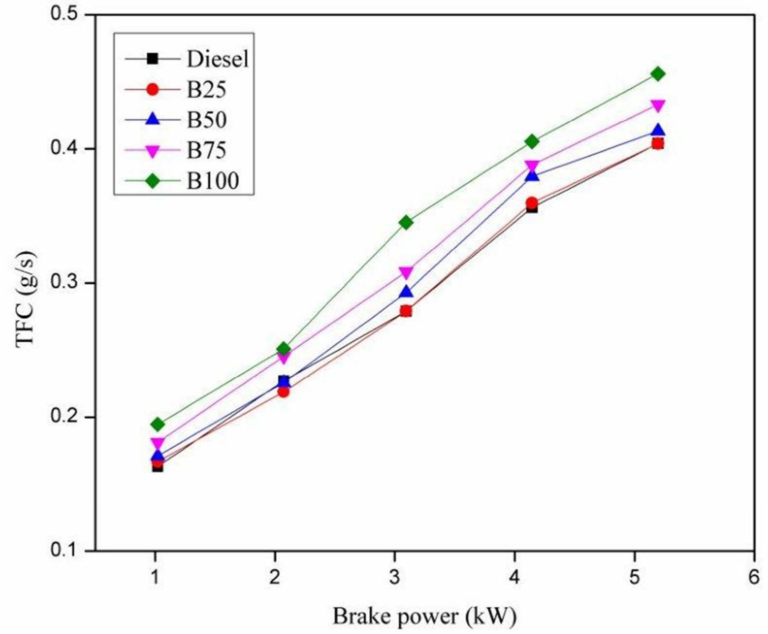


Figure 4.2 Variation of TFC with respect to brake power

Figure 4.1 shows the change in BSFC with respect to brake power for various blend fuels and diesel. It is clearly evident from the figure that BSFC of B25 blend is akin to that of diesel whereas; B75 and B100 blends show some discrepancies. BSFC of the engine depends upon the relationship between the amount of fuel injected and the calorific value of the fuel [205]. As KME has a lower calorific value, in order to produce the same power output, the TFC as visualized from Figure 4.2, is more for KME and its blends, thereby resulting in a higher BSFC. However, lower blends such as B25 show good agreement with diesel at most of the loads. The reason behind the comparable BSFC for B25 with diesel is that although the calorific value of B25 is slightly lower than that of diesel, the improved combustion due to the presence of inbuilt oxygen in it compensates the reduced energy. Moreover, the viscosity of B25 is comparable to diesel, while on the other hand, the higher blends such B75 and B100, experiences less complete combustion, due to lower calorific value and higher viscosity of KME. In compliance with these findings, Raheman et al [70] conceded increased BSFC with the increase in biodiesel proportion. In an another work, Usta et al [206], in their investigation on hazelnut soap stock/waste sunflower oil biodiesel, confessed the supply of more fuel due to lower calorific value of biodiesel.

4.1.3.2. Brake thermal efficiency

The thermal efficiency of the engine relies on the extent to which the fuel is burnt inside the combustion chamber [207]. Figure 4.3 shows the BTE of the engine fueled by various blend fuels and diesel. It can be seen from the figure that B25 has a better efficiency than diesel and other blend fuels under different loading conditions. For instance, the BTE of B25 was increased by 8.6% at lower load and 4% at higher load in comparison to diesel. This is due to the fact that KME has a higher cetane number and the presence of oxygen in the fuel is favorable for combustion. However, with the increase of KME blend ratio, there is a slight drop in BTE. This is mainly due to the combined effects of the increased viscosity of the fuel and the presence of inbuilt oxygen. The lower blends of KME have a lower viscosity and experience better atomization relative to higher blends; as a result, their thermal efficiencies are higher. However for higher blends of KME, the increased viscosity of the blend fuel affects the fuel atomization and predominate the combustion process, causing the efficiency to drop.

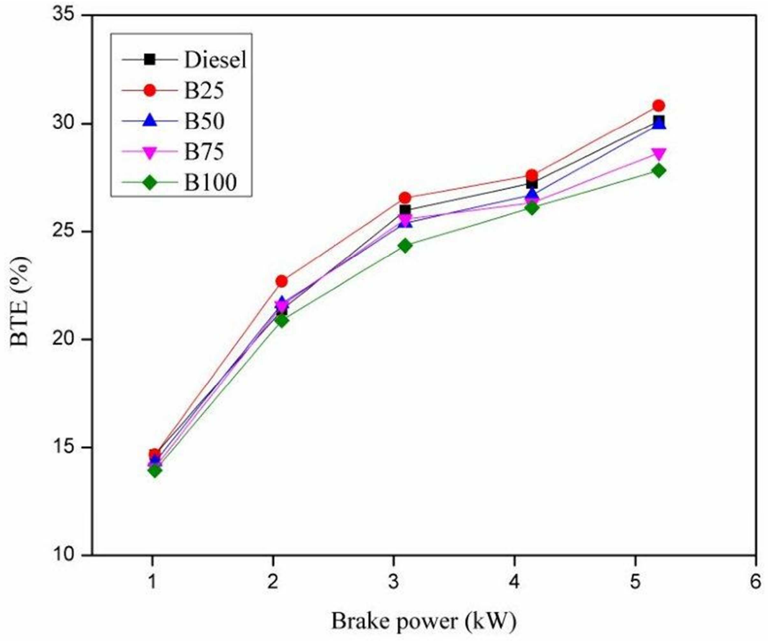


Figure 4.3 Variation of BTE with respect to brake power

4.1.3.3. Heat release rate and cumulative heat release rate

Cetane number of the fuel is primarily responsible for the ignition process [208] and therefore, the SOC (start of combustion) is little bit earlier for KME and its blends as their cetane number is higher than that of diesel (Table 3.1). It can also be observed from Figure 4.4 that the peak heat release rate for B25 lie in close agreement with diesel at maximum load of the engine. Nonetheless, the other blends such as B75 and B100 show a progressive decrease in peak heat release rate. For example, the peak heat release rate of B100 is 33% lower than that of diesel. This is because with the increase of KME percentage, the calorific value of the blend decreases, while the viscosity of the blend increases, affecting the fuel atomization and the ensuing combustion process, resulting in a lower peak heat release rate. Similar to this, Muralidharan et al [209] pointed out a decrease in peak heat release rate of biodiesel blends than diesel on account of higher viscosity and poor spray characteristics. Further, the reduced premixed combustion has had its impact on diffusion combustion as the accumulated heat release happens to get reduced for higher blends of KME. For better clarity and understanding, cumulative heat release rate curve has been drawn and is shown in Figure 4.5

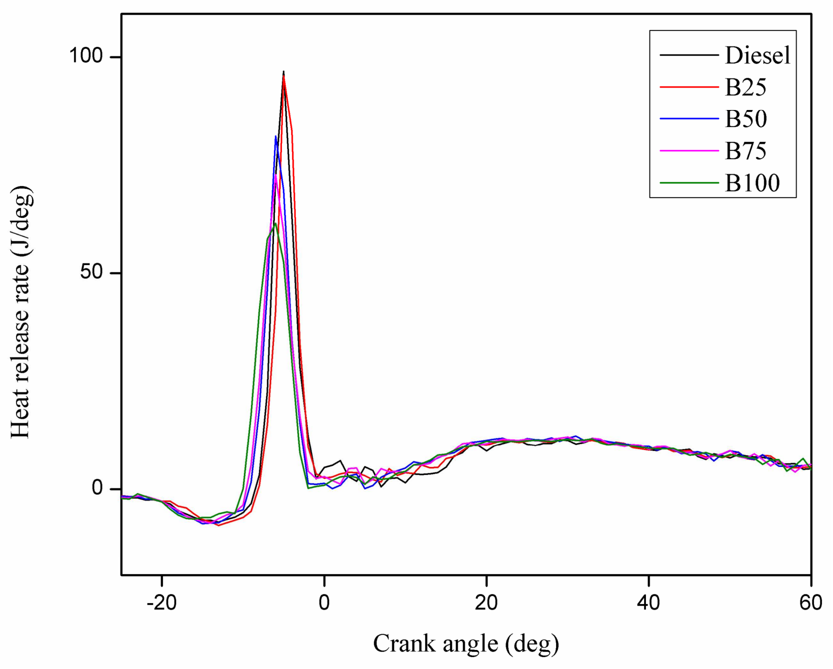


Figure 4.4 Variation of heat release rate with respect to crank angle

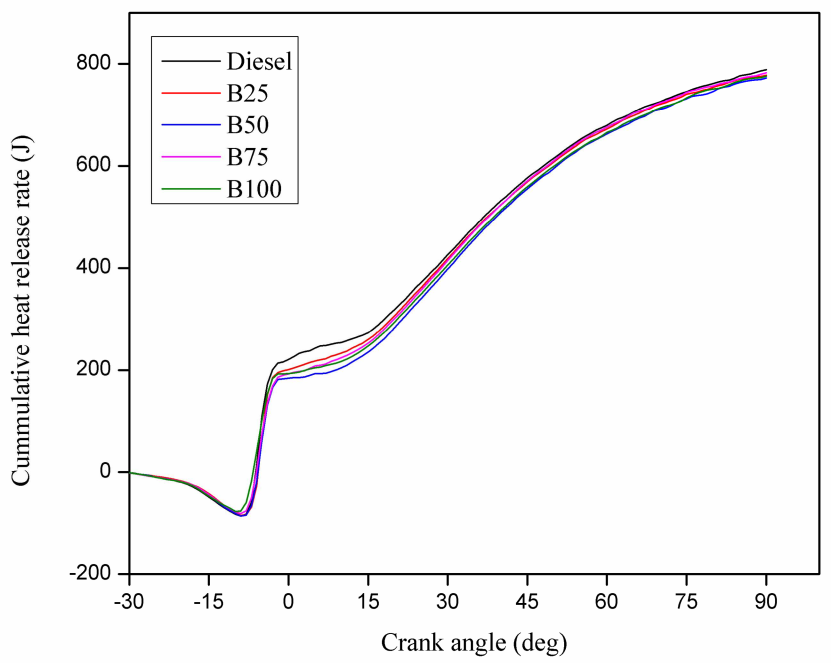


Figure 4.5 Variation of cumulative heat release rate with respect to crank angle

4.1.3.4. CO (carbon monoxide) emission

Figure 4.6 shows the CO emission for various blend fuels and diesel. It is noted that all the blend fuels emit higher CO emission, except B25, especially at full load condition, despite the presence of inherent oxygen within KME. This is due to the fact that more fuel is injected into the engine to produce the same power output as diesel (Figure 4.2), which increases the fuel/air ratio, resulting in incomplete combustion. At the same time, the increased viscosity of KME further deteriorates the combustion process resulting in more CO emission. However, for B25, the CO emission was observed to be in par with diesel, with a slight increase at full load condition.

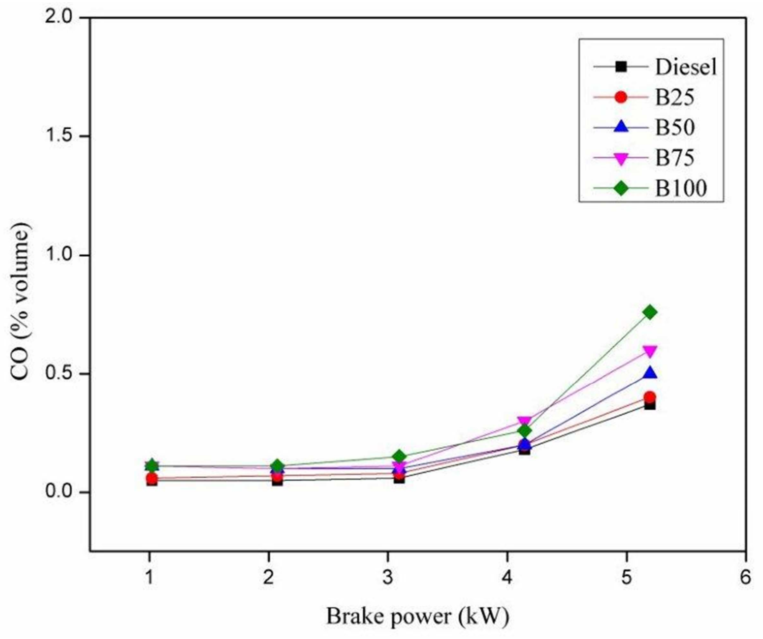


Figure 4.6 Variation of CO emission with respect to brake power

Since B25 doesn't confront with poorer atomization, and the presence of inbuilt oxygen has supported enhanced combustion, the results are in agreement with diesel. There are varied results with CO emission for biodiesel, as Sahoo et al [210], when comparing the emission of Jatropha and Karanja biodiesel, showed increased and decreased CO emission for Jatropha and Karanja, respectively. These distinctions might have arisen on account of feedstock type and biodiesel synthesis methodology. As a matter of fact, most of the researchers tend to report higher CO emission mainly because of higher viscosity of biodiesel, like the one presented here with KME.

4.1.3.5. NO_X (nitrogen oxide) emission

Diesel engine are prone to more NO_X emission due to higher heat release rate and rapid rise of temperature inside the combustion chamber [211]. The NO_X emission for various blends of KME increases with the increase in load due to the increased quantity of fuel injection, which when being burnt elevates the in-cylinder temperature. Apparently, from Figure 4.7, the NO_X emission for B25 blend is noticed to be slightly higher than diesel. The magnitude of peak heat release rate for B25 is almost similar to diesel and this accompanied by presence of excess oxygen paves way for the reaction of nitrogen molecules with oxygen at the temperature of burnt gas mixture, resulting in small increase in NO_X emission than diesel at higher loads. However, B100 and other higher blends shows slightly reduced NO_X emission than that of diesel since the combustion of B100 is predominated by the significant increase in viscosity and thereby, affecting the combustion process. In justification with this, Labeckas et al [212] indicated lower NO_X emission for pure biodiesel, Rapeseed methyl ester in their case, due to lower calorific value and slower evaporation of high viscous biodiesel.

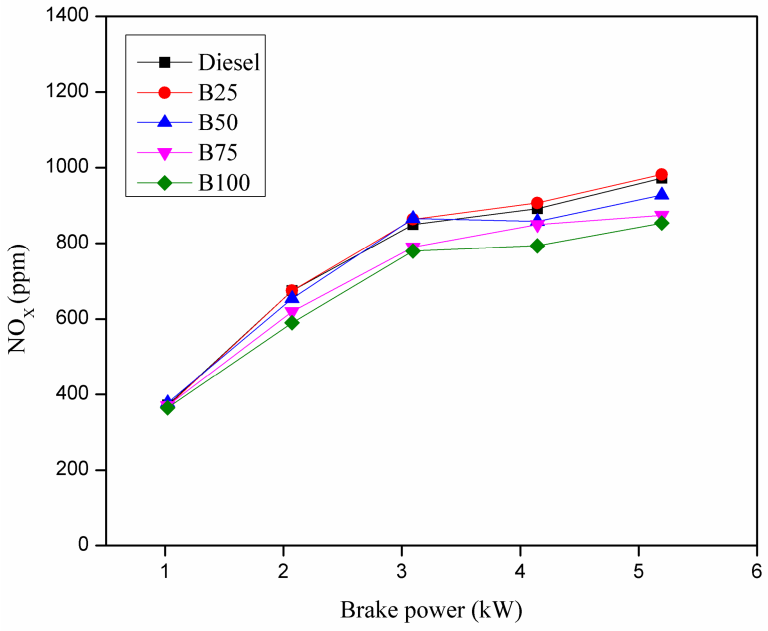


Figure 4.7 Variation of NO_X emission with respect to brake power

4.1.3.6. Smoke emission

The variation of smoke emission with respect to brake power for different blend fuels is shown in Figure 4.8 and it is found to increase with the increase in KME blend ratio. The smoke value of B25 happens to be in par with diesel. For all other KME blends, the smoke value is higher than diesel, with B100 blend reporting a 31.2% increase at full load condition. It is well known that soot precursors are formed during premixed combustion phase and if the premixed combustion phase is more pronounced, there is more time available for carbon particles to combine with oxygen and combust properly [213]. But in this case, the premixed combustion phase is less pronounced for higher blends of KME on account of shorter ignition delay and lower calorific value, which in effect, has caused for liberation of more smoke. The other potential reasons may include increased fuel/air equivalence ratio and viscosity of higher blends of KME. The deterrence's in combustion, resulting in increased smoke emission for biodiesel, has been remarked by Agarwal et al [135], which conforms the results of present study.

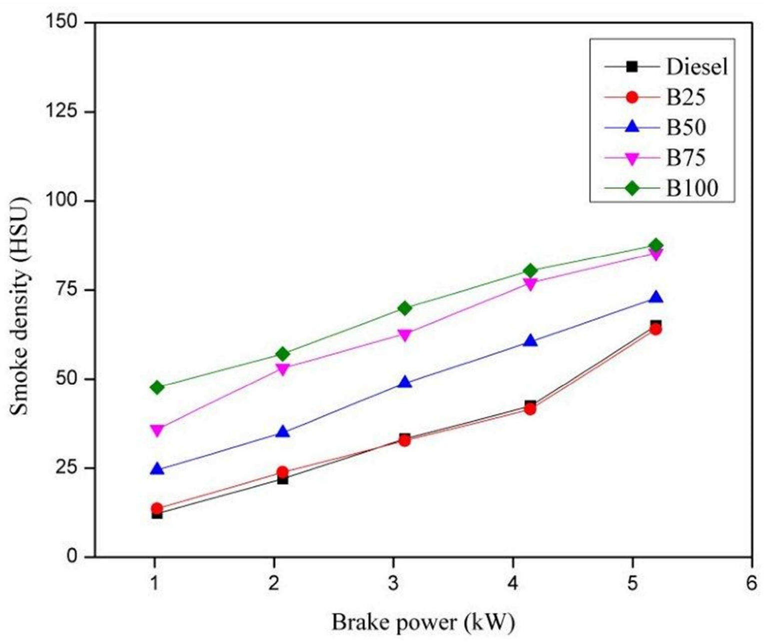


Figure 4.8 Variation of Smoke emission with respect to brake power

4.1.3.7. Exhaust gas temperature

The EGT of B25 is slightly lower than that of diesel as shown in Figure 4.9. Notably, higher ignition delay results in a delayed combustion and higher EGT [214]. For B25, SOC happens to be a bit earlier than diesel, inciting low temperature to the exhaust gases. This also explains the slightly increased efficiency of B25 compared to diesel. However, the EGT of higher blends of KME were noticed to be slightly higher than diesel, despite the higher cetane number of KME and excess oxygen within KME, as the combustion is deterred by the higher viscosity of KME, paving way for late combustion in the tail pipe.

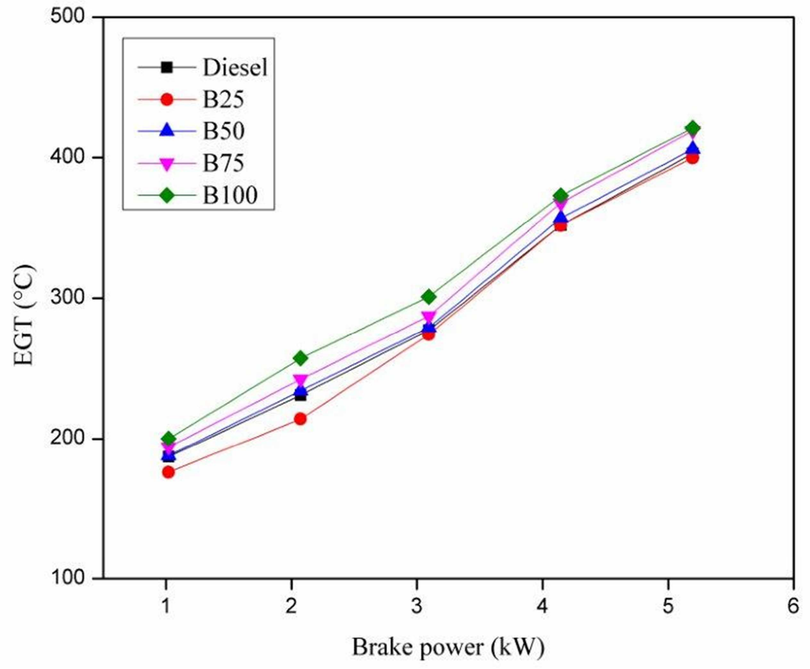


Figure 4.9 Variation of EGT with respect to brake power

4.1.4. Conclusions

In this study, KME, produced from inedible kapok oil, has been used as an alternate fuel for a diesel engine for the first time. Significantly, the potential benefits of kapok oil as source for fuel in diesel engine has been tapped. Kapok oil, extracted by steam treatment process followed by mechanical crushing, underwent alkali trans-esterification and the produced KME was tested in diesel engine. Systematic characteristic study of the fuel to identify the properties of the biodiesel was done and it was found to be in compliance with ASTM standard. Among the various blends tested in a single cylinder diesel engine, B25 blend claims a 4% increase in BTE than diesel and comparable emissions of HC, CO, NO_X and smoke with diesel. It is believed that the kapok oil would garner much attention and qualify as a viable source of renewable fuel among the other alternate fuels in the near future.

Associated publication

- Vedharaj S, Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Experimental investigation of kapok (Ceiba pentandra) oil biodiesel as an alternate fuel for diesel engine. Energy Conversion and Management. 2013; 75:773-9.

4.2. Effect of adding 1,4-Dioxane with kapok biodiesel on the characteristics of a diesel engine

4.2.1. Background

From the previous investigation of KME – diesel blends in a diesel engine, B25 was observed to evince better engine performance and emission than other blends. When compared to diesel, the engine characteristics for B25 were noted to be in par with diesel. To help improve the performance and emission for B25, in the current study, we decided to modify the properties of B25 by adding a fuel additive. Fuel additives, by virtue of their characteristics, alter the fuel properties in such a way that the combustion is improved. The comprehensive literature review on fuel additives, as described in chapter 2, manifest that 1,4-Dioxane has not been used as fuel additive with biodiesel thus far, despite its multipurpose benefits (Figure 2.1). Notably, in addition to improving the engine performance and emission, 1,4-Dioxane also enhances the blending of biodiesel with diesel and thus the mixing stability of the blend is improved. With all these considerations, 1,4-Dioxane, an indispensable additive, was added with the optimum blend (B25) in the current study, considering its potential to improve the fuel properties.

4.2.2. Methodology

In the current work, in an attempt to improve the performance and emission for B25 in an unmodified engine, we have decided to modify the fuel properties by adding 1,4-Dioxane with B25. The reported additive was procured from the commercial store and subsequently, it was added with B25 in the following composition, B25-5ml (B25 – 99.5% and 1,4-Dioxane – 0.5%) and B25-10ml (B25 – 99% and 1,4-Dioxane - 1%), and stirred well in an ultrasonic agitator. Subsequently, the fuel properties of B25, B25-5ml and B25-10ml were determined by ASTM standard methods and have been reported in Table 4.2. 1,4-Dioxane, when added with B25, improves the flash point as well as the cetane number of the blend. Further, the cold flow properties of the blend such as cloud point and pour point, and viscosity were improved, thereby enabling efficient pumping of the fuel without nucleation.

Table 4.2 Thermal and physical properties of B25 with and without 1,4-Dioxane

Property	B25	B25 -5ml	B25 -10ml
Density (kg/m^3)	850	853	851
Kinematic viscosity (*10^{-6} m^2/s)	4.1	3.76	3.65
Flash point (°C)	105	95	86
Pour point (°C)	-8	-10	-14
Cloud point (°C)	-2	-4	-6
Copper strip corrosion @100°C for 3 hours	Not worse than No. 1	Not worse than No. 1	Not worse than No. 1
Gross calorific value (kJ/kg)	41098	41012	40927
Sulphur content (%)	Less than 0.005	Less than 0.005	Less than 0.005
Calculated Cetane index	52	54	56

4.2.3. Results and Discussion

Heat release curve, a representation of amount of energy being released from the burning of fuel, for B25 with and without additive at full load condition, has been depicted in Figure 4.10. It could be noted from the figure that the peak heat release rate for B25 was in par with diesel, as there isn’t any big drop in its heating value when compared to diesel. However, the blends with additive shows a decrease in magnitude of peak heat release rate than diesel, with B25-10ml showing a lower magnitude of peak heat release rate than B25-5ml. This is because, the addition of 1,4-Dioxane in the blend ably reduces the ignition delay and as a result, the amount of fuel being burnt in the premixed combustion phase is reduced, decreasing the magnitude of peak heat release rate. The decrease in ignition delay with the increase of 1,4-Dioxane, as noted from Figure 4.10, could be attributed to the inherent nature of it to enhance the ignition attributes of the resultant blend. Conceptually, Dioxane molecules fragment at space and time when the fuel evaporates, and this liberates free radicals to improve the ignition quality of the blend. Incidentally, Ashok [215], demonstrated the shortening of ignition delay and the subsequent reduction in accumulation of air/fuel mixture by adding di-ethyl ether, an additive similar to 1,4-Dioxane, with emulsion fuel.

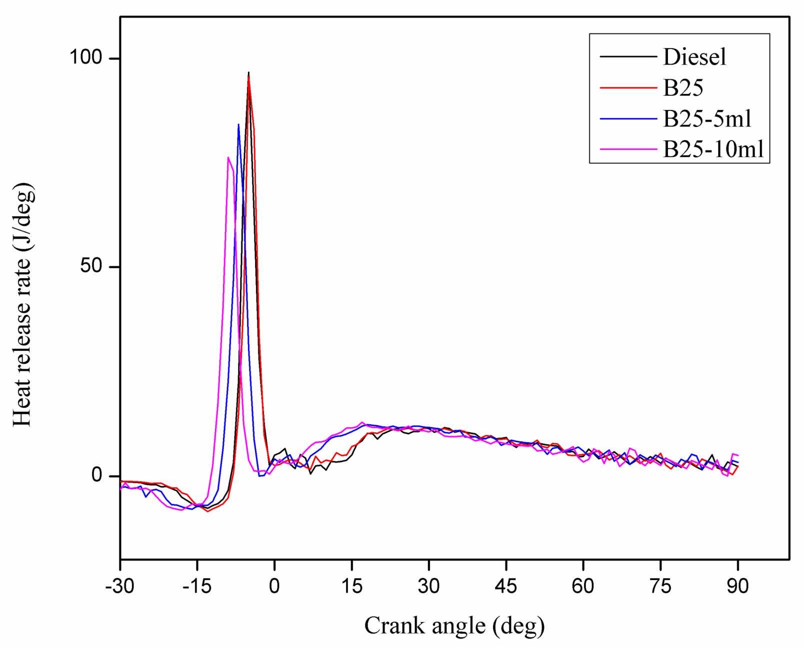


Figure 4.10 Effect of adding 1,4-Dioxane with B25 on heat release rate at full load condition

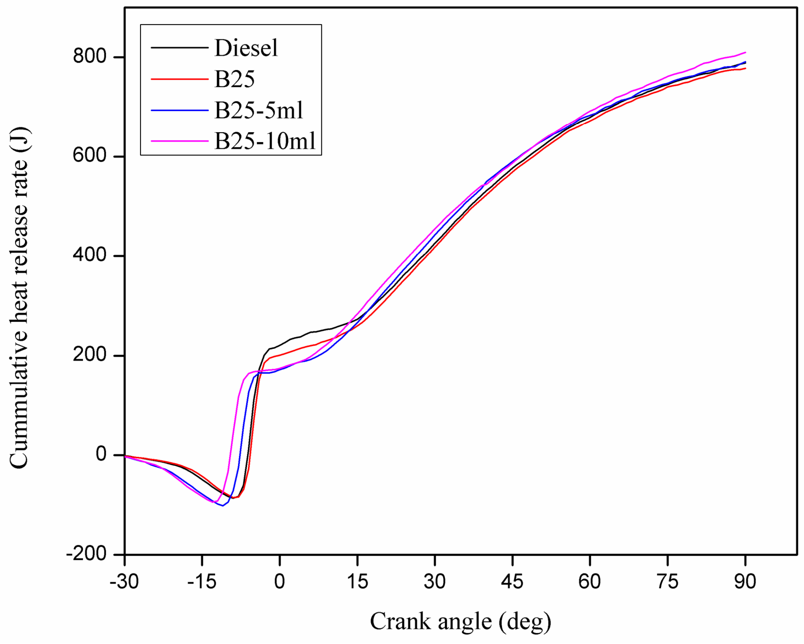


Figure 4.11 Effect of adding 1,4-Dioxane with B25 on cumulative heat release rate at full load condition

Despite the reduction in magnitude of peak heat release rate, the diffusion combustion phase, as noted from Figure 4.11, was more active for

B25-10ml. As a result, combustion is more complete, paving way for increased accumulated heat release rate. This could be attributed to the improvement in fuel properties after the addition of additives. In particular, the addition of 1,4-Dioxane improves the cold flow properties and in wake of this, the fuel atomization and evaporation are improved. At the same time, the oxygen enrichment from the additive and KME by itself, together with the improvement in other fuel properties, have promoted active diffusion combustion so as to increase the net energy released.

To help understand the effect of 1,4-Dioxane on the amount of fuel being burnt in respective combustion zones, percentage mass of fuel burnt, calculated from the net energy release rate at full load condition, for all the test fuels have been discerned in Figure 4.12. The figure clearly shows a reduction in mass of fuel burnt in premixed combustion phase and an increase of it in diffusion combustion phase with the increase in proportion of 1,4-Dioxane with B25. Notably, the mass of fuel burnt in premixed combustion phase was reduced to 24.86% for B25-10ml from 31.2% for B25. In compliance with this, Ladommatos et al [216] pronounced a decrease in mass of fuel being burnt in the premixed combustion phase, after improving the ignition attributes of the fuel being used.

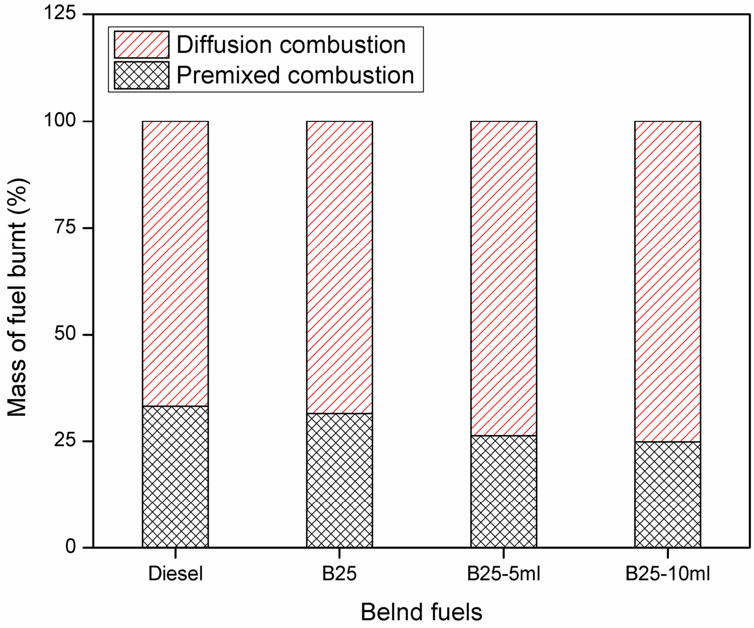


Figure 4.12 Effect of adding 1,4-Dioxane with B25 on mass of fuel burnt in premixed and diffusion combustion phase at full load condition

CO emission from a diesel engine is governed by various factors such as fuel/air equivalence ratio, in-cylinder temperature and presence of oxygen [70, 217]. Despite the presence of inbuilt oxygen, B25 showed slightly higher CO emission than diesel due to its slightly higher viscosity. However, the addition of 1,4-Dioxane enhances the combustion process and therefore, the CO emission for the blends with additive (B25-5ml and B25-10ml) is reduced than that of diesel. Furthermore, this reduction in CO emission could also be supported by their fuel properties (Table 4.2) such as reduced viscosity and improved cold flow properties. Notably, B25-10ml blend, as envisaged form Figure 4.13, depicts a 22.5% reduction in CO emission than B25 at full load condition. In a recent study, TJ Bruno et al [218] postulated the oxygen mass fraction of 1,4-Dioxane to be 0.36 and in light of this, better oxidation of CO was reported. By this token, in our study too, the promotion in oxidation of CO to CO_2 is certain due to the subtle increase in oxygen proportion, certainly from biodiesel as well as the additive.

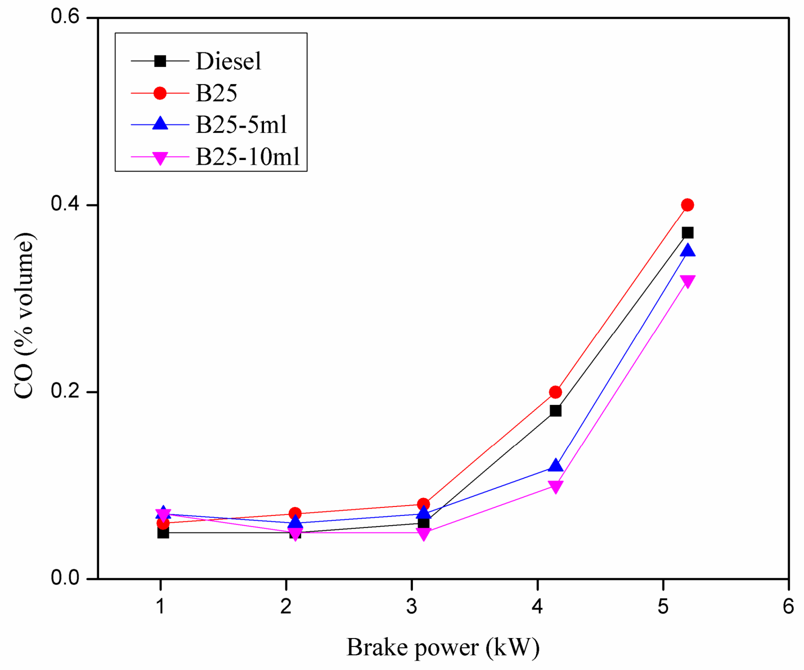


Figure 4.13 Effect of adding 1,4-Dioxane with B25 on CO emission

The HC emission for B25 with and without additive at respective loading conditions has been portrayed in Figure 4.14, highlighting the effect of additive on HC emission. From the figure, it could be inferred that the HC emission for B25-10ml is reduced by 25.3%, when compared to B25, at full load condition. For B25, the increased HC emission than that of fossil diesel is due to the incomplete combustion while for the blends with additive, the combustion is promoted so as to reduce the HC emission. The reason behind this is with the enhancement in ignition attributes of blends with additive (B25-5ml and B25-10ml) and the contribution of oxygen from both KME and 1,4-Dioxane, more complete combustion is enabled. Even in the past, Agarwal et al [64] conceded to the increase in HC and CO emission in face of incomplete combustion, caused by the higher viscosity of the fuel. However, later on, this effect was reportedly suppressed by the effect of additive to improve the ignition and combustion process, resulting in the reduction of CO and HC emissions [175], which is in compliance with the findings of the present study.

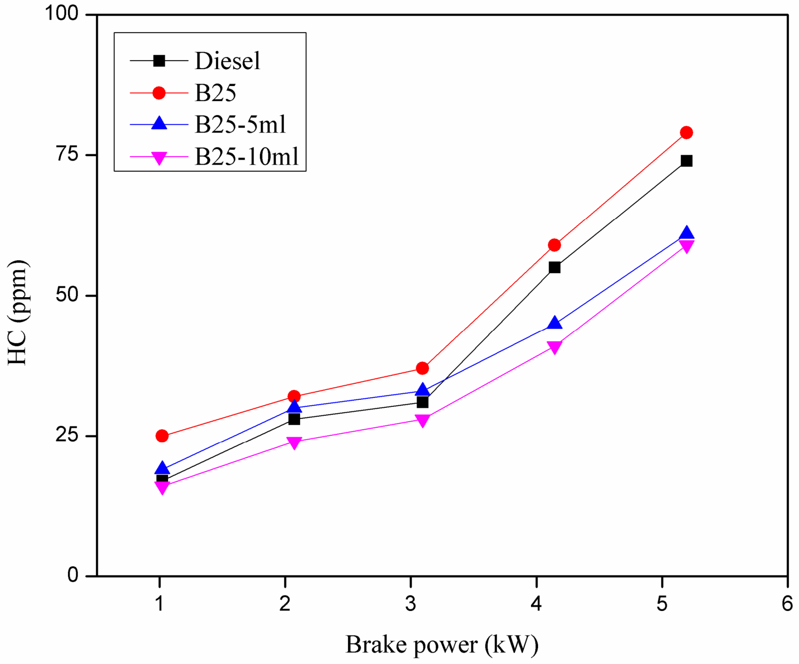


Figure 4.14 Effect of adding 1,4-Dioxane with B25 on HC emission

The blends with additive (B25-5ml and B25-10ml) are not subjected to improper soot oxidation due to inherent presence of oxygen within the fuel and additive and thereby, decreasing the smoke emission. In addition, since the cold flow properties and viscosity of the blend with additive are improved, the fuel atomization is more pronounced and thereby, the available oxygen easily penetrates the fuel droplets to properly oxidize the soot. It is worthwhile to link the reduced smoke emission for B25-5ml and B25-10ml, with the respective heat release curves of them. With the increase in proportion of 1,4-Dioxane with B25, the magnitude of premixed combustion is reduced and this might have increased the smoke emission, as premixed combustion phases are reported to be smoke free combustion zone [216]. In contrary, B25 with additive, despite the reduction in magnitude of premixed combustion, has shown reduced smoke emission, mainly due to the oxygen present in both biodiesel and additive, which has promoted the diffusion combustion phase, as described above. Notably, for B25-10ml, as seen from Figure 4.15, the smoke emission is reduced by 24.6% than B25 at full load condition, emphasizing more active combustion. The reduction in smoke emission is in compliance with the findings of Lin et al [185], who examined the intermediates of a cyclic oxygenated hydrocarbon (1,4-Dioxane) at low pressure with an equivalence ratio of 1.80, and found no aromatic intermediates. Further, reduction in smoke emission, when adding 1,4-Dioxane with ethanol – diesel blends, has also been reported by Sundar et al [172], which is in parallel with the finding of current study.

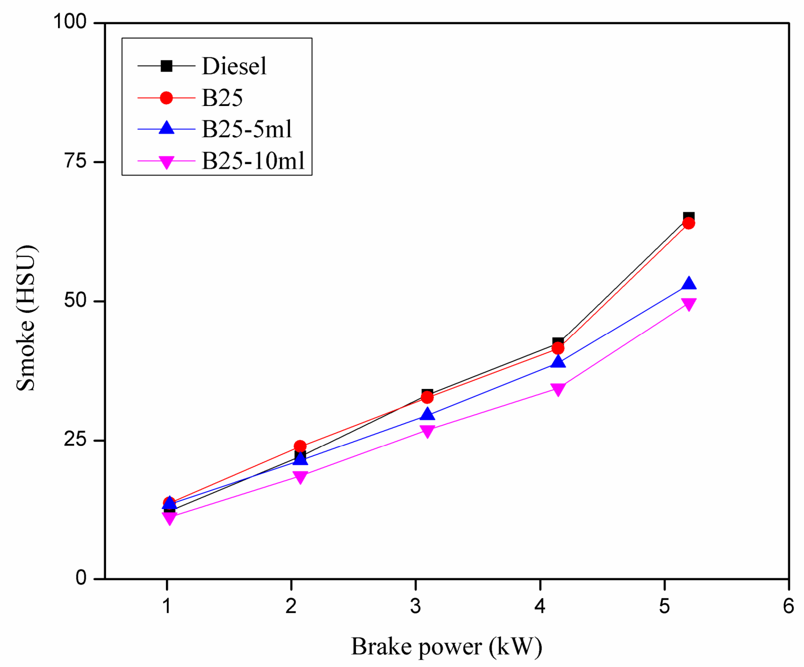


Figure 4.15 Effect of adding 1,4-Dioxane with B25 on Smoke emission

The high flame temperature and presence of surplus oxygen are being considered as propellants for the formation of NO_X in diesel engine [219]. However, B25-5ml and B25-10ml, despite the presence of inherent oxygen within them, were noticed to show a significant reduction in NO_X emission, as seen from Figure 4.16. From the heat release curve (Figure 4.10), it could be comprehended that the magnitude of peak heat release rate is lower for the blends with additive, as the SOC is early, which prevents the accumulation of air fuel mixture. Early SOC not only reduces the peak heat release rate, but also implicates softer changes in pressure and temperature [220]. Since the degree of smoothness of engine operation is enhanced and the in-cylinder temperature is reduced, the NO_X emission has been found to be lower for blends with additive. Similar conclusion were drawn by Vallinayagam et al [221], while investigating the engine characteristics using pine oil – diesel blend with ignition promoters, Iso-amyl nitrate and Di-tertiary butyl peroxide, in a stationary diesel engine. In the relentless pursuit to control both NO_X and smoke emission simultaneously, the shortening of the magnitude of premixed combustion phase by reducing SOC is regarded as an appropriate strategy [61], which has been realized in the current study by adding 1,4-Dioxane with the optimum blend of KME.

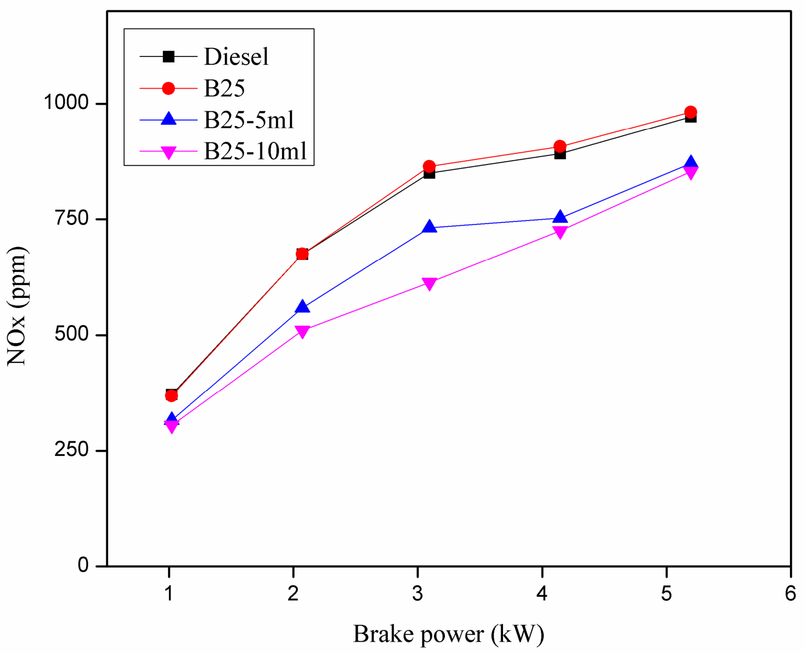


Figure 4.16 Effect of adding 1,4-Dioxane with B25 on NO_X emission

The BTE of the engine for B25 with and without additive at respective loading conditions has been shown in Figure 4.17. As noted from the figure, BTE for B25 was found to be slightly higher than diesel at all loading condition. A closer scrutiny of BTE curve reveals a noteworthy increase of

BTE for B25-10ml by 5.7% at full load condition, when compared to B25, due to improved combustion as explained above. In a comparison, Sundar et al [222], while investigating the effect of 1,4-Dioxane on ethanol blended diesel, reported an improvement in BTE, which is in concordance with the results of the present study. Furthermore, to help justify the increase in BTE with additive, the cumulative heat release curve (Figure 4.11) could be analyzed, which shows an increase in net energy released for B25-5ml and B25-10ml. When comparing B25, B25-5ml and B25-10ml, the accumulated heat release happen to get increased due to the improvement in combustion process in wake of improved fuel properties. This in turn has contributed holistically to the conversion of the accumulated heat release into useful piston work, thereby increasing the BTE for B25-5ml and B25-10ml.

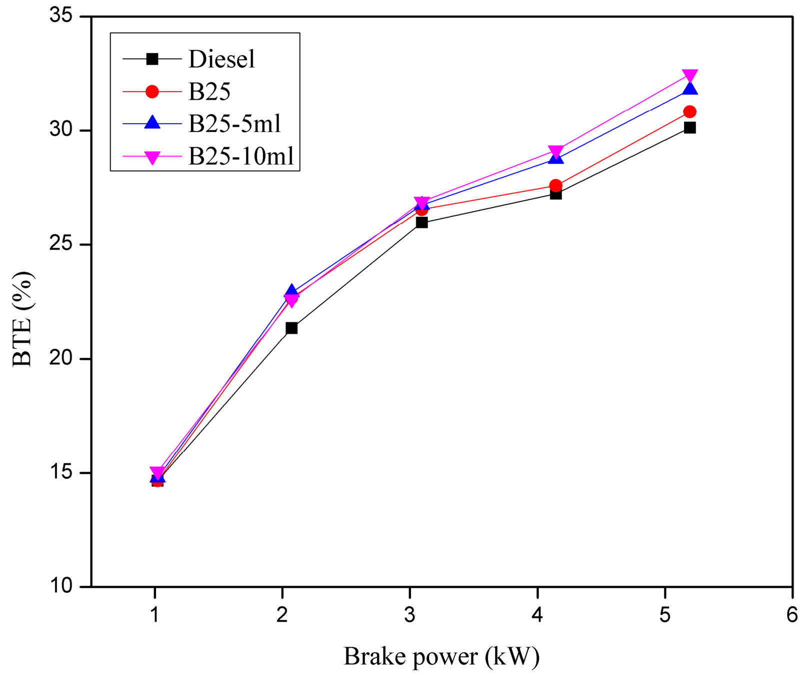


Figure 4.17 Effect of adding 1,4-Dioxane with B25 on BTE

The BSFC for B25 with and without additive was calculated from the total fuel consumption (TFC) for all corresponding loads and has been shown in Figure 4.18. For biodiesel with lower energy density, in order to produce the same power output, more amount of fuel has to be supplied than diesel, incurring more fuel consumption. Since KME has a lower calorific value, the BSFC was found to be slightly increased for B25 than diesel, which is the case for all biodiesel categories. Previously, Muralidharan and Vasudevan [209] have confided the increase in BSFC of the engine when using blends of waste cooking oil methyl ester with diesel, owing to the lower caloric value and higher viscosity of the biodiesel. However, with the addition of 1,4-Dioxane, the combustion process is improved on account of improved fuel properties and this in turn has slightly reduced the BSFC of the engine than that for B25 without additive.

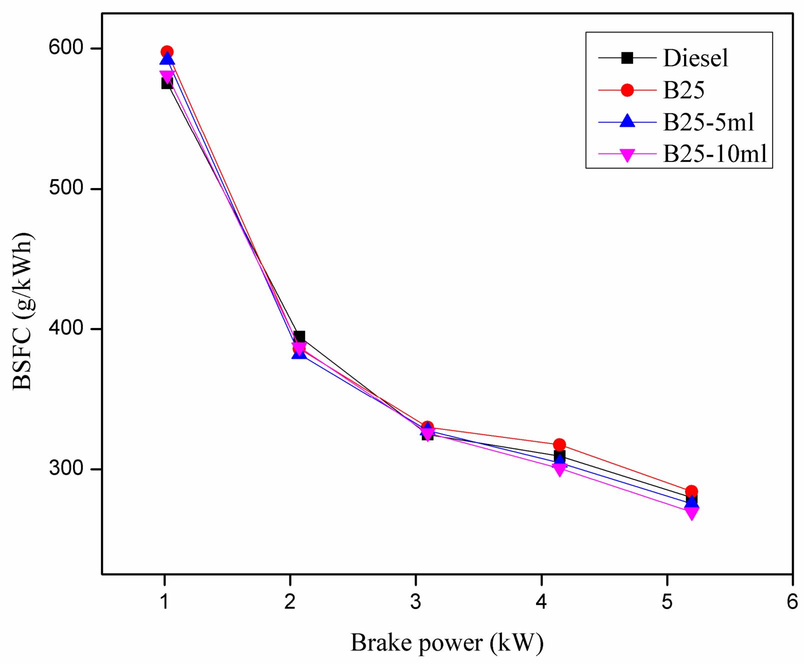


Figure 4.18 Effect of adding 1,4-Dioxane with B25 on BSFC

4.2.4. Conclusions

The energy crisis and notched up price of crude oil and petroleum, which is reported to have triggered a new interest in the field of alternate fuels, have impelled us to find an enviable renewable source of fuel. As a solution, KME, produced from inedible kapok oil, has been used as an alternate fuel for a diesel engine in the current study. Further, to stifle down the emission and improve the performance of the engine, multipurpose additive, 1,4-Dioxane has been added with B25 blend of KME. Significantly, the added additive has improved the cold flow and ignition properties of the blend, with another advantage of improvement in the blend stability. The combustion characteristics of the blend with additive (B25-5ml and B25-10ml) were noticed to be improved, while testing it in a single cylinder diesel engine, with significant reduction in emission and improvement in the performance.

Significantly, the following observation were derived out of the experimental investigation,

- The cetane number of B25-10ml showed an improved value of 56, which has had triggered proactive combustion process by shortening the ignition delay.
- The emissions such as CO, HC, NO_X and smoke were reduced by 22.5%, 25.3%, 15.2%, and 24.6%, respectively, for B25-10ml than B25. Noticeably, the emission of both NO_X and smoke were simultaneously reduced with the addition of 1,4-Dioxane with B25.
- The performance parameters such as BSFC and BTE, for B25-10ml were observed to be improved, when compared to B25, by 5.7%.

Associated publication

- Vedharaj S, Vallinayagam R, Yang WM, Chou SK, Lee PS. Effect of adding 1,4-Dioxane with kapok biodiesel on the characteristics of a diesel engine. Applied energy.2014 (Article in press)
- Vedharaj S, Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Influence of additive (1,4-Dioxane) on the performance and emission characteristics of kapok oil biodiesel. In proceeding of: International Conference on Applied Energy (ICAE) 2013, Pretoria, South Africa.

4.3. Reduction of harmful emissions from diesel engine fueled by kapok methyl ester by combined coating and SNCR technology

4.3.1. Background

In the consistent effort to improve the characteristics of a diesel engine when fueled by biodiesel, researchers have engineered some design modification strategies. When compared to the optimization of engine operating parameters, these design modification strategies are more effective. Notably, it offers the benefit of adaptation of higher blends of biodiesel, which have been earlier remarked to be used only up to 20% in an unmodified engine. The distinguished design change conjured up are alteration of the engine compression ratio, coating of engine components using insulating material and optimization of combustion bowl geometry, which has been elaborated in detail in chapter 2.

Among the various design modification techniques, thermal barrier coating of engine components has attracted the attention of many researchers. The ideology behind this technique is to reduce the heat losses from the engine, by coating the engine components with materials having poor thermal conductivity, so as to facilitate the conversion of accumulated heat into useful piston work. Further, from Table 2.2, which encapsulates the work on a coated engine fueled by biodiesel, it is clearly evident that though the intended objective of improved performance has been met after coating the engine components, the limitation of increased NO_X emission still persists for various biodiesel and vegetable oils. Thus far, no study has been initiated to curtail the NO_X emission from a coated diesel engine fueled by biodiesel, though the other emissions such as CO, HC and smoke were found to be lower. Regardless of the presence of various NO_X reduction techniques for a diesel engine such as optimization of injection timing, EGR, SCR and addition of NO_X reduction additives [79, 217, 223], required attention has not been paid to simultaneously improve the performance and reduce the NO_X emission from a coated engine.

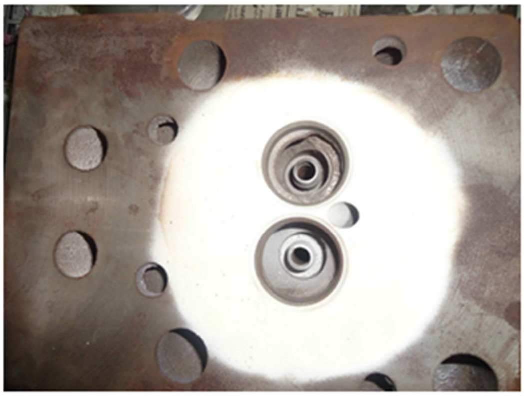
Due to the enormous task to be paid to achieve a design change, only a few studies have focused on it, when using biodiesel as renewable fuel Therefore, following the fuel modification study to improve the engine performance and emission, in the current study, we have decided to adopt the design modification strategy of TBC so as to improve the engine performance. Considering that design modifications would empower using higher blends of biodiesel [146], contrary to the reported adaptation of 25% biodiesel in an unmodified engine, herein we have used KME up to 50% with diesel (B25 and B50) in a coated diesel engine. Also, from the above discussion, it is evident that there exists an appeal for reduction in NO_X emission from a coated diesel engine fueled by biodiesel. Therefore, this research work would also focus on to reduce NO_X emission by implementing a urea based SNCR system in the exhaust pipe of a coated diesel engine, fueled by KME – diesel blends. Thus the objective of the study is not only to improve the engine performance by coating the engine components, but also to reduce the NO_X emission by implementing urea based SNCR system. Finally, the engine characteristics of the reported blends in a coated engine with SNCR and unmodified engine are analyzed and compared.

4.3.2. Methodology

4.3.2.1. Coating process

The engine components such as top surface of the piston, bottom face of the valves and the cylinder head portion associated with the combustion chamber were coated using PSZ. Plasma spray coating technique has been employed to coat the engine components meticulously; the photographs of the coated engine components are depicted in Figure 4.19. Prior to coating, the components are grit blasted so as to attain a surface roughness (Ra) value of 4, after which, the surfaces are cleaned using ethylene glycol. When the components are dried, PSZ is sprayed over cleaned surface and this ensures sufficient bond coat between the base substrate and the coating material. The thickness of the coating has been limited to 450 microns as increased thickness duly reduces the amount of air inducted in to the cylinder and this tends to decrease the volumetric efficiency of the engine, affecting the engine performance and emission.

Coated inlet and exhaust valve Coated piston



Coated cylinder head portion

Figure 4.19 Engine components coated with PSZ (partially stabilized zirconia)

4.3.2.2. After treatment process

In order to control NO_X emission from coated diesel engine, an additional SNCR circuit involving a tank with urea solution, 3 way control valve, small pump and flow pipes, was devised and fitted in the exhaust pipe, as show in Figure 4.20. The urea solution was prepared by mixing 30% of urea with 70% of water, widely recognized composition for urea based SCR systems [217], and was placed overhead in the tank. Further, the urea solution was sprayed into the exhaust manifold and the quantity of injection was controlled by maintaining adequate pressure in the flow lines through the pump and control valve assembly. In this study, urea was directly sprayed into the exhaust gases without the requirement of any catalyst and hence the name, non-catalytic SCR system. Typically, a catalytic converter was not preferred along with the SNCR system, given that the coated engine is reported to have decreased other emissions such as CO and HC already due to better combustion. Notably, this SNCR assembly was implemented only for coated engine and the emission results are compared with uncoated engine without SNCR. The selection of SNCR system to reduce NO_X emission than other strategies like EGR or retardation of injection timing is because of the fact that it does not compromises the engine performance, as modifications are only dealt in the tail pipe of the engine. Further, according to the reports of Casapu et al [224], urea – SNCR system is more amenable for stationary diesel engine, like the one used in the current study, than light commercial vehicles in face of complexity and large dimensions of the system. Therefore, the selection of urea – SNCR system for the current study was reasonable.

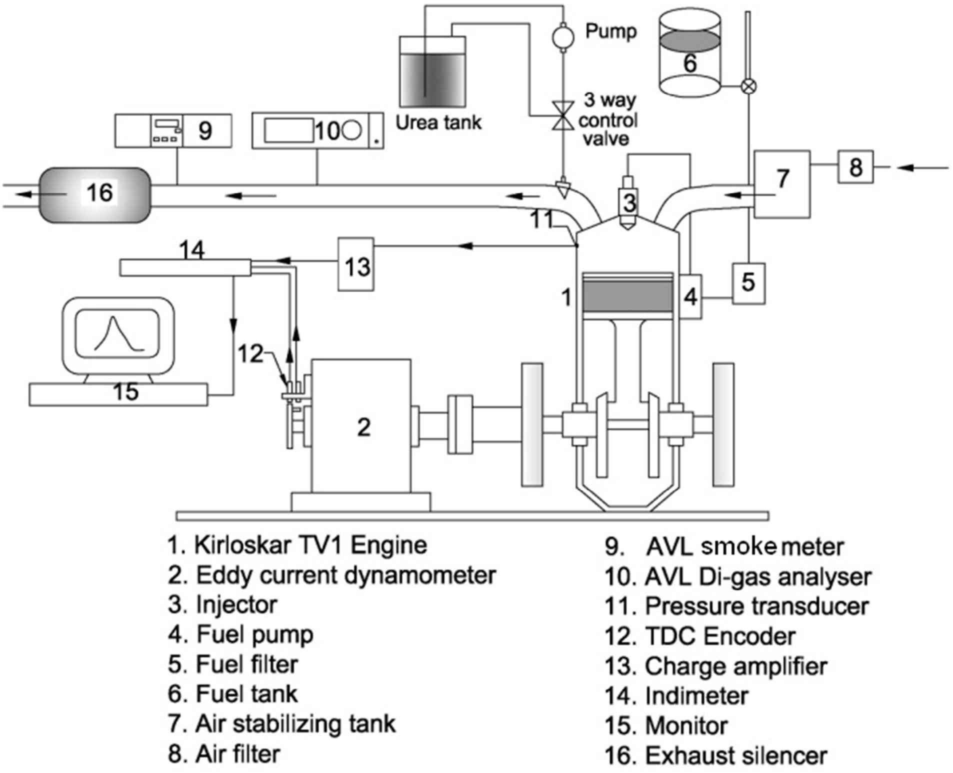
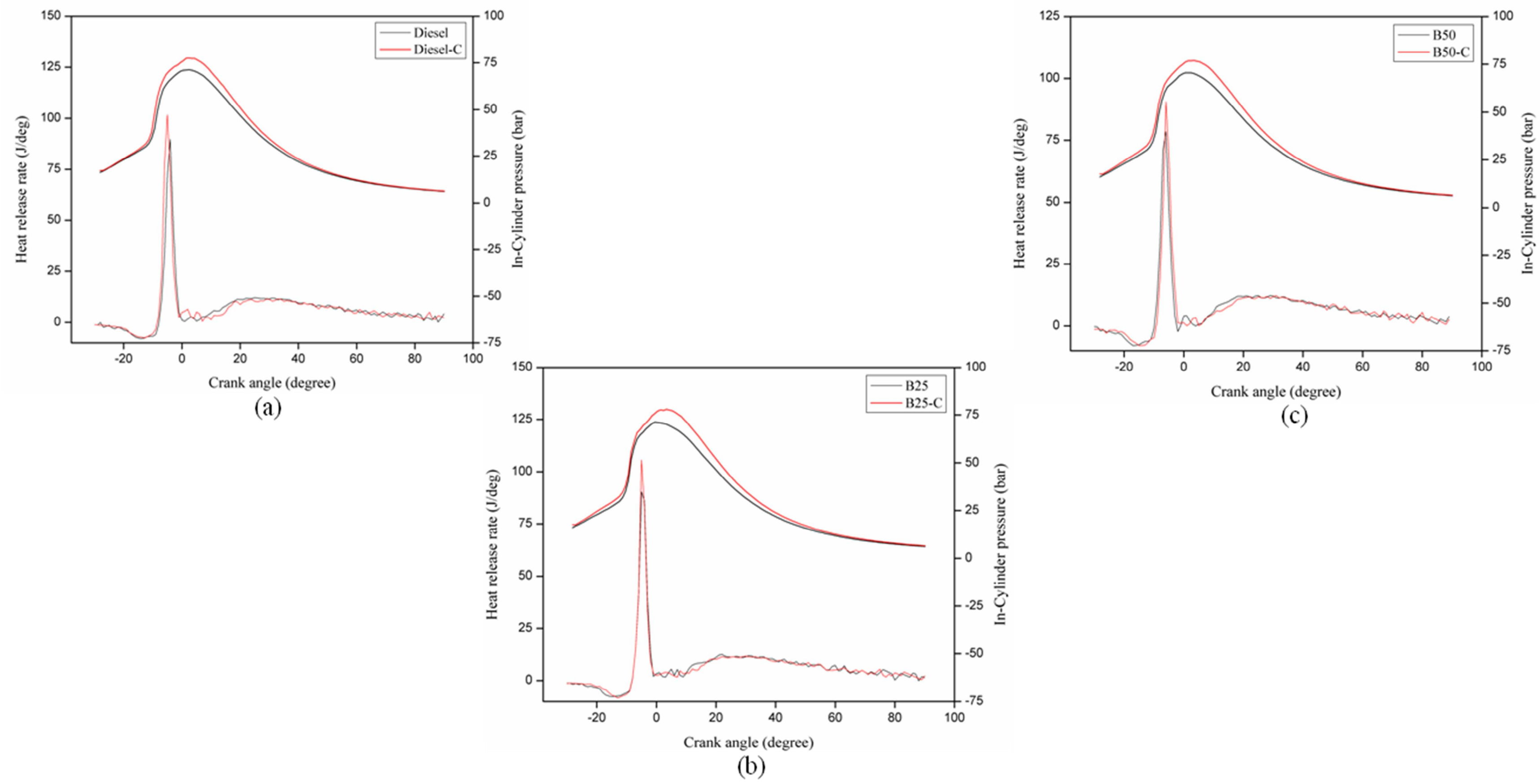


Figure 4.20 Schematic diagram of the engine experimental setup with SNCR assembly

4.3.3. Results and discussion

Before appraising the effect of TBC on engine performance, it is worthwhile to analyze its impact on combustion process. In this connection, the variation of heat release rate and in-cylinder pressure for diesel, B25 and B50 in coated and uncoated engine, at full load condition, have been shown in Figure 4.21 (a), (b) and (c), respectively. It can be seen from the figures that



(a)

(b)

(c)

Figure 4.21 In-cylinder pressure and heat release rate comparison for (a) Diesel (b) B25 (c) B50 in coated (-C) and uncoated engine at full load condition for all the tested fuels, both the peak heat release rate and in-cylinder pressure of the coated engine are higher than that of uncoated engine due to the fact that heat lost were reduced in a coated engine. These results are in consonance with the results of Prasath et al [142], wherein, an improvement in in-cylinder pressure of around 3 bar has been reported for coated engine over normal diesel engine when fueled by Jatropha methyl ester. Furthermore, by comparing Figure 4.21(a) and Figure 4.21(c), it could be noted that the peak heat release rate for B50 is lower than diesel both in coated as well as uncoated engine; mainly due to its lower calorific value. Another reason is the shorter ignition delay of KME because of its higher cetane number, which is in agreement with the reports of Sarin [61]. Conceptually, the early start of combustion, accompanied by poor evaporation of KME, has yielded less amount of prepared fuel for premixed combustion, contributing to reduced peak heat release rate.

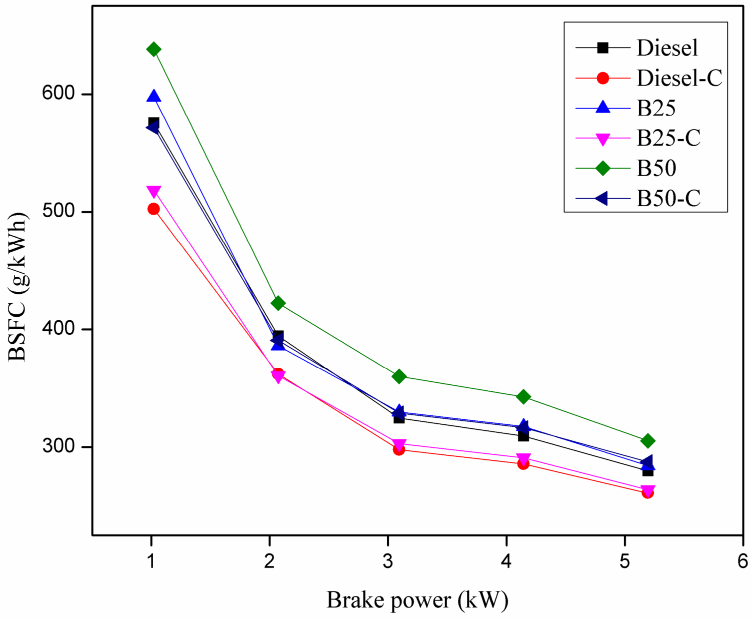


Figure 4.22 Variation of BSFC for diesel, B25 and B50 in a coated (-C) and uncoated engine

The performance parameters such as BTE and BSFC have been analyzed to appreciate the effect of TBC on engine performance. For uncoated engine, BSFC was noticed to be increased with the increase of KME in the blend ratio, as seen from Figure 4.22. This trend could be explained by the distinct property of KME i.e lower calorific value than diesel, which demands larger quantity of fuel to produce the required power output, resulting in higher BSFC. Similar reports on increase in BSFC for various biodiesel have attributed lower calorific value as the prime reason for it [14, 206]. However, for coated engine, the heat trapped inside the engine cylinder and the inherent presence of oxygen within the fuel has promoted better combustion for B25 and B50 and thereby, lowering the BSFC of the coated engine. Similar such conclusion has been drawn by Hazar et al [137], when testing canola methyl ester in a low heat loss diesel engine.

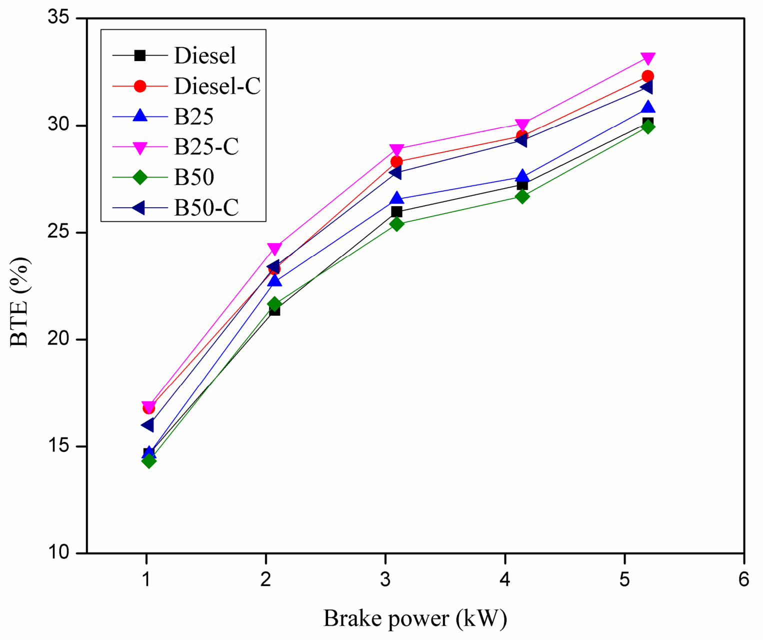


Figure 4.23 Variation of BTE for diesel, B25 and B50 in a coated (-C) and uncoated engine

In general, the presence of oxygen within the renewable biodiesel promotes better oxidation of hydrocarbon, resulting in increased BTE. However, higher viscosity and lower calorific value of B50 caused a slight decline in efficiency compared to diesel and B25, which is clearly evident from the present investigation in an uncoated engine. On the other hand, in a coated engine, the BTE of the engine, as shown in Figure 4.23, gives a clear picture of improvement in engine performance for B50 as the heat loss to the surrounding has been minimized by the insulation of engine components. This reduced heat loss not only increases the energy available for converting into useful piston work, but also improves the combustion process. As a result, an obvious higher efficiency has been achieved for all test fuels in coated engine.

Remarkably, BTE was increased by 9% for B50 in a coated engine than in uncoated engine at full load condition. In the past, improvement in BTE of a coated diesel engine fueled by sunflower oil biodiesel was reported by Hasimoglu et al [126], which is in concordance with the improved efficiency for B50.

The major emissions such as CO, HC, smoke and NO_X for diesel, B25 and B50 in coated and uncoated engine have been analyzed In light of higher viscosity, the combustion is said to be incomplete for B50 in uncoated engine, resulting in higher CO and HC emission than diesel, which are shown in Figure 4.24 and Figure 4.25, respectively. However, B25 showed comparable CO and HC emission with diesel, as its viscosity is not much higher and further, presence of oxygen within the fuel could have promoted oxidation of CO and HC to CO_2 and H_2O. In general, many experimental investigation have shown more active combustion of biodiesel, due to the inherent possession of oxygen within its molecular structure, resulting in reduced CO and HC emission [60, 75, 225]. Nonetheless, there are also contradictions to the above said fact as the higher viscosity and boiling point of biodiesel affects the combustion process [226, 227]. This is why B50 is reported to have shown higher HC and CO emission than diesel in uncoated engine.

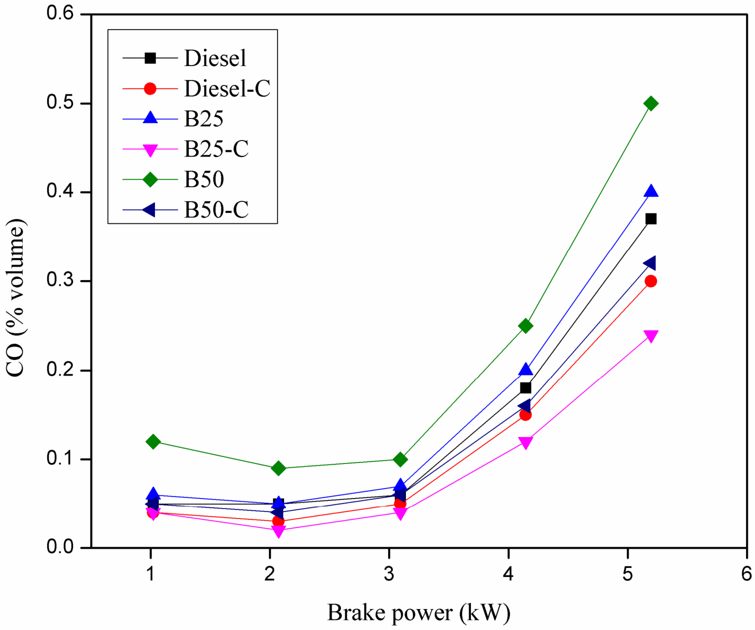


Figure 4.24 Variation of CO emission for diesel, B25 and B50 in coated (-C) and uncoated engine

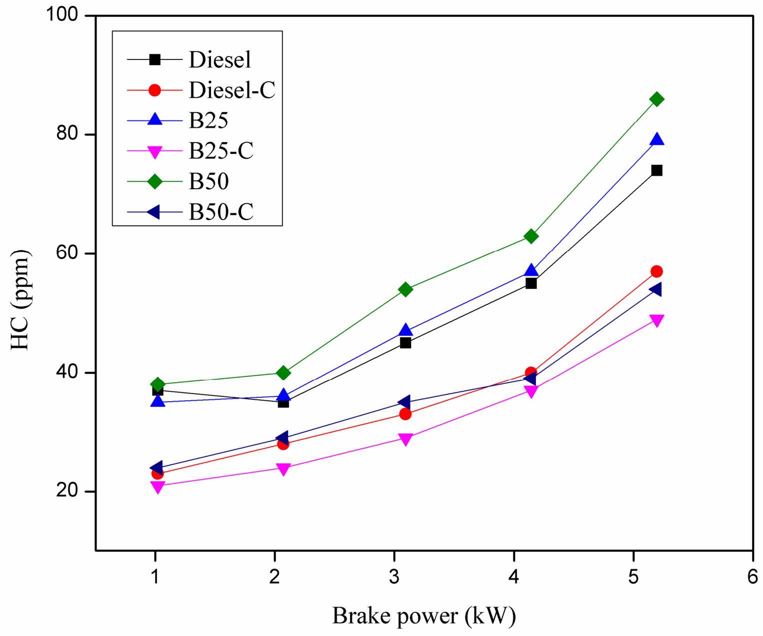


Figure 4.25 Variation of HC emission for diesel, B25 and B50 in coated (-C) and uncoated engine

It is very interesting to compare the CO and HC emission from coated engine and uncoated engine, and analyze the impact of coating on engine out emissions. Apparently, all the blend fuels showed decreased CO and HC emission in coated engine when compared with uncoated engine. This decrease can be judged based on the expected increase in in-cylinder temperature, due to the reduced heat losses to the coolant, in coated engine. The increase in temperature is believed to promote the oxidation of CO to CO_2, thereby reducing the CO emission by 40% for B50 in coated engine than that in uncoated engine. The same is the case for HC emission, with B50 in coated engine showing 35.3% reduction in HC emission than that for uncoated engine, perhaps slightly better than diesel too. Similar such reductions in HC and CO emission were also noted by Hazar et al [138] and Musthafa et al [139], when using cotton and pongamia methyl ester in a coated diesel engine, complying with the findings of the current study. Categorically, it has been reported that SCR systems reduces HC and NO_X emissions, while the CO emission increases [228]. On the contrary, in the current study, an appreciable increase in CO emission has not been envisaged for B25 and B50 in coated engine. This is because of the profound impact of coating and effective utilization of the heat energy in accomplishing more complete combustion within the combustion chamber itself.

In general, when biodiesel is being utilized as an alternate fuel for diesel engine, the NO_X emission is reported to be increased due to the inborn oxygen within fuel, fuel injection advance and other features pertaining to fuel chemistry [229]. However, there are contradictions to the above said phenomenon, as few researchers consider that the lower peak heat release rate, caused by higher cetane number of biodiesel, reduces the in-cylinder temperature so as to impede the formation of NO_X [230]. Incidentally, this latter occurrence, lower peak heat release rate to reduce NO_X emission for B50, has happened in the present study with uncoated diesel engine, as seen from Figure 4.26. The reasons for this are explained as follows: due to the higher viscosity and lower boiling point of KME, the atomization and evaporation of it are affected and therefore, the quantity of well mixed fuel available for combustion is reduced. Following this, the lower cetane number of KME advances the combustion process and with the reduced quantity of fuel being available for combustion, coupled by the lower calorific value of KME, the magnitude of peak heat release rate is decreased and this reduces the in-cylinder temperature to decrease the NO_X emission for B50.

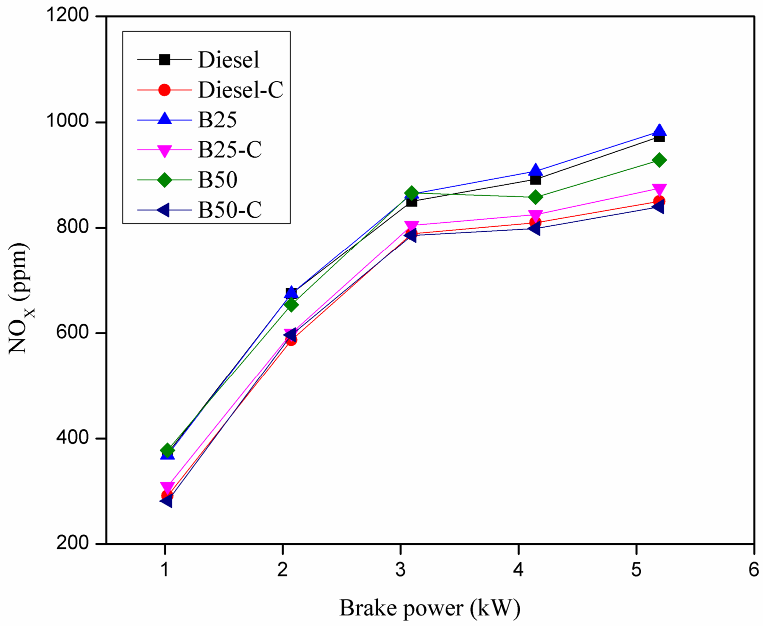


Figure 4.26 Variation of NO_X emission for diesel, B25 and B50 in coated (-C) and uncoated engine

On the other hand, it is widely noted that coated engine tends to increase the in-cylinder temperature and this together with the presence of oxygen within the biodiesel would cause an increase in NO_X emission, as high temperature and presence of nitrogen as well as oxygen in air are reported to be crucial elements in the formation of NO_X [231]. Substantially, Aydin et al [141] and Iscan et al [140], demonstrated an increase in NO_X emission when using sunflower oil and waste corn oil in a coated engine, perhaps for the same reason as noted above. In the event of increasing the performance of a diesel engine fueled by KME blends through coating of engine components, similar phenomenon is believed to arise. To avert the expected increase in NO_X emission for the blend fuels in the current experimental study using PSZ coated engine, urea based SNCR system, which is regarded as an effective after treatment technique [232], has been fitted in the exhaust pipe. With the SNCR fitted coated engine, the NO_X emissions for B25 and B50 were successfully reduced, as shown in Figure 4.26. The ideology behind NO_X reduction with urea – SNCR system is: when urea is sprayed in the exhaust pipe, it gets decomposed and hydrolyzed in ammonia (NH_3), while the formed ammonia then reacts with NO and NO_2 and breaks it down to N_2 and H_2O. Consequently, NO_X emission for B50 in coated engine with SNCR has been reduced by 13.4% than that in uncoated engine. In parallel with these conclusions, Xu et al [233] and Liu et al [234] had already reported a drastic reduction in NO_X emission by implementing urea based NO_X reduction system. However, when compared to diesel, the NO_X emission for B50 was noticed to be slightly lower due to deterrence in combustion and the subsequent reduction in in-cylinder temperature, caused by the higher viscosity of KME, and for the other reasons with the early start of combustion as explained above. It could be pointed out that the NO_X emission for lower blend, B25, was shown to be higher than diesel, as the properties are not much varied, which is in compliance with the general scenario of increased NO_X emission for biodiesel. The temperature of the exhaust gas at respective loading condition would have an effect on the NO_X reduction potential as the reaction of urea with it is depend on the temperature. To have a better understanding of this, the EGT for diesel and blend fuels in coated and uncoated engine has been drawn and shown in Figure 4.27. Evidently, the coated engines tend to exhibit higher EGT due to the reduction in heat losses and this ought to enhance the NO_X reduction in a coated engine.

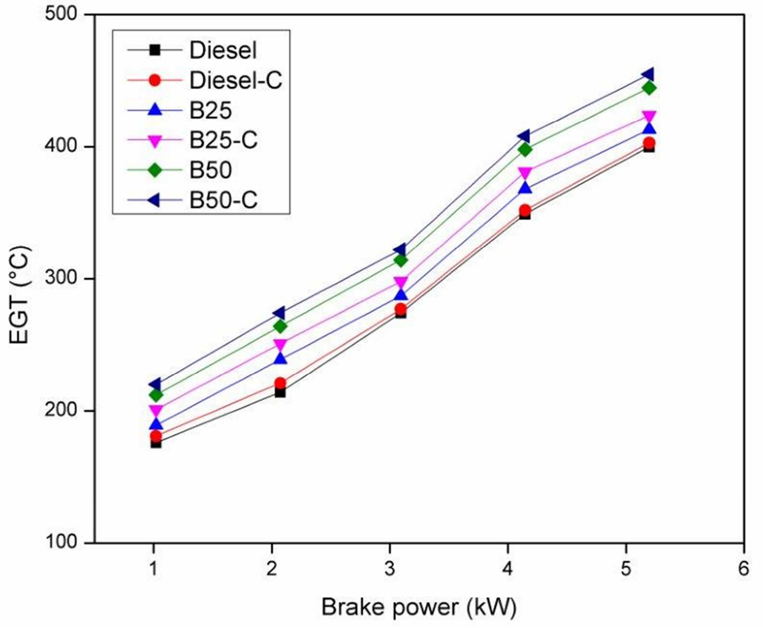


Figure 4.27 Variation of exhaust gas temperature for diesel, B25 and B50 in coated (-C) and uncoated engine

There always exists a tradeoff between NO_X and smoke in a diesel engine fueled by any kind of fuel. However, in our case, this tradeoff has been refrained with the realization of coating and implementation of urea – SNCR system, as both NO_X and smoke are simultaneously reduced for B50. Notably, a 21.4% decrease in smoke emission for B50 in coated engine than that in uncoated engine, as noted from Figure 4.28, has been realized. Characteristically, the soot precursors formed in the fuel rich zones of spray are oxidized by the oxygen from KME and this is ameliorated by the enhanced combustion temperature, following the prevention of heat loss through coating. To back up this, Di et al [235], in their study using oxygenated fuel (ethanol) as substitute for diesel, acceded to the profound oxidation of fuel in the diffusion combustion phase and reported effective reduction in smoke emission. In general, when the premixed combustion is more pronounced, the soot formations are reduced as the amount of fuel being burnt in diffusion controlled combustion is reduction. In our case, since premixed combustion is more pronounced for B50 in a coated engine, as seen from Figure 4.21, the smoke emission are noted to be reduced than that in an uncoated engine.

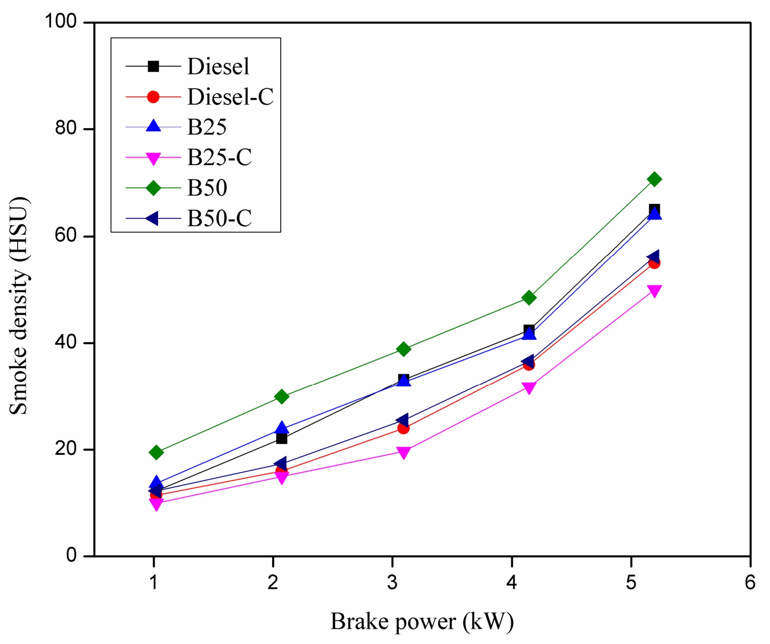


Figure 4.28 Variation of Smoke emission for diesel, B25 and B50 in coated (-C) and uncoated engine

4.3.4. Conclusions

The first objective of this investigation was to improve the performance of a diesel engine by coating the engine components using PSZ, a commensurate insulating material. Secondly, the increased NO_X emissions from the coated diesel engine, due to rise in temperature inside the combustion chamber, has been identified and efforts were taken to reduce it by implementing urea – SNCR system in the exhaust pipe. Further, this study has also thrived to duly utilize kapok seed oil, an underutilized bio oil, to synthesize biodiesel (KME) and experimentally investigate the engine characteristics in a coated diesel engine. From the experimental investigation, the performance and combustion characteristics are found to be improved for the blend fuels in coated engine, with a 9% increase in BTE for B50 in coated engine than uncoated engine. Further, the major emissions from the coated engine such as HC, CO and smoke for B50 were found to be reduced by 35.3%, 40% and 21.4% than uncoated engine, and with the incorporation of urea – SNCR systems, the NO_X emission was also reduced by 13.4% than uncoated engine. Previously, many research studies on coated diesel engine with biodiesel, categorically reported better engine performance and reduction of HC, CO and smoke emissions at the expense of higher NO_X emission.

However, distinctly, this study has duly noticed the problem of higher NO_X emission with coated engine fueled by biodiesel and subsequently, an effective after treatment technique in the likes of SNCR was incorporated to reduce the rampant impact of NO_X emission on atmosphere, implicating much greener environment.

Associated publication

- Vedharaj S, Vallinayagam R, Yang WM, Saravanan CG, Chou SK, Chua KJE, Lee PS. Reduction of harmful emissions from diesel engine fueled by kapok methyl ester by combined coating and SNCR technology. Energy Conversion and Management.2014:79:581-589.
- Vedharaj S**,** Vallinayagam R, Yang WM, Chou SK, Chua KJE, Lee PS. Experimental study on thermal barrier coating of a diesel engine powered by kapok biodiesel. In proceeding of: 12th International Conference on Sustainable Energy technologies (SET-2013) 2013, Hong Kong.

4.4. Modification of combustion chamber geometry for the operation of kapok biodiesel in a diesel engine

4.4.1. Background

Having realized the utilization of higher blends of KME by combined coating and SNCR technology, we have initiated another design modification strategy of optimizing the combustion bowl geometry in the current study. In the previous study, with coated engine components, B50 was noted to show only comparable engine performance and emission with diesel, though B25 showed enhanced engine characteristics. To attain better engine efficiency and emission results with higher blends of KME, in the current study, we endeavored to operate KME – diesel blends in a diesel engine with various combustion chamber geometries. As such, three different combustion bowl geometries were used for operating different blends of KME such as B25, B50, B75 and B100 in a diesel engine. Finally, performance, emission and combustion characteristics of the engine with different combustion bowl geometries for the reported blends have been discussed.

4.4.2. Methodology

In the event of optimization of combustion chamber geometry for kapok biodiesel and its blends, three different shapes of combustion chamber geometry such as TRCC (trapezoidal combustion chamber), TCC (toroidal combustion chamber) and HCC (hemispherical combustion chamber) were selected. In the design aspect every combustion chamber, fabrication is done in such a way that the volume of the combustion bowl is not altered so as to maintain the same compression ratio for all configurations. The photographic view of the different combustion chambers, employed in the current work, has been depicted in Figure 4.29. In a comparison, the lip of the TCC touches the combustion chamber wall and offers better squish than other combustion chambers, while TRCC is shown to have larger surface area. Experiments are carried out in diesel engine, after assembling and dis-assembling the variety of combustion chambers sequentially, following the methodology explained in the previous section of this chapter.

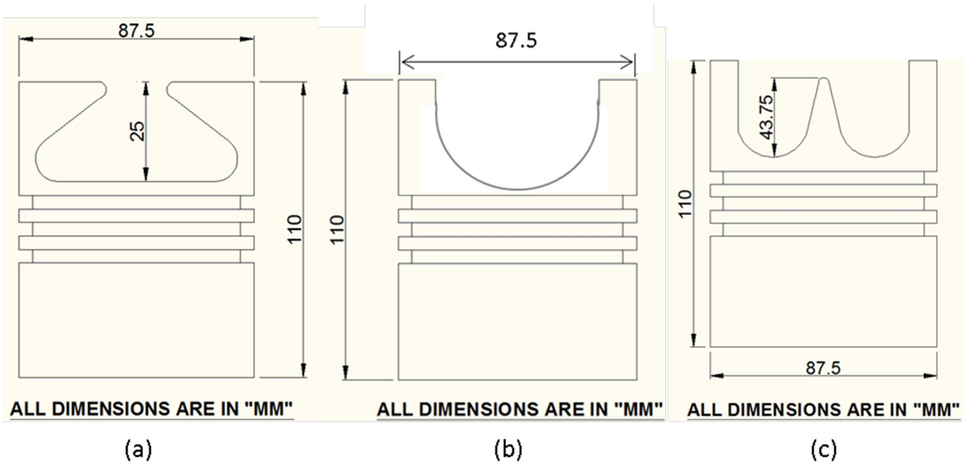


Figure 4.29 Combustion chamber geometries (a) TRCC (b) HCC and (c) TCC

4.4.3. Results and discussion

The performance, combustion and emission characteristics have been analyzed for different blends of KME with various combustion chamber geometries such as TRCC, TCC and HCC and are discussed below. The variation of BTE for KME – diesel blends with various combustion chamber geometries at low (20%) and full (100%) load conditions has been discerned in Figure 4.30 and Figure 4.31, respectively. As inferred from the figure, it was noted that TCC was able to show an increase in BTE for blends up to B50 and after which, BTE was observed to decline, while HCC was noticed to show increase in BTE for blends up to B25. Significantly, for B25 with HCC, the presence of oxygen within the fuel and a better calorific value than other KME – diesel blends have promoted active combustion of it, showing an increased BTE. However, for blends beyond B25 with HCC, the higher viscosity of KME appears to have affected the fuel atomization and the subsequent air fuel mixing process, as reported for other categories of biodiesel [236, 237], resulting in lower BTE than diesel.

With TCC, despite the higher viscosity, the improvement in squish has increased the swirl and promoted better air/fuel mixing, thereby increasing the BTE by 5.2% for B50 than diesel. Noticeably, the enhanced air flow is believed to improve the fuel evaporation and this together with the presence of oxygen from KME has triggered proactive combustion for B25 and B50. Notably, the better utilization of oxygen and the enhanced air movement to improve the BTE has been remarked in the past [238, 239], which coincides with the outcome of the current study as reported above. For blends beyond B50, even with TCC, BTE was found to be decreased than diesel as the higher viscosity and lower calorific value of KME has deterred the fuel atomization, air/fuel mixing and the ensuing combustion process. Undesirably, TRCC did not support better combustion for any of the selected blends. This is because, TRCC has higher surface area and this ought to increase the heat losses from the combustion chamber, meanwhile, the sharp angle is not favorable for the formation of squish, and part of fuel may deposit on the sharp angle, resulting in the decrease of engine power output and thereby decreasing the BTE.

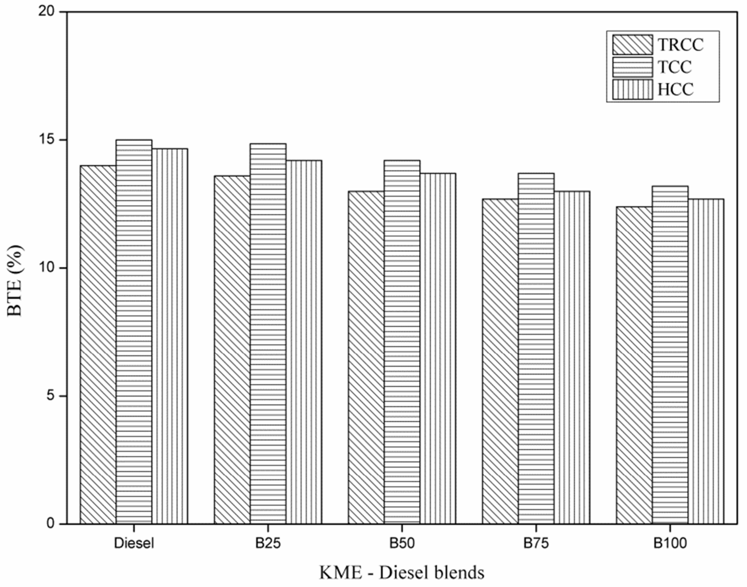


Figure 4.30 Effect of combustion chamber geometry on BTE for various KME – diesel blends at low load condition

The scenario of BTE with various combustion chamber geometries at low load condition has a reverse trend to evince, as exhibited in Figure 4.30. At low load, regardless of the type of combustion chamber geometry, the BTE of the engine was observed to decrease slightly with the increase in proportion of KME with diesel. Characteristically, the presences of oxygen in KME tend to dilute the air/fuel mixture and therefore, the fuel to air equivalence ratio is reduced, decreasing the in-cylinder temperature. Predominantly, the in-cylinder temperature that is lower at low load condition has affected the combustion of high viscous KME and this is further compounded by other adverse properties of KME such as lower calorific value, higher boiling point and flash point. The decrease in BTE for bio derived fuels with inherent oxygen at low load condition had already been demonstrated by many researchers [240, 241], which is in concordance with the results of current study. Notably, though TCC has improved the squish and swirl motion, the negative impact of lower fuel to air equivalence ratio has deteriorated the efficiency than diesel at low load condition. Over and all, either at low or full load condition, TCC has shown better BTE for diesel as well as KME – diesel blends than conventional HCC and TRCC.

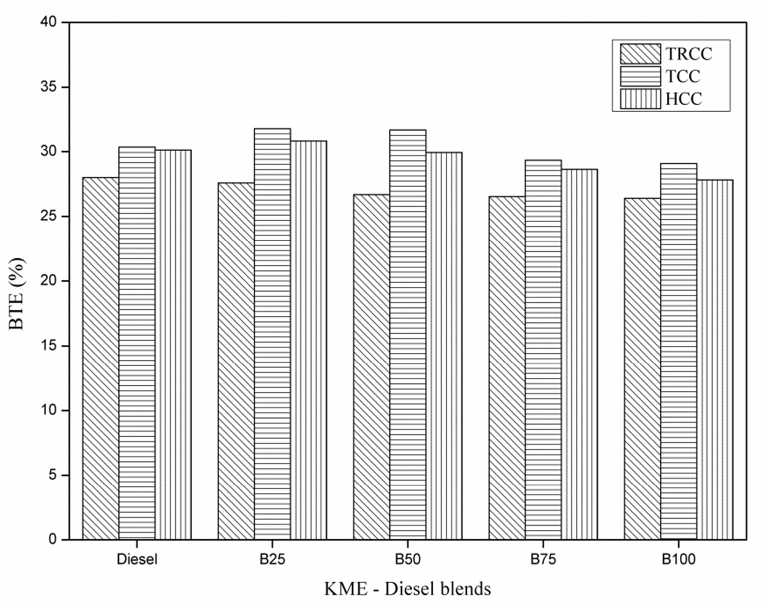


Figure 4.31 Effect of combustion chamber geometry on BTE for various KME – diesel blends at full load condition

The maximum heat release rate for KME – diesel blends with various combustion chamber geometries has been portrayed in Figure 4.32 and Figure 4.33 at low and full load conditions, respectively. As evident from the figure, the increase in peak heat release rate than diesel is appreciable up to B25 with HCC and for the remaining blends of KME, the maximum heat release rate is found to be lower. Also, TRCC, because of its distinct shape, has shown a lower peak heat release rate for all test fuels than diesel. The reasons for the decrease in maximum heat release rate for higher blends of KME with HCC and TRCC can be explained as follows: Since KME being a high viscous fuel with higher boiling point, the quantity of prepared air/fuel mixture readily available for combustion is reduced after the delay period and this has reduced the rate of energy release. Furthermore, the lower calorific value of KME reduces the amount of net energy release, lowering the maximum heat release rate for higher blends of KME with HCC and TRCC, respectively, than diesel. Substantially, many research studies have also conceded to the decrease in peak heat release rate when using biodiesel from different feedstock [242-244].

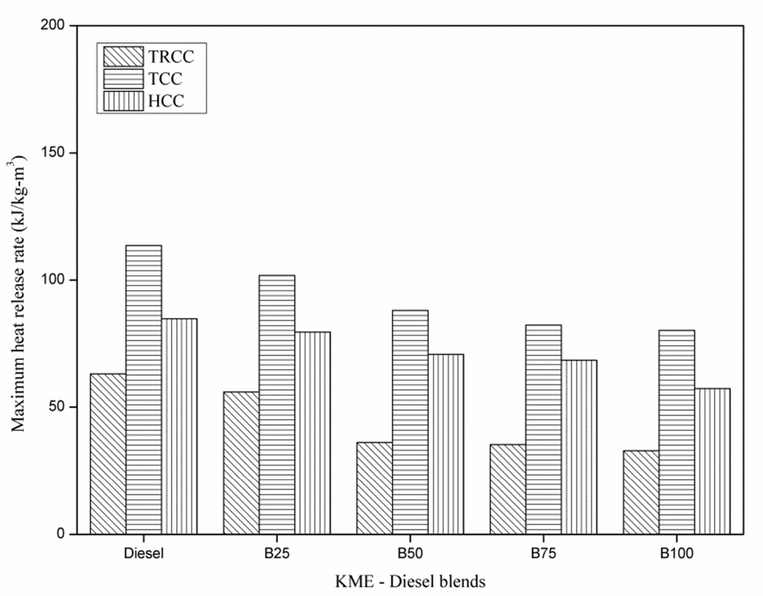


Figure 4.32 Effect of combustion chamber geometry on maximum heat release rate for various KME – diesel blends at low load condition

Significantly, with TCC, peak heat release rate has been scrutinized to be higher for blends up to B50 than diesel, while other blends of KME showed a drop in peak heat release rate. For TCC, the improved air flow motion has inflicted better evaporation and mixture formation for blends up to B50, facilitating faster burning of fuel to increase the peak heat release rate when compared to other combustion chamber geometries. Characteristically, the peak heat release rate for B50 with TCC is increased by 7.2 than that with HCC at full load condition. Therefore, from the present test results, TCC has shown an improvement in engine combustion and performance for higher blend of KME, B50, than diesel at full load condition, while the conventional HCC was reported to show increased BTE and peak heat release rate than diesel only for B25 at the respective loading condition. On the other hand, at low load condition, similar to BTE, the maximum heat release rate for all combustion chamber geometries were noted to be decreased with the increase in addition of KME with diesel due to the above mentioned reasons of lower in-cylinder temperature and fuel to air equivalence ratio.

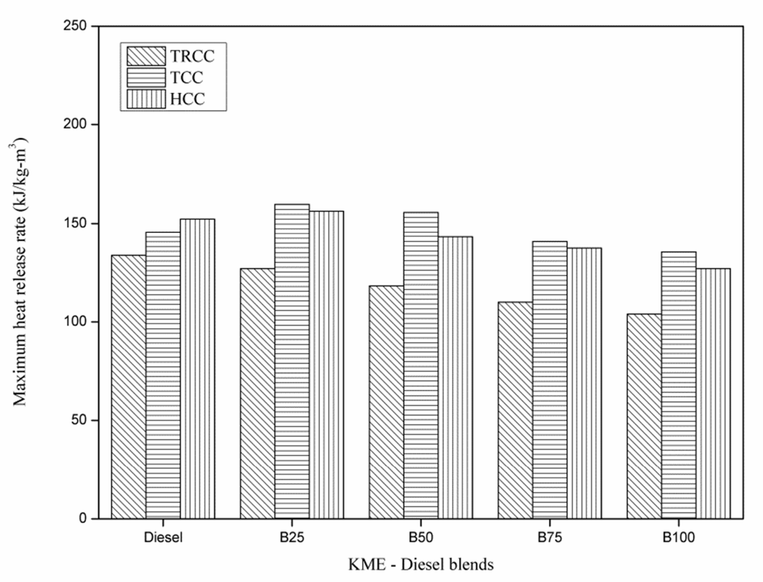


Figure 4.33 Effect of combustion chamber geometry on maximum heat release rate for various KME – diesel blends at full load condition

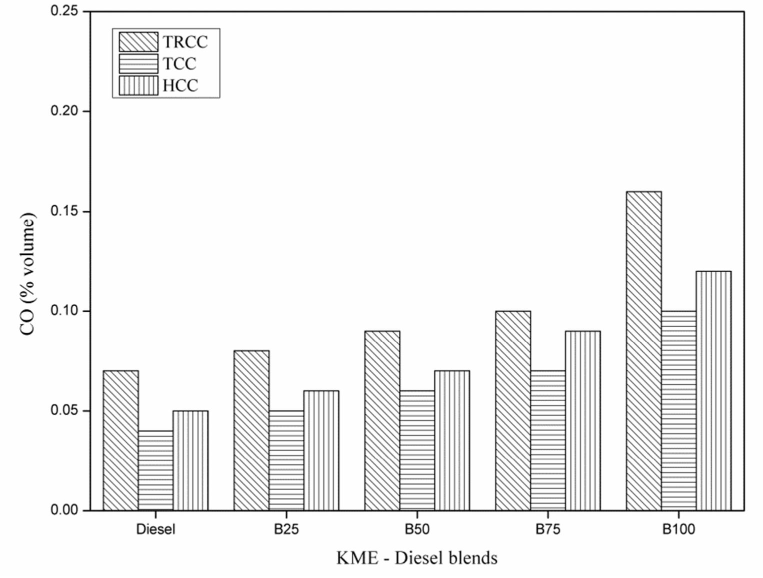


Figure 4.34 Effect of combustion chamber geometry on CO emission for various KME – diesel blends at low load condition

It is worthwhile to shed some focus on the effect of combustion chamber geometry on the pollutant emission from a diesel engine fueled by KME – diesel blends. As such, gaseous emissions such as CO, smoke and

NO_X were measured for various blend of KME and are compared for different bowl geometry shapes.

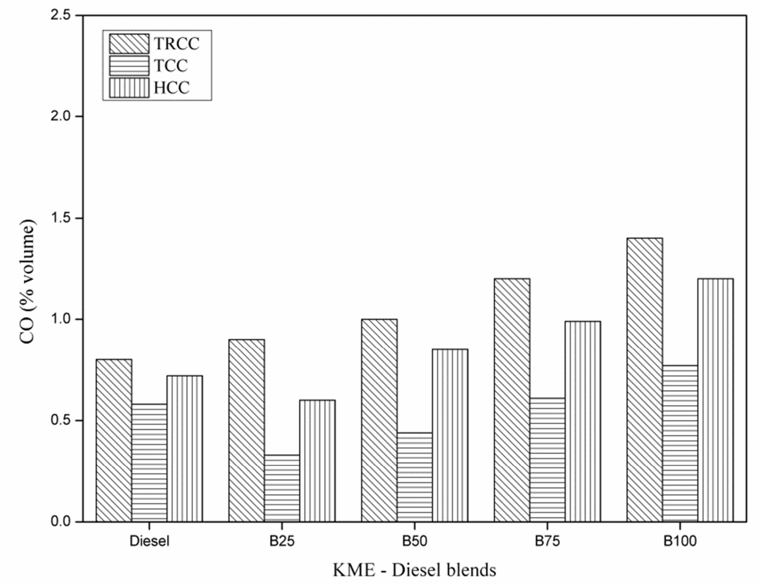


Figure 4.35 Effect of combustion chamber geometry on CO emission for various KME – diesel blends at full load condition

Figure 4.34 and Figure 4.35 represents the CO emission for KME – diesel blends with various combustion chamber geometries at low and full load conditions, respectively. The traditional HCC evinces a comparable CO emission for B25 with diesel and for higher blends; CO emission is noted to be increased as the viscosity of KME predominates the combustion process, resulting in incomplete combustion. In addition, due to the lower calorific value of KME, more fuel is being injected to produce the same power output and this increases the fuel to air equivalence ratio, thereby resulting in increased CO emission. On the other hand, TCC showed reduced CO emissions for all test fuels than that with HCC and TRCC, due to better air/fuel mixing and the following more complete combustion. Considering the emissions with TCC alone, addition of KME up to 50% with diesel showed reduced CO emissions than diesel. Notably, the CO emission for B50 with TCC was reduced by 15.7% than diesel, while it was found to be 27.8% lower than that with HCC at full load condition. For blends beyond B50, despite enhancement in air/fuel mixing process, the negative effect of higher viscosity had cost for the penalty of increased CO emission than diesel. Furthermore, for TRCC, irrespective of the blends, the CO emissions were noted to be increased than HCC and TCC due to poor squish and unique shape of the combustion bowl, trapping hydrocarbons at its sharp edges so as to hinder the fuel oxidation process. While at full load condition, there was substantial decrease in CO emission for B25 and B50 in HCC and TCC, respectively, the trend is more likely different at low load condition, reporting an increase in CO emission with the increase in addition of KME with diesel. The lower in-cylinder temperature and the excessive dilution of the air/fuel mixture are the reason noted for the increase in CO emission with KME – diesel blends, notwithstanding the different combustion chamber geometries being used.

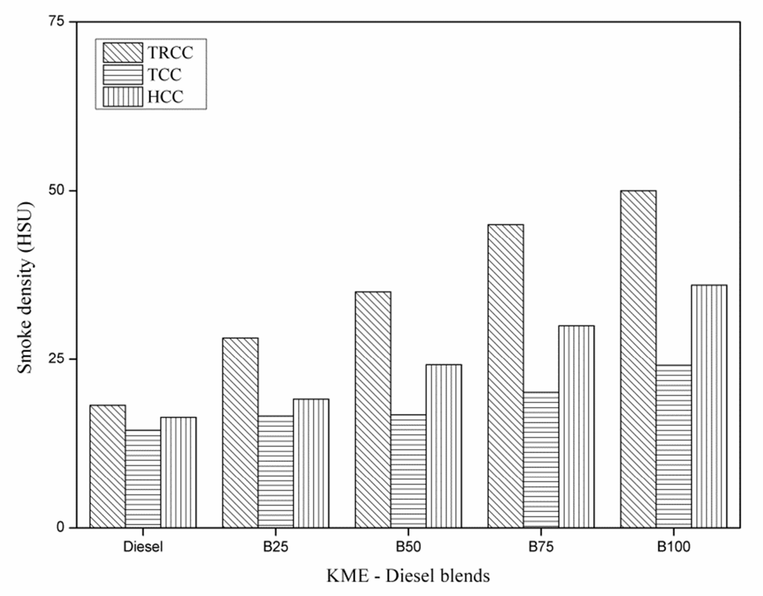


Figure 4.36 Effect of combustion chamber geometry on smoke emission for various KME – diesel blends at low load condition

The much reported trade-off between NO_X and smoke emission in a diesel engine has been well noted and analyzed herein for various blends of KME at low and full load condition. Among the various combustion chamber geometries, smoke emission as inferred from Figure 4.36 and Figure 4.37, was observed to be lower for all test fuels with TCC than that with HCC and TRCC for the reason of enhanced swirl motion of air and the consequent active combustion. With TCC, B50 showed a 7.8% reduction in smoke emission than diesel, while B75 and B100 discerned higher smoke emission despite the presence of oxygen within KME. This is because; the oxidation of soot particles is hindered for higher blends of KME due to the lower in-cylinder temperature, caused by the detoriation in combustion. On the other hand, at low load, the smoke emission was observed to be increased with the increase in KME in the blend, irrespective of the type of combustion chamber geometry being used.

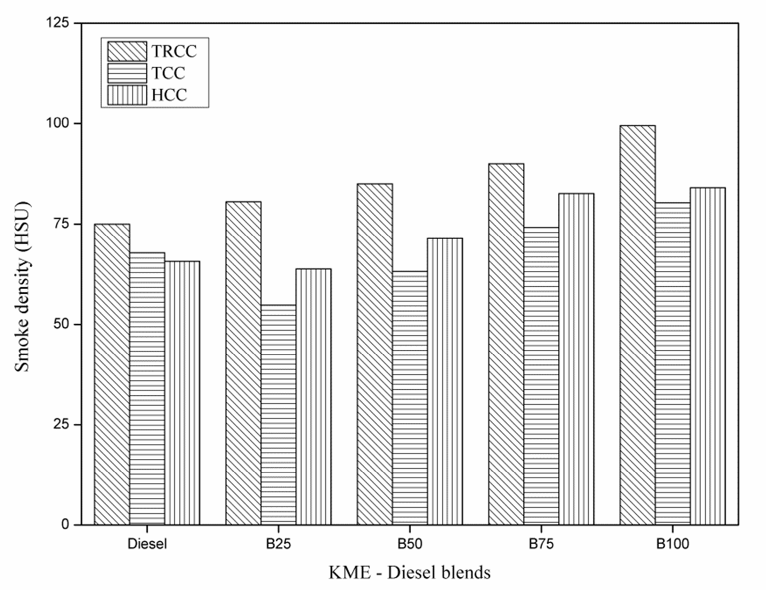


Figure 4.37 Effect of combustion chamber geometry on smoke emission for various KME – diesel blends at full load condition

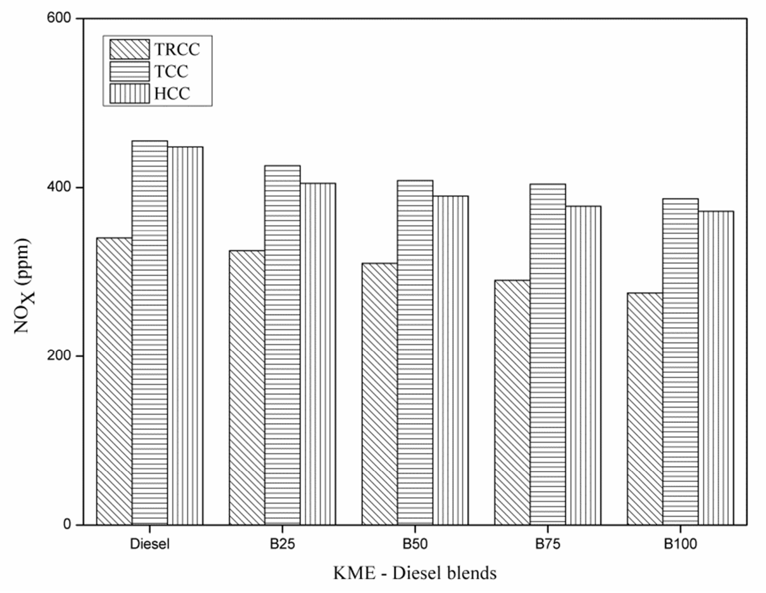


Figure 4.38 Effect of combustion chamber geometry on NO$_X$ emission for various KME – diesel blends at low load condition

A completely opposite scenario to the smoke emission, as it deemed to be, was observed with NO$_X$ emission at full and low load condition from Figure 4.38 and Figure 4.39for different test fuels with various combustion chamber geometries. The observed higher NO_X emission for all test fuels with TCC than other geometries was held accountable due to the higher in-cylinder temperature in respect of better combustion. Substantially, the increased NO_X emission with TCC compared to HCC has been reported previously by Jaichander et al [161] when using Karanja methyl ester. However, only B25 and B50 evinced higher and comparable NO_X emission for TCC, while higher blends of KME showed decreased NO_X emission because of ineffective combustion. In another interpretation, with HCC, only B25 showed comparable NO_X emission with diesel, whereas the other higher blends manifested decreased NO_X emission. In contrast, for all other blends, TRCC showed lower NO_X emission due to the combined effect of weak swirl ratio and increased viscosity of KME, which has had deterred the combustion process on whole.

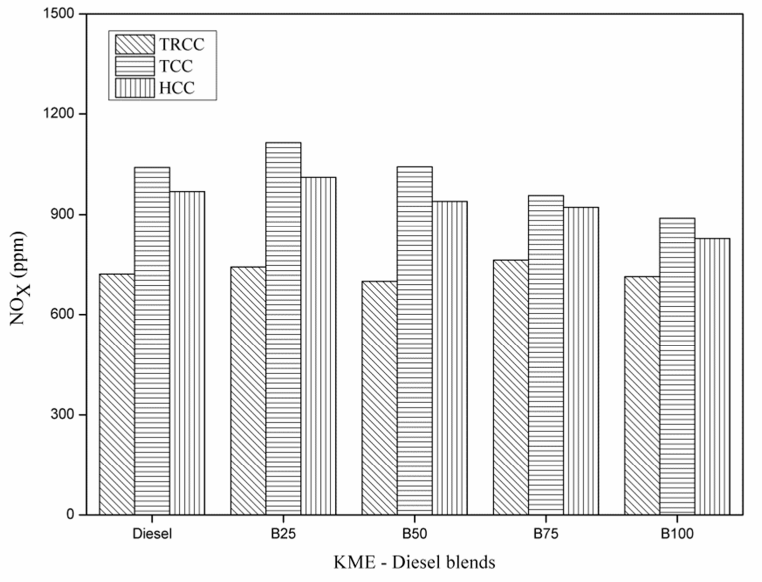


Figure 4.39 Effect of combustion chamber geometry on NO_X emission for various KME – diesel blends at full load condition

4.4.4. Conclusions

Experimental investigation was carried out to optimize the combustion chamber geometry for the operation of kapok biodiesel in a single cylinder diesel engine. As such, three different combustion chamber geometries viz HCC, TRCC and TCC, with constant compression ratio to make the comparison unanimous, were chosen. In this connection, blends of KME with diesel such as B25, B50, B75 and B100 were chosen and tested in a diesel engine with different combustion chamber geometries. From the experimental investigation, TCC was found to show better combustion and performance than other combustion chamber geoemtries for all test blends. However, when compared to diesel, TCC showed increased BTE only up to B50 blend and beyond which, a decline in engine performance was reported. Similarly, the CO and smoke emission were noticed to be 15.7% and 7.8% lower for B50 than diesel in TCC, while NOX emission was shown to be in par with diesel. It is noteworthy to point out that, with the conventional combustion chamber (HCC), the engine was able to show better performance and emission for only B25 blend, while in TCC, blends up to B50 showed better engine characteristics. In the final disposition, among the various combustion chamber geometries, the improvement in which the engine characteristics such as performance, combustion and emission could be rated goes in this trend: TCC>HCC>TRCC. In our previous study with coating, B50 evinced only comparable engine characteristics with diesel, while herein, improved engine performance and emission was achieved for B50 in TCC.

Associated publication

- Vedharaj S, Vallinayagam R, Yang WM, Saravanan CG, Lee PS. Optimization of combustion chamber geometry for the operation of kapok biodiesel in a diesel engine. Fuel (under review)