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A comprehensive review on the assessment of fuel additives effects on combustion behavior in CI engine fuelled with diesel biodiesel blends.

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Abstract

Development in transport technology is not only one of the major issues but also the demand increases with population growth that forces to increase the number of vehicles, which in-turns increase the emissions resulting in global warming. The world's present transportation systems are greatly dependent on petroleum which depletes rapidly due to limited reserves of fossil fuel. In addition, transportation is responsible for more than 25 percent of the world's greenhouse gas (GHG) emissions, and this share is rising which is a threat for future. As an alternative, biodiesel has drawing attention due to its renewability, biodegradability, high conductivity, sulfur content, flash point, aromatic content, increased lubricity etc. with less carbon monoxide and carbon dioxide emission. On the other hand, as the viscosity of biodiesel is greater than diesel due to its large molecular mass and chemical structure, problems like pumping, combustion, atomization in the injector system, injector deposit, plugging of filters, carbon deposits on piston and head of engine occur. Most of the previous study concluded that although particulates emissions from

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biodiesel fuelled engines are much less than gasoline, NO_X emissions increases significantly. The adjustment of ignition delay in the premixed combustion phase, faster rate of fuel burn, advanced start of combustion, low radiation heat transfer and variable adiabatic flame temperature is mainly responsible for NO_X formation and other emissions. Hence fuel additives may play an important role to make up the problems and meet up various specified standards. Researchers have used a lot of additives to improve the quality of biodiesel such as metal based additives, oxygenated additives, cetane improver, ignition promoter, cold flow improvers, antioxidants and lubricity improvers etc. This literature review characterizes the combustion behavior of diesel engine fuelled by diesel, biodiesel and its blends including additives. It was found that combustion characteristics were improved introducing additives with diesel and biodiesel blends, while exhaust emission also reduced.

Keywords: Biodiesel, Additives, Performance, Emission, Combustion.

1. Introduction

The energy demand after 20th century has drastically increased due to worlds rapid industrialization, accelerated economic growth, increased human standards of living, modern technology transportation system and power sector [1] depended only on limited petroleum or fossil fuel reserve which possessing 26–27% each of total energy consumption and will be replaced completely by biofuels by 2050 [2]. Oil is the world's essential wellspring of vitality and chemicals with a present interest of around 12 million tons every day (84 million barrels a day) [3] with a projection to increment to 16 million tons every day (116 million barrels a day) by 2030. While 30% of the worldwide oil utilization represents transport, a striking 60% of the rising interest anticipated that for 2030 corresponds to transport [4]. The combustion of fossil fuels in the transportation sector is the primary source of greenhouse gas and pollutant emissions [5-7]. Due to greater fuel economy, higher efficiency, excellent reliability and lower CO_2 emissions, diesel engines are widely used. But burning of this fuels are not environment friendly and produced some other harmful emissions resulted in global warming, which led the scientists and researchers to find out renewable alternative fuel for heavy duty diesel engine [8-13]. As a renewable fuel biodiesel has receiving great attention due to its biodegradability, non-toxicity, lower emission, ecofriendly and more reliable in behavior, which produced and formulated from vegetable oil and animal fat [14-16]. But biodiesel exhibits low aromatic and sulfur contents with high lubrication and octane number [17]. Furthermore higher viscosity and large molecular mass of biodiesel leads to lower volatility and poor fuel atomization, injector coking, piston ring sticking, incomplete combustion, problems in cold weather country due to adverse impact on cold flow property [1, 18, 19] and more importantly a significant increase of NO_X emission [20, 21]. Emissions from diesel engines seriously threaten the environment and are considered one of the major sources of air pollution [22]. The fourth assessment Report of United Nations Intergovernmental Panel on Climate Change (IPCC) stated that greenhouse gas emissions like nitrogen oxides (NO_X), methane and carbon dioxide (CO_2) are the main cause of global warming. An increase in the average global temperature by 2 °C will result in the deaths of hundreds of millions of people [23]. Pollutants also affects the ecological systems and creates environmental problems, produce carcinogenic compounds that leads significant endanger to human health. Pollutants from combustion like oxides of nitrogen (NO_X), carbon monoxide (CO), particulate matter (PM), total hydrocarbons (THC), acid rain, and photochemical smog as well as depletion of the ozone layer has increase concerned and driven few countries to manage emissions and give directives for implementation and consistence [24].

Combustion of diesel engine is an important factor which has great impact on engine performance and emission characteristics. Efficient combustion is desirable, which depends on atomization and evaporation of fuel, blending with surrounding gases, self-ignition, oxidation, turbulence incited by air and fuel stream, the possible interaction of the fuel stream with the cylinder walls, heat exchange between the fuel and the surrounding gases, and between combustion gases and the cylinder walls etc. [25]. The distinctions in physical and chemical properties of diesel and biodiesel fuels influences the combustion attributes. Due to shorter ignition delay of biodiesel and its blends, the premixed combustion phase occurs earlier compared to neat diesel fuel. Both the premixed combustion phase duration and diffusion combustion phase duration increased with all biodiesel–diesel blends than neat diesel. Higher premixed combustion phase duration of biodiesel–diesel blends, is responsible to increase the NO_X emission. The maximum rate of pressure rise ($ROPR_{max}$) and the maximum heat release rate (HRR_{max}) of biodiesel are generally lower than that of diesel. Moreover, the brake specific fuel consumption increases a little bit with biodiesel and its blended fuel due to variation in physical properties, combustion and heat release characteristics of biodiesel compare to diesel fuel [26, 27].

Several experimental studies has been performed to explore the combustion behavior of diesel engine fuelled by biodiesel by altering parameters like, injection timing, injection pressure, engine load, engine speed, compression ratio, fuel blends etc. Most of them concluded that, biodiesel fuelled engine showed lower ignition delay and HRR with early start of combustion, increased PM and NO_X emission and decreased power loss [28]. The combustion phasing [29] combustion temperatures [21, 30] Presence of oxygen content [31] and distinctive chemical composition [32] of diesel and biodiesel is responsible for this. High viscosity, density and low volatility characteristics of biodiesel resulted in problems in long term engine performance tests. While combustion quality is influenced by size of fuel molecule, inadequate atomization performance and fuel entrances in the cylinder which are affected by higher viscosity of biodiesel [33, 34]. Larger chemical structure of biodiesel fuel is attributed to the higher viscosity that create problems like injector coking, ring sticking and gumming in diesel engines [1]. Biodiesel also showed increase in PM and NO_X emissions. To improve this properties and solve the problems, fuel additives is taken as an alternative and most attractive solutions [24]. A lot of studied has been conducted using additives along with diesel, biodiesel and their blends to characterize combustion behavior [35-37]. Kinoshita et al. [35] reported that the ignition delay of biodiesel with crude glycerine increased the ignition delay (ID). Iranmanesh et al. [36] investigated the fuel properties and combustion characteristics of karanja biodiesel in diesel engine with 5%, 10%, 15% and 20% by volume of DEE, and showed that physicochemical properties like calorific value, viscosity, specific gravity and liquidity profile were found according to the ASTM standards with improved combustion and cold starting problems. Li et al. [37] studied the influences of multifunctional diesel fuel additive with rapeseed oil to aim the combustion performance and concluded that additives diminished the ignition delay (ID), enhanced the premixed combustion and gives better combustion efficiency.

Many investigations have been performed using additives to find out the combustion characteristics and their impacts on engine performance and emission with varying load, speed, injection timing, and injection pressure. They have also drawn conclusion regarding to the effects. The present study emphasized to compare the combustion behavior of diesel engine fuelled by diesel, biodiesel and their blends including additives by reviewing a lot of qualified papers and accumulating information from them. So that an efficient volume of additives with diesel, biodiesel can be invented and will implemented to optimize the combustion with lowest emission and highest performances. It will also help to further research with additives for future investigation.

2. Combustion behaviour in diesel engine

Diesel engines works on the principle of compression ignition. Combustion in a compression ignition (CI) engine is an unsteady process happening at the same time at numerous spots in a non-homogeneous mixture at a rate controlled by fuel injection. The combustion in the compression ignition engine depends on compression process into the cylinder to increase the temperature and pressure of air so that during fuel injection the mixture of air-fuel auto ignites. It is necessary to inject the fuel finely scattered, so that it atomized and evaporates quickly to mix rapidly with swirling hot air in combustion chamber. To ensure desired high temperature and pressure hence auto ignition of the mixture occur into the cylinder, compression ratios of modern CI engines range from 12 to 24 [25, 38, 39].

The combustion procedure in CI engines can be categorized into three major sections, as shown in **Fig.1**.

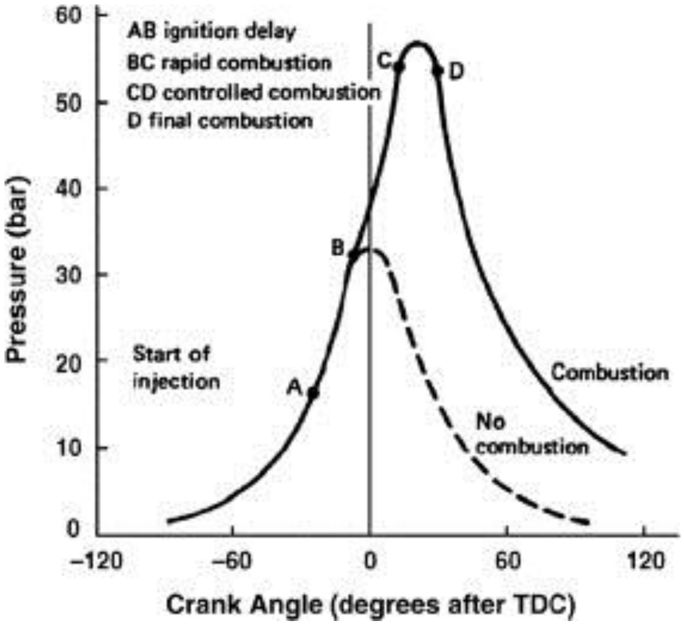


Fig. 1. Combustion matters in CI engine [25, 39].

2.1. Ignition Delay

Among the major combustion parameters, ignition delay is one of the most important combustion property, which is defined as the time period between the start of injection (SOI) and the start of combustion (SOC) during which each fuel droplet gets ready for combustion by being atomized, vaporized, mixed with air, ignited through auto ignition, and burned [9, 11]. Ignition delay period in diesel engine exhibits huge impact on engine design, performance and emission and variation depends on either diesel, biodiesel or their blends fuel used. Functionally, the ignition delay (ID) can be divided into two parts, such as the physical delay and chemical delay as shown in **Fig. 2** [40].

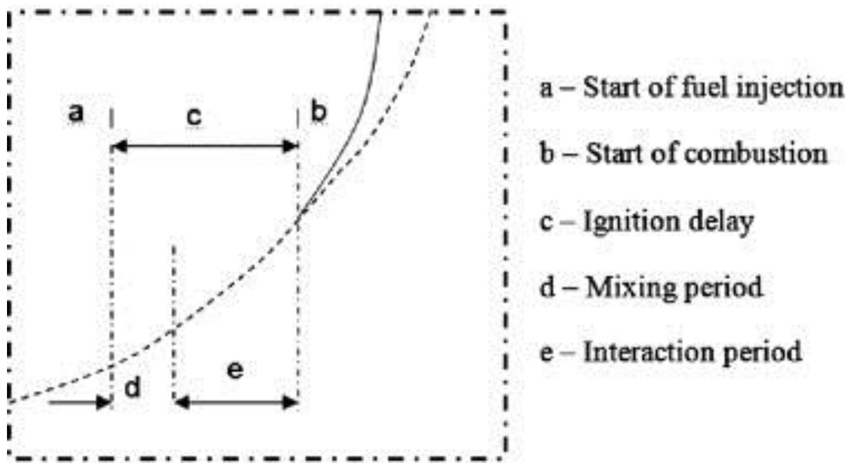


Fig. 2. Ignition delay mechanism [40].

Physical delay is the period between start of injection and the arrival of chemical reaction conditions. During this time, the fuel is breaking up, vaporized, blended with air and enhanced to self-ignition temperature. Viscosity represents the physical delay of fuel ignition process. Physical delay increases as viscosity increased and vice versa. During chemical delay time, reactions begin gradually and afterward quicken until combustion occur. Generally, chemical delay was found greater compared to physical delay depending on the temperature of the circumferences. When chemical reactions are quicker at higher temperatures then physical delay becomes greater than the chemical delay.

2.2. Rapid or uncontrolled Combustion

During this stages of combustion auto ignition occur as some of the mixture has been injected into the cylinder in the ID stage and begin to burn as a premixed charge. As a result a rapid pressure rise is observed depending on the length of ID and mass of fuel present in the combustion chamber [39, 41].

2.3. Controlled Combustion

By controlling the rate of fuel injected into the cylinder that mixes with compressed hot air, can control combustion efficiently. As the piston returns away, the in-cylinder mixture cools rapidly due to expansion, resulting in a great decrease in the rates of chemical reaction (often termed as frozen). Which means that, the reaction rates are insignificant, leaving the system such a condition that may be far from chemical equilibrium. High levels of NO_X and PM are examples of chemical products that are "frozen" well above their equilibrium levels [37].

3. Influence of combustion on Performance and emission

Diesel engine combustion is an important but complex phenomenon. The performance and emission of diesel engine depends on combustion efficiency. Many researchers have studied the engine performance, emission and combustion of diesel engine fuelled with biodiesel. Most of them reported that the major factors of combustion that effects on performance and emission are heat release, ignition delay, combustion phases, maximum heat release rate (HRR_{max}) in premixed phase, combustion duration [25, 42]. More specifically emission such as NO_X, PM, THC, HC, CO formation and performance such as Break Specific Fuel Consumption (BSFC), Break Specific Energy Consumption (BSEC), and Brake Thermal Efficiency (BTE) are affected by combustion parameters. The effects of combustion on performance and emission varied with various parameters like biodiesel feedstock's (sources), contents of biodiesel, cetane number, advance injection timing and combustion, oxygen contents, engine load, engine speed, density and viscosity [1].

3.1. Combustion Chemistry and engine emission

Combustion is a complex phenomenon which creates heat and includes numerous free radical species and responsive intermediates in chain spreading, chain propagation and termination reactions. To understand the ignition and emission matters like formation of pollutants, quantitative chemical information is necessary along with nature and amount of undesirable and potentially noxious products [43]. Combustion chemistry perspectives are included especially in ignition, heat release and elimination forms. They have fundamental impact on harmful pollutants emission signature with expansion of biofuels in diesel or biodiesel. For instance, particulate emission can be decreased by expansion of ethanol [44] however undesired aldehyde may increment altogether [45]. Additionally an increased NO_X emission is seen if there should be an occurrence of biodiesel ignition [46]. The biodiesel class of compounds is particularly diverse chemically, and to comprehend suggestions for the burning methodology it is important to consider prototypical analysis [43].

Biodiesel fuels are methyl and ethyl esters of unsaturated fats from plant and animal provenance [47]. Biodiesel is produced by artificially responding lipids (e.g., vegetable oil, animal fat) with an alcohol to create unsaturated fat esters. The unsaturated fat profile of biodiesel compares to that of guardian oil or fat, which is a key variable that impacts its fuel qualities [48]. Biodiesel can be mixed with petroleum diesel or utilized as a perfect fuel as a part of current automotive, exploiting its low sulfur and aromatics content and of the considerable diminishing in

CO, unburned hydrocarbons, and particulates in the exhaust gasses [49]. Biodiesel fuel contains branched and unsaturated long carbon chains. Higher fuel molecules and chemical variability attributes them to develop the combustion details [50].

Several features of the combustion reactions for methyl esters like methyl palmitate ($C_{17}H_{34}O_2$), methyl stearate ($C_{19}H_{38}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), and methyl linolenate ($C_{19}H_{32}O_2$), are similar to those of large *n*-alkanes, such as *n*-hexadecane, because of the common alkyl chains [51]. Mechanisms have a tendency to become complex, not just due to the extent of the fuel molecules, additionally as a result of the extra reactions of oxygen-containing species. For example, low-temperature ignition of methyl decanoate was displayed with 3012 species and 8820 reactions [52]. Vital pathways for ester ignition incorporate alkyl peroxy radical reactions, isomerization reactions, and H-atom exchange [53]. Methyl esters can deteriorate into two different reactive oxygen carriers which could contribute to soot-precursor lessening, or the O-C-O structure in the molecule may frame CO_2 [43]. Ignition timing is truly diverse notwithstanding for a homologous arrangement of methyl esters, with methyl butanoate being the most safe fuel to auto ignition. It was reported that the reactivity increases with the length of the alkane chain. High reactivity is attributed to the methoxy radical. More generally, alkyl and alkyl ester radicals add to O_2 to form RO_2 radicals in the low-temperature region, and they deteriorate in the high-temperature region to form olefins and unsaturated esters which may then react further in same elementary reactions [54]. The combustion reactions of ethyl esters show unthinking contrasts from those of methyl esters. Mole fractions for C_2- to C_6- hydrocarbons are higher in the ethyl formate flame as an outcome of the ethyl group and carbon development reactions. However, they are still lower than those seen in comparable fuel-rich hydrocarbon flames, affirming a propensity of ester fuels to lessen soot precursors. Concerning oxygenated intermediates, H-deliberation from the methoxy group of the methyl ester drives especially to formaldehyde, and H- deliberation from the ethoxy group of the ethyl ester prompts more prominent mole divisions of acetaldehyde [55]. Ethyl esters can deteriorate through a unimolecular disposal reaction creating C_2H_4 by means of a six-membered pericyclic transition state. This ethene elimination reaction may be the motivation behind why ethyl esters may light all the more quickly [56].

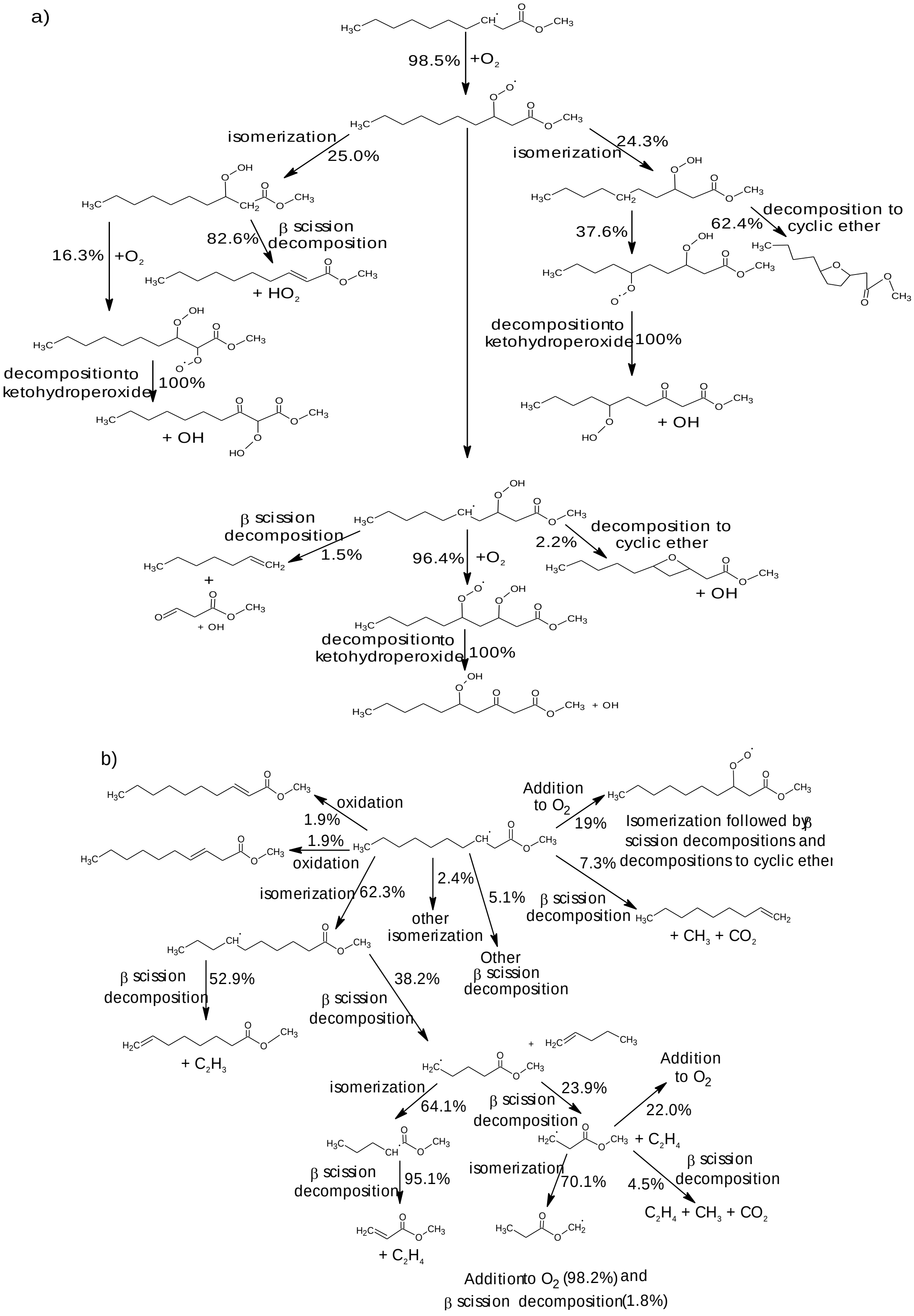

a)
98.5%
$+O_2$
isomerization
25.0%
isomerization
24.3%
16.3%
$+O_2$
β scission decomposition
82.6%
$+ HO_2$
decomposition to cyclic ether
62.4%
37.6%
decomposition to ketohydroperoxide
100%
decomposition to ketohydroperoxide
100%
+ OH
+ OH
β scission decomposition
1.5%
96.4%
$+O_2$
2.2%
decomposition to cyclic ether
+ OH
+ OH
decomposition to ketohydroperoxide
100%
+ OH
b)
oxidation
1.9%
1.9%
oxidation
Addition to O_2
19%
Isomerization followed by β scission decompositions and decompositions to cyclic ether
7.3%
β scission decomposition
$+ CH_3 + CO_2$
isomerization
62.3%
2.4%
other isomerization
5.1%
Other β scission decomposition
β scission decomposition
52.9%
$+ C_2H_3$
38.2%
β scission decomposition
isomerization
64.1%
β scission decomposition
23.9%
Addition to O_2
22.0%
$+ C_2H_4$
β scission decomposition
95.1%
$+ C_2H_4$
isomerization
70.1%
4.5%
β scission decomposition
$C_2H_4 + CH_3 + CO_2$
Addition to O_2 (98.2%) and β scission decomposition (1.8%)

Fig. 3. Flow decomposition paths of a radical formed by abstraction of a secondary H-atom from methyl decanoate at a residence time of 1s and a temperature of (a) 650 K and (b) 900 K [57].

Fig. 3 demonstrates the destiny of the radical that is gotten from methyl decanoate supply of an optional H-atom by OH radicals. A ROO radical is framed that isomerizes to three distinctive more radicals of QOOH structure at low ignition temperature of 650 K **(Fig. 3a)**. The next stages in the oxidation include ketohydroperoxides and four- and five-membered cyclic ethers. During higher ignition temperature of 900 K **(Fig. 3b)**, isomerization is seen to further C_{11} alkyl ester radicals. The reaction scheme also includes unsaturated compounds. As to decenoate oxidation, the double bond inhibits certain H-atom-transfer isomerization reactions. The vicinity and position of a double bond in this manner has an imperative impact on the low-temperature reactivity of the ester molecule [57]. Isomeric mediums are essential for biofuel ignition as a results of extra chemical functional groups in the fuel particle that offers ascend to distinct reaction sequences and potential fuels might likewise have distinctive isomers [43]. Blending of biofuels as additives in diesel biodiesel blends may spread up more chemical pathways through the interaction of the decomposition and oxidation of all the compounds in the mixture. Hence different types of isomeric additives blends with biodiesel may solve the existing problems of biodiesel fuelled engine.

3.2. Combustion & Emission

At primary phase of fuel injection, the in cylinder pressure and temperature were lower a little bit with higher ignition delay and forms greater fuel rich zone with advanced SOI timing, which is responsible for increased CO emission. But at a constant SOI timing, CO emissions decreases with increasing fuel injection pressure [58]. The retarded injection timing increase CO emission due to a longer heat release [59]. The in-cylinder pressure and temperature drops with retarded SOI timing that increases the HC emission with increasing fuel injection pressure. With retarded SOI timing NO_X emission decreased and reached to lowest when SOI timings is near TDC but begin to increase again when SOI timings were further retarded after TDC. Up to 4.125 °CA ATDC SOI timing the peak of premixed heat release tends to increasing but at 5.625 °CA SOI timing the peaks of premixed heat release and NO_X concentration reduced [58].

Lower gas pressure and in-cylinder temperature showed lowest NO_X emission at 25% load [60]. Decreasing maximum heat release rate (HRR_{max}) in premixed combustion phase lowered the in-cylinder gas temperature and NO_X emissions but increased amount of fuel injected at full load increase the NO_X emissions. Deterioration of atomization and combustion lowered the HRR_{max} lengthen the premixed combustion duration at full load [61]. Advanced SOI of B5 increase the NO_X emission [62] whereas B10 showed lowest NO_X emissions at all load but due to its high viscosity the smoke emissions increased by deteriorating the atomization and combustion [63, 64]. Shorter delay of CD of B5 leads to lower the smoke emission and longer delay of CD of B10 leads to higher the smoke emissions [65]. The deterioration of combustion together with high fuel density caused a decrease in NO_X [66, 67]. Higher cetane number of biodiesel cause decrease in flame temperature and NO_X [68, 69]. B5 showed shorter ignition delay than neat diesel and offered complete combustion with low total hydrocarbon (THC) emissions [68, 70]. But THC emissions of B10 were higher than B5 and neat diesel at all load due to larger spray droplet size of higher density and viscosity characteristics fuel which deteriorates the combustion [71-73].

Combustion temperature, the oxygen concentration and the duration of combustion is mainly responsible for NO_X formation [74-76]. Early start of combustion due to lower premixed burned fraction decreases the NO_X emissions [63, 69, 76]. At the initial stage of diffusion combustion higher amount of oxygen content causes, biodiesel produced excess NO_X with higher in-cylinder temperatures [77-79]. Moreover, NO_X formation rates in the post flame gas region increased because of the longer existing time with the increase of the overall Combustion Duration [28, 79]. Combustion occurred earlier because of higher cetene number and lower aromatic content of biodiesel causes shorter ID period, which improved the THC emissions due to formation of over-lean regions. Also the longer CD with the increase in the engine loads due to higher boiling point of biodiesel also leads to improve the THC emissions [76, 80-83]. The higher rate of fuel flow with oxygen content and higher combustion temperatures became effective parameters with the increasing engine load to improve CO emissions [30, 80, 84-87]. In addition, early start of combustion and longer combustion duration increases the possibility of CO oxidation to CO_2 with the biodiesel addition for the higher engine loads [65, 80, 84, 88-91]. Presence of oxygen content in the biodiesel leads to clean and complete combustion which reduce the CO and HC emissions. Advanced injection timing with biodiesel reduce CO and HC emissions but increases the NO_X formation due to increases the fuel existing time in pump-line-nozzle injection system [27].

3.3. Combustion & performance

Delayed combustion duration (CD) has negative effects on the engine performance [92-94]. Increasing percentages of biodiesel in the blends showed early SOC which increases the pumping work and heat loss and increase the combustion duration cause heat release in the expansion stroke contributes less work [90]. Retarded start of injection timing showed minimum break specific fuel consumption (BSFC) with increasing fuel injection pressure. But at a constant start of injection timing thermal efficiency increase with increasing fuel injection pressure [58]. Break thermal efficiency (BTE) increased with increasing fuel injection pressure at full load for biodiesel [95]. Lower in-cylinder pressure and temperature increases the Break Specific Energy Consumption (BSEC) of increasing proportion of biodiesel–diesel in blends at low load, because biodiesel having higher injection duration and combustion duration. Increasing in BSEC in-turn lowered the brake thermal efficiency (BTE) than neat diesel. Poor atomization and mixture formation is attributed to slow down the combustion and lower BTE [27]

3.4. Impact of additives on performance and emission

A lot of research have been performed including additives in diesel, biodiesel and their blends. Rashedul et al. [96] reviewed the performance and emission of biodiesel with additives in diesel engine reported that oxygenated additives in blends is not enough efficient to improve brake power and less efficient to decrease fuel consumption. While antioxidant additives and metal based additives improves the brake power, decrease fuel consumption than other additives. On the other hand, Oxygenated additives, metal based additives and antioxidant additives showed reduced NO_X emission. Metal based additives, ethanol, methanol decreased the CO and HC. Smoke opacity of blend fuel with additives also diminished with DEE, ethanol and metal based additives. Misra et al. [97] reported that ethanol as an additives is more significant to improve combustion performance and emission. The National Renewable Energy Laboratory's (NREL) report named "NO_X Solutions for Biodiesel" reported that di-tertiary butyl peroxide and ethylhexyl nitrate, which are both cetane improvers effectively reduce the NO_X emission. NREL also reports that tertiary butyl hydroquinone, an antioxidant, is an effective NO_X reducing agent, with slight PM increase [25]. Kannan et al. [98] studied that, using $FeCl_3$ as fuel borne catalyst to diesel engine increase BTE by 6.3% due to decreased fuel consumption by 8.6%. Including 1% of 4-nonyl phenoxy acetic acid additives increase BTE and decreased the exhaust emissions [99]. Keskin et al. [100] mentioned that specific fuel consumption of tall oil with metallic additives showed decreasing trends than biodiesel. Chen et al. [101] illustrated that emulsified bio-solution/palm-biodiesel/diesel blends showed benefits to save energy and decreases the polycyclic aromatic hydrocarbons and particulate matter. Usually, catalysts do not affect the engine performance significantly but delay the ignition time and reduce the unburned hydrocarbon (HC) and the particulate matter (PM). However, overall performance can be enhanced by adding additives with the fuel [102].

4. Fuel additives

4.1. Introduction to fuel additives

Fuel additives are natural substances dissolvable in fuels. Around 20 properties of fuels can be enhanced, kept up or bestowed new advantageous attributes by the including of little measures of specific chemicals named fuel additives. Fuel added substances are included little focuses from a few ppm to a few thousand ppm. It is imperative that added substances which enhance a few properties ought not to disintegrate different properties of fills and its quality when all is said in done. Some of these additives may help to keep up fuel quality (e.g., antioxidants, stabilizers, corrosion inhibitors, and biocides). Others may help the development of fuel through the dispersion chain and into the vehicle tank (e.g., flow improvers, pipeline drag reducers, demulsifies, and antifoams); may be included for legal reasons (e.g., colors and markers) or can address particular concerns from engine manufactures (e.g., deposit control additives and lubricity improvers) [103]. Fuel additives in diesel, biodiesel and their blends improves the fuel characteristics of hence showed the following benefits [24, 96]:

- Secured of fuel tanks, channel lines and other from greatly lavish erosion.
- Secured of fuel system equipment's in the diesel engine from catastrophic untimely wear.
- Diminished pumping expenses and energy use in long-distance fuel pipelines.
- Lessened refinery preparing expected to meet diesel cetane, octane and details.

- Improvement of cold flow in middle distillates, boosting utilization of bio fuel.
- Changes of stability to enhance storage for long time of fuels through-out the working theatre.
- Fuel sparing from improved vehicle performance and economy.
- Decreases noxious emissions;
- Enhance fluid stability over a more extensive scope of conditions.
- Improve the viscosity number, diminishing the rate of change of viscosity with temperature.
- Enhance ignition by decreasing delay time, flash point, etc.; and
- Diminish wear with agents that adsorb onto metal surfaces and conciliatorily give chemical to-chemical contact as opposed to metal-to-metal contact under high-load conditions.

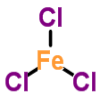
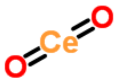
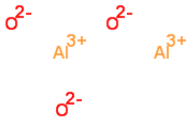
However, as fuel additives comprise of several chemicals, some of them are harmful for the environment. Then there are certain bio elements inside the additives which can cause potential harm to the engine if not used properly [104]. Higher proportion of alcohol causes extra release of rust, debris, sediment and gunk and further clogging and damage to engine components and filters [105]. It is very difficult to use ethanol fuel in cold weather [106]. Higher concentration of antioxidants showed a remarkable increase of acid values at antioxidant levels of 1000 mg/kg [107].

4.2. Application of various types of fuel Additives in diesel Engine

4.2.1. Metal based additives

Introducing metal based additives with diesel and biodiesel fuel can improves the fuel properties and meet up the problems of incomplete combustion and exhaust emissions [96]. Catalytic effect is the key principle of metal based additives which working as combustion catalyst to accelerate the combustion, decreased fuel consumption and emissions for hydrocarbon fuels. Various metal based additives used are cerium (Ce), cerium–iron (Ce–Fe), platinum (Pt), platinum–cerium (Pt–Ce), iron (Fe), manganese (Mn), barium, calcium and copper [98, 108]. Metal based additives like Nano CuO, $CuCl_2$, $CoCl_2$, $FeCl_3$ and $CuSO_4$ are sometimes implemented as fuel borne catalyst (FBC) for biodiesel. It was observed that, addition of FBC in biodiesel made the cylinder gas pressure and heat release rate high with lower ignition delay at optimized operating conditions [98]. Metal based additives are also effective to reduce emission either by mixed with water to create hydroxyl radicals that increase soot oxidation, or react directly with carbon atoms in the soot, hence reducing the oxidation temperature [109-111]. Whereas, addition of FBC to biodiesel showed a slight increase in NO and CO_2 emission at optimized operating conditions [98]. The addition of CON and CNT in Diesterol blends increases the CO emission to 22.2% than the E20 fuel blend, but there was no remarkable change in NO_X emission [112]. **Table 1** showed the chemical structure and molecular formula of often used Metal based additives.

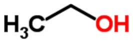
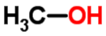
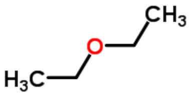
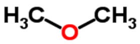
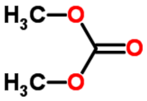
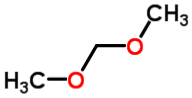
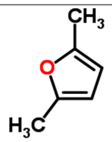
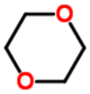
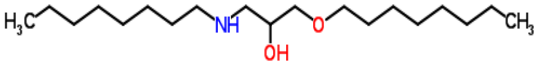
Table 1: Chemical structure and molecular formula of different Metal based additives [113].

Name	Structure	Molecular Formula
Fecl$_3$		Cl_3Fe
Cerium (IV) oxide		CeO_2
Alumina		Al_2O_3

4.2.2. Oxygenated fuel additives

Oxygenated fuel additives are additives that contains oxygen content with them. They are very useful to improve fuel properties, combustion quality and octane rating. The oxygenate added substances by and large utilized are alcohol (ethanol, methanol, butanol and propanol and so forth.), ether (ethyl tertiary butyl ether, methyl tert-butyl ether, di-isopropyl ether, dimethyl ether, diethyl ether and so on.) and ester (dicarboxylic corrosive esters and acetoacetic esters) functional group [114]. Oxygenated fuel permits the fuel in engine to combust more completely. Because of the vast majority of the fuel is burning, there are minimum measure of destructive chemicals protected into the climate. Consequently, the chemical structure of biodiesel and the utilization of added oxygenated additives directly affect properties like viscosity, density, and behavior at low temperatures, volatility, and the cetane number [115-118]. Oxygenated additives also have been considered for decreasing the ignition temperature of particulates depending on oxygen content and local oxygen concentration of fuel [24, 119]. The vicinity of some oxygenated added substances (ethanol, 1-octylamino-3-octyloxy-2-propanol, and N-octyl nitramine) brings about the development of a lubricant film with helpful against wear properties. The increase volatility of the blends is also evidence as a lower flash point at atmospheric temperature [120-122]. Oxygenated additives like diethyl ether, ethanol, n-butanol etc. help to decrease the in-cylinder temperature because of their high latent heat of evaporation [96]. But there are some limitation of oxygenated additives, specifically the lower carbon fuels showed lower calorific value contrasted with diesel fuel, miscibility and stability issues when mixed with diesel fuel [123] low cetane number, high heat of vaporization, high auto-ignition temperature [47, 124, 125] and inadequate lubricating behaviors [126]. Due to contain higher oxygen content they tends to increase NO_X slightly [127]. **Table 2** showed the chemical structure and molecular formula of often used oxygenated additives.

Table 2: Chemical structure and molecular formula of different oxygenated additives [113].

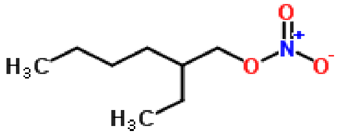
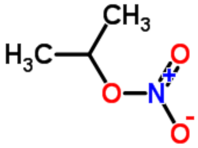
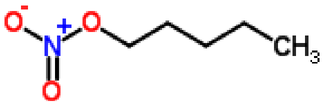
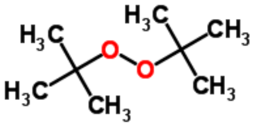
Name	Structure	Molecular Formula
Ethanol		C_2H_6O
Methanol		CH_4O
n-Butanol		$C_4H_{10}O$
Diethyl ether		$C_4H_{10}O$
Dimethyl ether		C_2H_6O
Dimethyl Carbonate		$C_3H_6O_3$
Dimethoxy methane		$C_3H_8O_2$
2,5 Dimethylfuran		C_6H_8O
1,4 dioxane		$C_4H_8O_2$
1-octylamino-3-octyloxy-2-propanol		$C_{19}H_{41}NO_2$

4.2.3. Cetene number improver additives

Cetane number is the quantity measure of how well and easily diesel fuel combusted. Diesel engines work well with a cetane numbers from 48 to 67 varying on several factors such as oil processing and environmental conditions from where the feedstock was collected and mainly the fatty acid composition of the base oil. Engine running on low cetane index diesel fuels are difficult to starts on cold climatic area, exhibits abnormal levels of emissions, developed low power and consumed more fuel [127, 128]. Larger amount of alkanes, alkenes and naphthenes and lower amount of aromatics keeps the cetane rating higher. An increase in cetane index lowered the ignition delay [129]. To launch the oxidation of the fuel in the engine in fluid stage before the arrangement of vapor-air mixture and in this manner quicken the development of hydro-peroxides and accordingly to give quite, uniform and stable ignition in the engine, various additives are used. These additives are alkyl nitrates (2-ethyl-hexyl nitrate, octylnitrate, isopropyl nitrate, amyl nitrate) and di-tert-butyl peroxide. They initiate oxidation of cycloalkanes (naphthenes) and aromatics containing in large amounts in diesel fuels, breakdown during combustion to form free radicals, which increase the rate of decomposition of the hydrocarbon components of fuel, diminish ignition delay, and thus facilitate the start of engine [103]. Cetane number is particularly influenced by the structural features of the different fatty esters. The vicinity of double bonds in unsaturated fats will bring down the cetane number quality, and afterward methodologies are tended to move the fatty pool of vegetable oil toward immersed moieties which enhance the ignition nature of the derived biodiesel, however the oxidative solidness may compromise cold flow properties [130, 131]. Hess et al. [132] investigated the effect of antioxidant on NO_X emissions using 80% diesel and 20% biodiesel blend and reported that, the 2-ethyl-hexyl nitrate (2-EHN) additive improved the cetane number of the fuel decrease the ignition hence reduce the NO_X emissions.

There is a slight increase of HC emission of ethanol blended diesel with CN improver at overall engine operating conditions. It was found that, both 0.2% and 0.4 % CN improver showed same HC emissions to that of diesel fuel. But during low load the ignition delay of the blends cannot be resumed to diesel fuel only through the CN improver [128]. **Table 3** showed the chemical structure and molecular formula of often used cetane improver and ignition promoter additives.

Table 3: Chemical structure and molecular formula of different cetane improver and ignition promoter additives [113].

Name	Structure	Molecular Formula
2-ethyl-hexyl nitrate		$C_8H_{17}NO_3$
Octylnitrate		$C_8H_{17}NO_3$
Isopropyl nitrate		$C_3H_7NO_3$
Amyl nitrate		$C_5H_{11}NO_3$
Di-tert-butyl peroxide		$C_8H_{18}O_2$

4.2.4. Ignition promoter additives

Improved ignition is distinguished as a decline in the ignition delay time, which measured as the time between the start of fuel injection and perceptible ignition. Quite engine operation, decreased NO_X emission, and quicker engine startup at cold weather depends on lower ignition delay [133]. On the other hand a high ignition delay will prompt the possible ignition being exceptionally quick, bringing about an unsuitably high rate of pressure rise in the burning chamber, producing high noise, whilst incomplete combustion, loss of power and expanded emission will likewise happen. Alternately, decreasing the ignition timing results in enhanced start ability, lower noise and reduce emission [130]. The ignition delay reduced with an increase in aromatic hydrocarbons and increases with an increases in n-paraffin and olefin content in fuels [134]. Implementation of ignition promoters reduces this difficulties. Ignition promoters have traditionally been given to alkyl nitrates (e.g., amyl nitrate, hexyl nitrate, and octyl nitrate), but azo compounds and alkyl peroxides have also been proposed [135, 136]. The CO emission during the heavy engine load does not change remarkably. The HC emission can be increased by adding DTBP [137]. Whereas addition of 50% diesel and 50% biodiesel along with DTBP decreased HC emission by 34% compared to diesel-biodiesel blends [138].

4.2.5. Lubricity additives

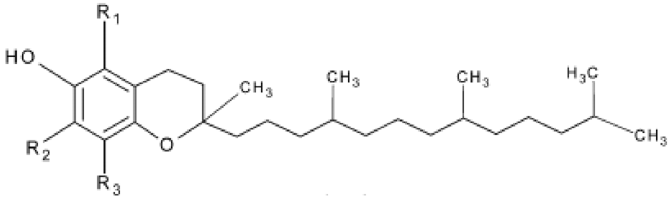
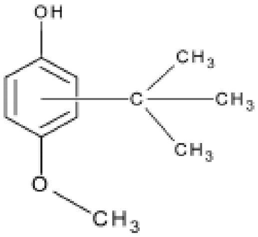
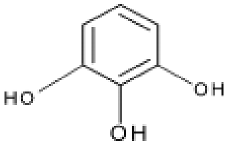
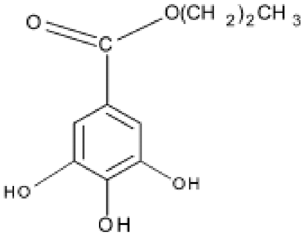
Introducing lubricity additives in the fuel increased the fuel lubricity. They embody a scope of surface-dynamic chemicals. They have an affinity for metal surfaces, and they construct a boundary films that restrict metal-to-metal contact that prompts wear under light to high loads. A lot of research demonstrated that the expansion of lubricity added substances is redundant in low-sulfur diesel−biodiesel mixes once vegetable oil methyl esters upgrade the fuel lubricity [139-141].

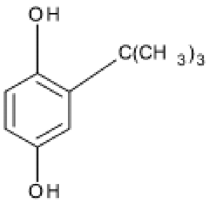
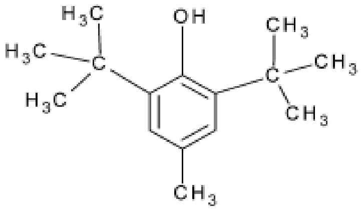
The additives in the fuel gives a stable film on the metal surface and considerably diminishes the wear scar width [142]. Lubricating improver additives are powerful in restoring lubricity lost in serious refinery transforming, consequently allowing ordinary engine operation, reliability and service life [143]. Lately, unsaturated fat methyl esters normally known as biodiesel, have effectively been utilized as diesel fuel lubricity improvers [144]. The lubricity changes saw from vegetable-oil-based methyl ester additives are more prominent than that watched when the methyl ester of one and only unsaturated fat is included at the same fixations. Past studies have demonstrated that unsaturated fat esters got from vegetable oils have expanded diesel fuel lubricity at amassing's of under 1% [144, 145]. Biodiesel fuels have chemistry like some lubricity additives and when mixed with diesel fuel gives notably change to the fuel's lubricating properties, most of the time killing the requirement for extra lubricity additives. The biodiesel content exceeds 2–3% in the finished fuel, a lubricity additive would typically be considered unnecessary [130]. Biodiesel is corrosive in nature against copper and brass. Using biodiesel showed excessive engine wear [1].

4.2.6. Antioxidant additives

Antioxidants agents are frequently diminishing operators, for example, hindered phenols, aromatic amines and diamines, or mixtures of aromatic diamines (e.g., phenylenediamines) and alkyl phenols. Oxidation creates free radicals which can begin chain of oxidation reactions in fuels. Antioxidants work by interfering with this chain reactions (evacuating free radical intermediates), restricting the creation of hydroperoxides, peroxides, dissolvable gums, or insoluble particulates. Antioxidants agents do this by being oxidized themselves rather fuels [103]. Oxidation leads to deterioration, prompts decay, bringing about fuel obscuring and the formation of gums and sediment. Antioxidants improve biodiesel stability and restrain its propensity to deteriorate in long term storage [146-148]. Presence of unsaturated fatty esters in biodiesel make it much able to the auto oxidation or oxidation begins for long time storage of biodiesel. After oxidation of biodiesel and its diesel blends the viscosity, density and corrosive worth expanded, as the iodine quality lessened with rising storage time [96, 149, 150]. Amine-based added substances, in some cases consolidated with dispersants, are utilized to control the strength of diesel fuel. Hydro-preparing uproots the majority of the receptive species to make ultra-low sulfur diesel fuel which creates an extremely stable diesel fuel obliging the utilization of little, if any, stability additive. Biodiesel, while regularly low in sulfur, corrupts through an oxidative procedure that can be controlled, normally utilizing impeded phenol antioxidant agents. It is essential to treat biodiesel when it is created, as any corruption will be to a great extent irreversible. Both gasoline and diesel fuel are sporadically contaminated with metals, such as copper, that can catalyze the creation of gums and residue. Hence, metal deactivators may be utilized at low levels to kill the synergist impact of these metals. Most biodiesel antioxidant packages contain a metal deactivator to control catalytic degradation [130]. Antioxidant concentration highly impacts on engine performance and emission. The BSFC of biodiesel fuel with antioxidants is not as much as that of fuel without antioxidants. Besides, an antioxidant can significantly reduce NO_X formation during engine operation [48]. B20, B20 + BHA, and B20 + BHT showed reduced power of 1.02%, 0.44%, and 0.68% compared to that of B0 respectively. This is due to the combined effect of their lower energy content, i.e. lower calorific value, and higher viscosity compared to B0. Introducing antioxidant in the biodiesel blends showed an average enhancement of CO emission of 8.6–12.3% compared to B20, as it prevents the conversion of CO. Because of decreasing the formation of oxidative free-radical, antioxidant addition in the blends showed a mean increase in HC emission of 9.1–12.0% than B20 [151]. Pyrogalol (PG) showed some compatibility problems, and it may not be readily solubilized in blends with larger SME ratios [107]. **Table 4** showed the chemical structure and molecular formula of often used cetane improver and antioxidant additives.

Table 4: Chemical structure and molecular formula of different antioxidant additives [48].

Name	Structure	Molecular Formula
α-tocopherol		$C_{29}H_{50}O_2$
Butylated hydroxyanisole (BHT)		$C_{11}H_{16}O_2$
Pyrogalol (PG)		$C_6H_6O_3$
Propyle gallate		$C_{10}H_{12}O_5$

Tert-butylhydroxyquinone		$C_{10}H_{12}O_3$
Tert-butylhydroxytoluene		$C_{11}H_{16}O$

The reaction path diagram of combustion of some fuel additives are given below. Where **Fig. (a-d)** represents the reaction path diagram of (a) Ethanol (b) Methanol (c) *n*-butanol (d) Cerium oxide combustion and **Fig. (e)** represents the oxidation process of antioxidants.

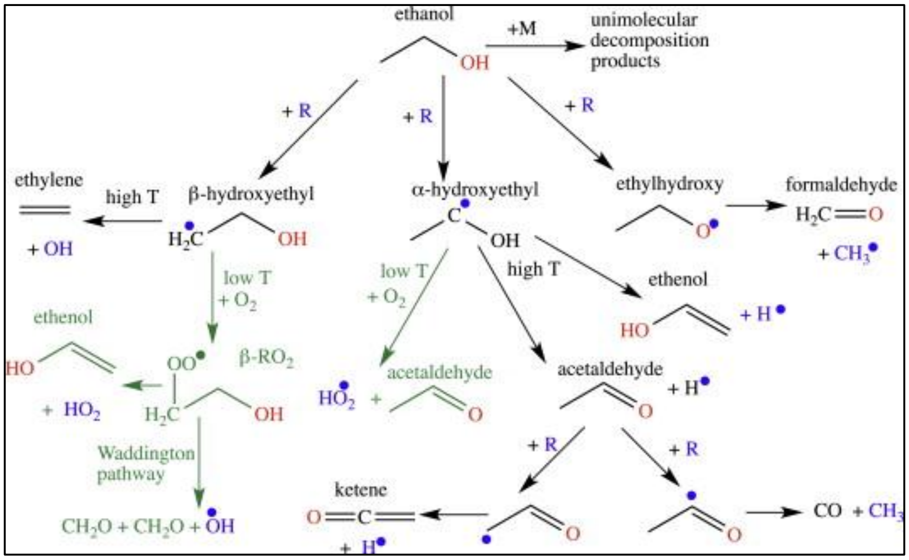


Fig. (a) Reaction path diagram for ethanol combustion [152].

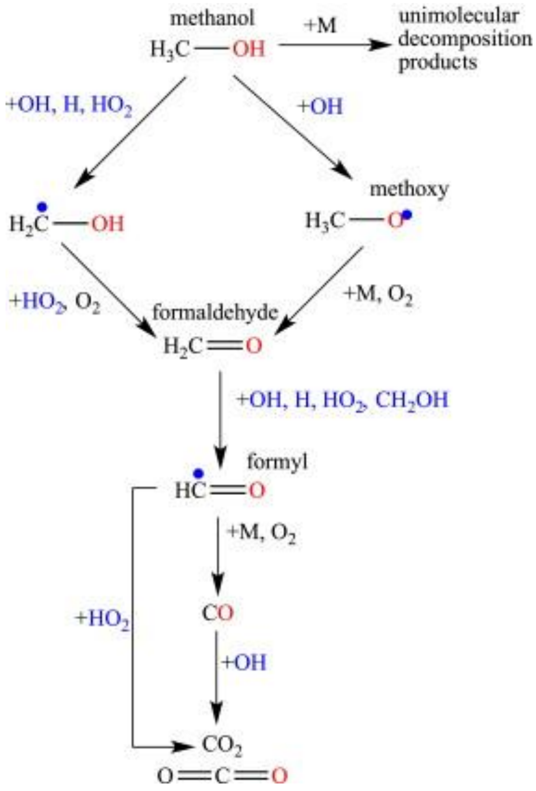


Fig. (b) Reaction path diagram for methanol combustion [152].

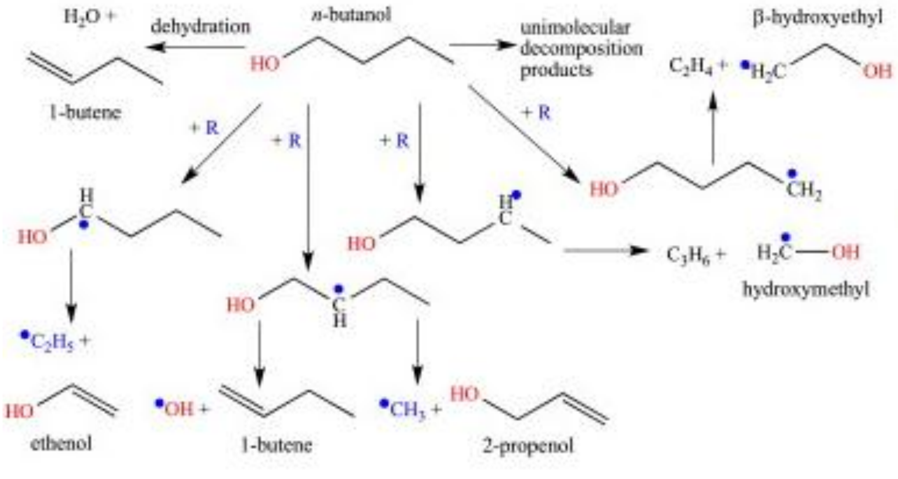


Fig. (c) Reaction path diagrams for high-temperature combustion of *n*-butanol [152].

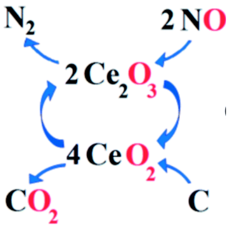


Fig. (d) Cerium oxide role in combustion process : it absorbs oxygen from NO mediates produced due to the high temperature of combustion chamber, then donates this oxygen to the soot (C) particles produced by incomplete combustion of hydrocarbons and converts them to CO_2 molecules [16].

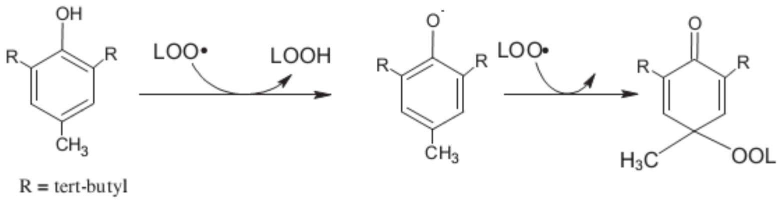


Fig. (e) Antioxidants form stable radical intermediates with moderate resonance delocalization, which hinders the oxidation of fuels [153].

5. Fuel properties, Fatty acid composition and engine combustion.

5.1. Fuel properties and engine combustion.

The fuel properties of biodiesel will influence the engine performance and emissions followed by combustion, since it has distinctive physical and chemical properties than petroleum-based diesel fuel. Biodiesel contains about 10-15% of oxygen by weight [154] and has higher cetane number, high viscosity, and specific gravity that influenced on fuel quantity, injection timing, and spray characteristics. Combustion is also influenced by fuel viscosity [19]. Biodiesel has lower heating value of almost 12% than the diesel fuel that reduced power. But although increase in amount of fuel injected increased the heating value, while the injection duration increased due to change in start of injection which in-turn affects the ignition delay. However, higher cetane number of biodiesel decreases the ignition delay and advances the combustion timing [155]. The lower compressibility of biodiesel and its blends facilitates to quick pressurization of the injected fuel into the pump that can accelerate the pressure wave towards the injectors to advance the injection timing. The higher density of biodiesel is also responsible to advance in the injection timing. Moreover, the higher viscosity increase the injection line pressure thus lower vapor content in a high pressure injection system advances the injection timing which leads to decrease in ignition delay [25, 73].

The choice for correlation of the fuel-bound oxygen in the mixes as the fundamental regular property, which is a parameter emphatically impacting the burning conduct by means of the neighborhood fuel-air proportion in the different "zones" and, thusly, the temperatures and emission, was demonstrated exceptionally effective. Whatever is left of the critical properties of the bio-fuels blends, for example, principally bulk modulus of elasticity, kinematic viscosity, lower heating value and latent heat of evaporation accomplish by need diverse qualities for the same estimation of the fuel-bound oxygen in the mixer. Biofuels increase the kinematic viscosity that decreases the fuel evaporation rate and poor mixing behavior leads to a monotonic increases the soot emissions for the vegetable oil blends. On the other hand, the low kinematic viscosity of DEE may have brought on again a long way from ideal fuel evaporation and blending in the spray, as confirm by the delayed lower pressures and temperatures, which regardless did not have any unfavorable impact on the residue and NOx discharges or the brake thermal efficiency. The lower heating value of the bio-fuels blends has a normal increment of the brake specific fuel consumption due to increases the fuel-bound oxygen, which increases the proportion of lower heating value fuel blends, consequently obliging more fuel to accomplish the same power output. The higher latent heat of evaporation, as in the case of bio-alcohols and DEE, causes lower temperatures during evaporation and thus higher ignition delays and lower gas temperatures after combustion. Lower cetane index of bio-alcohols and DEE blends with diesel fuel showed longer ignition delay and displacement-delay of heat release rate diagram, whereas bio-diesel and the vegetable oil cause lower ignition delays and displacement-advance of the HRR diagram was found. All things considered, it ought not be overlooked that there is an inconspicuous interchange of the dissipated fuel-air and temperature in the different "zones" concerning the heat released by the combusted measure of fuel, as affected by the ignition attributes, latent heat of evaporation, lower heating value (LHV), cetane number and so on, which determine the last burning temperature and oxygen lack or excess [156].

However, introducing additives in diesel, biodiesel and their blends improves many of the major properties, hence improved combustion. Rashedul et al. [96] concluded that addition of metal based additives improve the flash point, decrease the pour point and viscosity of biodiesel enough than that of other additives. Oxygenated additives lessen the density and viscosity and increase the oxygen content of biodiesel than other additives. Higher combustion efficiency owing to higher oxygen content, lower density and viscosity of oxygenated additives [18]. The addition of antioxidant improve flash point, cetane number and oxidation stability but decrease calorific value of biodiesel.

Table 5 showed the changes in values of various physico-chemical properties like density, viscosity, flash point, fire point, cetane index, oxygen content, sulfur content, latent heat of evaporation etc. of different proportion of diesel, biodiesel and their blends fuel with and without additives.

Table 5: Comparison of fuel properties of biodiesel with and without various fuel-additives to blends.

Biodiesel feedstock	% of additives used		Fuel Properties												Refs.
			Density at 20 °C	Viscosity at 40 °C	Flash Point °C	Fire Point °C	Pour point °C	Cetane number	Calorific value (MJ/Kg)	Oxygen content (% mass)	Sulfur content (% mass)	Carbon content (% mass)	Hydrogen content (% mass)	Heat of evaporation (KJ/Kg)	
Diesel ($C_{12}H_{23}$)	-		0.82	3.4	71		1	45	43.2	13.4	<10	87.4	-	-	96
Diesel	Ethanol (C_2H_5H)	5%	0.833 [a]	4.05	58.6	72.4	-	45.53	44.09	1.8	-	84.8	13.4	-	157
Diesel	2, 5-DMF	30%	0.85	2.32 [c]	-	-	-	-	39.73	5.27	-	83.2	11.53	-	158
Ultra low sulfur diesel (ULSD)	-		0.840	2.4	-	-	-	52	42.5	0	<10	86.6	13.4	250-290	159

Waste cooking oil	-		0.871	4.6	-	-	-	51	37.5	10.8	<10	77.1	12.1	300	159
Waste cooking Palm oil	$FeCl_3$ as a Fuel Borne Catalyst (FBC)	5 µ mol	0.8658	4.55	170	190	9	67.4	38.1	-	-	-	-	-	98
		15µ mol	0.8652	4.52	167	186	9	68.1	38.21	-	-	-	-	-	
		25µ mol	0.8646	4.54	167	185	9	68.9	38.32	-	-	-	-	-	
		35µ mol	0.8652	4.56	166	184	9	69.2	38.28	-	-	-	-	-	
		50µ mol	0.8658	4.57	165	183	9	69.6	38.43	-	-	-	-	-	
Jatropha biodiesel & Diesel	Ethanol	20%	0.832^b	2.38	14	-	-3	50	39.93	7.77	-	78.69	13.54	-	160
		30%	0.834^b	2.4	12.5	-	-9	50	38.96	12.21	-	74.49	13.30	-	
		40%	0.820^b	2.018	12	-	-12	41	36.33	14.53	-	72.07	13.41	-	
Waste cooking oil & (ULSD)	Ethanol	5%	0.842	-	-	-	-	-	41	3.3	-	-	-	-	159
		10%	0.839	-	-	-	-	-	40.3	5	-	-	-	-	
		20%	0.833	-	-	-	-	-	38.9	8.2	-	-	-	-	

RME	-	-	0.884	4.79	178	-	-	53.4	-	10.9	-	-	-	-	161
RME - diesel blends	Ethanol	10%	0.844	-	-	-	-	-	40.75	3.9	-	-	-	-	44
		20%	0.84	-	-	-	-	-	39.03	7.79	-	-	-	-	
		30%	0.834	-	-	-	-	-	37.54	11.1	-	-	-	-	
Soybean biodiesel	-		0.865	4.78	-	-	-	49	41.20	-	-	-	-	-	162
Soybean biodiesel & Diesel	Ethanol (4%) Isopropanol (1%) Alumina (100 mg)		0.840	3.37	-	-	-	52	42.59	-	-	-	-	-	
Soybean biodiesel & Diesel	Ethanol	5%	0.840	-	-	-	-	-	40.94	-	-	-	-	266	163
	Diethyl ether $(C_2H_5)_2O$		0.837	-	-	-	-	-	41.41	-	-	-	-	242	
Soybean biodiesel & Diesel	Methanol (CH_4O)	5%	0.842	-	-	-	-	-	39.68	7.13	-	-	-	264	164
		10%	0.843	-	-	-	-	-	38.84	9.08	-	-	-	294	

Jatropha biodiesel	-		0.861	4.27	202.5		2	53.5	39.83	-	-	-	-	-	165
Jatropha biodiesel	Ethanol	5%	0.875[a]	5.29	147.9	167.4	-	48.85	41.24	12.2	-	76	11.8	-	157
Jatropha biodiesel & diesel	Ethanol	5%	0.842[a]	4.31	77.4	92.4	-	46.23	43.49	4	-	82.9	13.1	-	157
Jatropha biodiesel & Diesel	n-butanol $(C_4H_{10}O)$	5%	0.834	3.29	87.5	-	-	-	43.40	-	-	-	-	-	165
		10%	0.831	3.24	79.5	-	-	-	43.15	-	-	-	-	-	
	Diethyl ethar	5%	0.830	3.22	83.5	-	-	-	43.39	-	-	-	-	-	
		10%	0.823	3.15	71.5	-	-	-	43.10	-	-	-	-	-	
Cottonseed oil biodiesel	-		0.871	5.28	-	-	-	51	37.5	10.8	<10 mg/kg	77.1	12.1	300	166
Cottonseed oil biodiesel & diesel	Ethanol	5%	0.867	-	-	-	-	-	37.1	11.9	-	76	12.1	324.5	
		10%	0.862	-	-	-	-	-	36.7	13	-	74.8	12.2	349.2	
		15%	0.852	-	-	-	-	-	36.2	14.1	-	73.7	12.2	374.2	
	Methanol		0.843	3.1345	43	-	-	92.4	-	-	-	-	-	-	167

Neem oil biodiesel	-		0.867	4.5	165	-	-	51	41	11	-	-	-	-	20
Neem oil	Diethyl ethar	5%	0.859	4.2	148	-	-	54	40.6	11.44	-	-	-	-	20
		10%	0.851	3.89	127	-	-	58	40.3	11.88	-	-	-	-	
		15%	0.844	3.57	102	-	-	61	40.0	11.26	-	-	-	-	
Kapok biodiesel	-		0.850	4.1	105	-	-8	52	41.09	-	<0.0005	-	-	-	168
Kapok biodiesel and diesel	1,4-Dioxane ($C_4H_8O_2$)	0.5 %	0.853	3.76	95	-	-10	54	41.01	-	<0.0005	-	-	-	
		1%	0.851	3.65	86	-	-14	56	40.92	-	<0.0005	-	-	-	
Karanja biodiesel	-		0.889	5.71	181	-	-	52.8	39.13	10.8	-	-	-	-	169

a Density at 25 °C

b Density at 15 °C

c viscosity at 20 °C

5.2. Impact of Fatty acid composition on fuel properties and engine combustion.

Pinzi et al. [64] studied the impact of fatty acid composition of biodiesel on combustion behavior in a diesel engine. The author concluded that, the viscosity of vegetable oil raises with the carbon chain length, while the lubricity increases slightly. However, enhancing the degree of unsaturation resulted in lower the viscosity, but there is no remarkable change in lubricity. The calorific value of the fuel also depends on chain length and as the degree of unsaturation rises the calorific value reduces [170]. Mehta et al. [171] also drawn the similar conclusion about the effect of carbon chain length and degree of unsaturation on calorific value of the fuel. The CN of the fuel enhances with carbon chain length and reduces along with the degree of unsaturation [172, 173]. The adiabatic flame temperature also varies with carbon chain length and degree of unsaturation. An increasing adiabatic flame temperature implies an increase in neighboring burning temperature in the ignition chamber and leads to generate large amount of NO_X [47, 174]. **Table 6** represented the fatty acid composition of different vegetable oils.

Hellier et al. [175] investigated the effects fatty acid composition of biodiesel on diesel engine combustion characteristics. It was reported that, the majority of the vegetable oils showed the range of ignition delay between ±0.6 CAD than that showed by base diesel, however a greatly lessened rates of peak heat release rate was found. Whereas, with an increase in C: H ratio (carbon to hydrogen ratio) an increased ignition delay was observed. The HRR_{peak} reduced with reducing the viscosity of vegetable oils. The peak pressures raises as the degree of unsaturation increases, i.e. in case of large unsaturated fatty acid (C18:2). It was found that increasing degree of unsaturation advanced the SOC because of increasing CN and bulk modulus which in turns reduced the ignition delay. As the chain length increases, the initial cylinder pressure increased to a little extent [64].

Table 6: Fatty acid composition (wt. %) of vegetable oils [176].

Fatty acid		Palm	Olive	Peanut	Rapeseed	WCO [177]	Soyabean	Neem oil [178]	Cotton Seed [179]	Jatropha curcas L [178]	Sunflower	Karanja [178]	Grape	H.O. Sunflower	Almond	Corn
Lauric	C12:0	0.1	0	0	0	-	0	-	-	-	0	-	0	0	0	0
Myristic	C14:0	0.7	0	0.1	0	-	0	0.2–0.26	-	1.4	0	-	0.1	0	0	0
Palmitic	C16:0	36.7	11.6	8	4.9	38.8	11.3	14.9	24.3	12.7	6.2	3.7–7.9	6.9	4.6	10.4	6.5
Palmitoleic	C16:1	0.1	1	0	0	-	0.1	0.1	-	0.7	0.1	-	0.1	0.1	0.5	0.6
Stearic	C18:0	6.6	3.1	1.8	1.6	4.1	3.6	20.6	2.2	5.5	3.7	2.4–8.9	4	3.4	2.9	1.4
Oleic	C18:1	46.1	75	53.3	33	47.9	24.9	43.9	16.4	39.1	25.2	44.5–71.3	19	62.8	77.1	65.6
Linoleic	C18:2	8.6	7.8	28.4	20.4	0.2	53	17.9	54.9	41.6	63.1	10.8–18.3	69.1	27.5	7.6	25.2
Linolenic	C18:3	0.3	0.6	0.3	7.9	-	6.1	0.4	0.1	0.2	0.2	-	0.3	0.1	0.8	0.1

Arachidic	C20:0	0.4	0.3	0.9	0	-	0.3	1.6	-	0.2	0.3	4.1	0.3	0.3	0.3	0.1
Gadoleic	C20:1	0.2	0	2.4	9.3	-	0.3	-	-	-	0.2	2.4	0	0	0	0.1
Behenic	C22:0	0.1	0.1	3	0	-	0	-	-	-	0.7	-	0	0.7	0.1	0
Erucic	C22:1	0	0	0	23	-	0.3	-	-	-	0.1	-	0	0	0	0.1
Lignoceric	C24:0	0.1	0.5	1.8	0	-	0.1	-	-	-	0.2	-	0	0.3	0.2	0.1
Nervonic	C24:1	0	0	0	0	-	0	-	-	-	0	-	0	0	0.4	0
Saturated [180]	-	49.3	14	16.9	7.365	-	15.65	-	25.9	-	10.1	-	-	-	-	12.948
Monounsaturated [180]	-	37	72	46.2	63.276	-	22.783	-	17.8	-	45.4	-	-	-	-	27.576
Polyunsaturated [180]	-	9.3	14	32	28.142	-	57.74	-	51.9	-	40.1	-	-	-	-	54.677

6. Effect of additives on combustion behaviour

An et al. [181] investigated the combustion characteristics of waste cooking oil biodiesel with ethanol as additives. Simulations were performed for each blend with or without advanced injection timing of 2°, 3° and 5° crank angle for each load. They reported that increasing percentage of ethanol in the blend with no injection advance, decrease the peak cylinder pressure at light load (10% loads) by 15.3%, 25.1% and 40.0% for 5%, 10% and 20% ethanol respectively. Chen et al. [44] studied the combustion characteristics of rapeseed oil in addition of ethanol as fuel additives and found that both 20% and 30% ethanol in biodiesel lengthen the ignition 1.2 CA and 2.5 CA compared to diesel respectively. The HRR_{max} with ethanol blended fuel was found higher because of prolonged ignition delay and faster rate of evaporation of ethanol in the premixed combustion phase which also leads to increase the peak pressure in the cylinder [182-184]. The ethanol also shortens combustion duration in the order of 69.6° CA, 54° CA, and 48° CA for E0, E10, and E30 respectively. Kannan et al. [157] investigated the impact of ethanol addition to jatropha methyl ester through port injection on combustion characteristics. They found that, the maximum in-cylinder peak pressure for 5% ethanol with neat diesel and diesel-jatropha blends were found at about 67 bar and 66 bar respectively. Ethanol in diesel showed an increase in pressure of almost −5° to −1° (BTDC) with delayed maximum peak pressure of 8° (ATDC) than that of neat diesel and JME. Results showed a slowly rise of pressure from -10° to -2° (BTDC) at premixed stage but at diffusion stage the maximum peak pressure reached at about 15° (ATDC) which expanded up to 50° (ATDC) successively. They also reported in this case that 25% of biofuels addition may show a nearest ignition behavior to that of diesel. Anbarasu et al. [166] studied the effect of ethanol in cottonseed oil biodiesel operated diesel engine on combustion. It was observed that, the heat release rate of BE blends decreases from 99 kJ/m^3 degree to 61 kJ/m^3 degree for diesel and BEB15, respectively. It was found that the maximum cylinder pressure decreases from 71.5 bar to 70 bar for the blends of BEB5 and BEB 15, respectively. This is due to the cooling effect of the higher blends of ethanol. Ethanol percentage in the blend retarding the start of combustion and decrease the combustion duration [159]. Hulwan et al. [160] investigated the combustion behavior of jatropha biodiesel-diesel-ethanol blends of high ethanol contents of 20%, 30% and 40% with advanced injection timing. The observation showed that, adding high proportion ethanol content showed higher cylinder pressure but the peak cylinder pressure occurs later at low loads. Results demonstrated that the ID increment around 40–50% at 1600 RPM with 21° injection timing. Labeckas et al. [161] studied the effect of ethanol and diesel-biodiesel (rapeseed methyl ester) blends on combustion properties at different air fuel. Results demonstrated that, the auto ignition delay of E15B showed 15.4% higher compared to standard diesel at richer air–fuel mixture of 1.5 at engine speed of 2200 rpm. It was also reported that the increment of auto ignition delay was 43.4%, 18.9%, 14.0% for overall lean, 21.1%, 22.6%, 22.4% for moderate and 14.9%, 21.3%, 15.4% for richer air–fuel mixtures at 1400, 1800 and 2200 rpm speeds for E15B blend. The angle of average maximum heat release rate moved from − 0.8° BTDC (DF) to + 2.0° ATDC (E15B) CADs with increased fuel mass from 0.4 wt.% to 6.1 wt.% for lean air–fuel mixture *of* λ=5.5 at low speed of 1400 rpm. The maximum pressure in the cylinder increased by 2.1 bar (3.1%) and 1.2 bar (1.9%) when running E15B blends against values of 68.1 bar and 64.6 bar of neat diesel operating on richer air-fuel mixtures λ=1.5 at 1400 and 2200 rpm speeds. There was also a rise in maximum in-cylinder pressure of 1.65 bar/° and 0.61 bar/° higher than ordinary diesel running on richer air-fuel mixtures λ=1.5 at 1400 and 2200 rpm speeds found respectively. The maximum heat release rate increased in the range of 114.7 to 146.7 kJ/m^3 deg (27.9%) and 93.9 (DF) to 111.3 (E15B) kJ/m^3 deg (18.5%) for richer mixtures of 1.5 at 1400 and 1800 rpm speeds.

Shaafi et al.[162] studied the combustion characteristics using alumina as a nano-additive with two modified fuel blends, B20 (Diesel–soybean biodiesel) and diesel–soybean biodiesel–ethanol blends. Results found that adding alumina with diesel–soybean biodiesel–ethanol blends increased the ignition delay at lower loads but as load increased the ignition delay decreases compared to neat diesel due to increased temperature. A sharp increasing in the cylinder pressure was observed up to 7° ATDC from 7° BTDC in the case of adding alumina to the fuel blend. The Peak Pressure for alumina added fuel blend at all the loads increases to 64.61 bar, whereas for neat diesel and B20 blend, the values are 63.03 bar and 62.41bar respectively. Addition of alumina nanoparticles in the blends give higher heat release as 62 J/CA, whereas it is 51.60 J/CA, 53.12 J/CA for neat diesel and B20 blend respectively. In spite of lower calorific value of alumina added fuel blend, it has higher instantaneous HRR between 6.5° CA and 1° BTDC that enhances the combustion rate and leads to complete combustion. Kannan et al.[98] investigated the influences of metal based additive on combustion characteristics of ferric chloride ($FeCl_3$) as a fuel borne catalyst (FBC) blended to waste cooking palm oil based biodiesel. It was concluded that, a slightly higher maximum cylinder gas pressure (CGP_{max}) of 75.8 bar and 366.1 °CA with FBC added biodiesel and 74.3 bar and 367.2 °CA without FBC added biodiesel was found respectively at optimized operating condition. Advanced injection timing and increased injection pressure attributed to this as they perform earlier SOC and shorter ID of biodiesel. FBC added biodiesel showed a HRR_{max} of 29.2 J/°CA, which is 4.6% higher than that of biodiesel without FBC and 6.2% higher than that of diesel at optimized operating condition. Higher amount of fuel accumulated and injected earlier at the compression stroke due to lower ignition delay is responsible for this[185]. A reduction in ignition delay was found with the increase in injection pressure from 220 to 280 bar due to better atomization and proper mixing of fuel with air[186], but accelerating the injection timing from 23° BTDC to 25.5° BTDC increases the ignition delay. FBC in biodiesel showed lower ignition delay of 10 °CA, which is slightly lower than that of biodiesel without FBC at optimized operating condition. Addition of FBC in biodiesel showed lowest combustion duration of 52.8 °CA at optimized operating condition. Improved combustion rate in premixed and controlled combustion phase's leads to higher gas temperature and reduced CD at higher BMEPs. Selvan et al. [112] investigates the effect of Cerium Oxide Nanoparticles (CON) and Carbon Nanotubes (CNT) as fuel-borne additives in diesterol blends on combustion. The main findings of the experimental analysis showed that, the peak pressure for the E20-CON 50-CNT 50 blends was found as 10.7 MPa at CA of 367°, whereas for the E20 blend it is 7.9 MPa at CA of 377°. Introducing CON provide oxygen and CNT prompts the combustion in the diesterol blend which rises the peak pressure cause increase the cylinder gas pressure. The blending of CON and CNT reduced the ignition delay and leads to earlier start of combustion, that resulted in lower heat release rate and advanced peak heat release rate was found. The HRR_{max} was observed as 67 J/CA at the crank angle of 370° for the E20-CON 25 and CNT 25 blend, whereas it is 85 J/CA at the crank angle of 376° for the E20 blend.

Imtenan et al. [165] studied the combustion behaviour of a diesel engine fuelled with diesel–jatropha biodiesel blend with of 5–10% *n*-butanol and diethyl ether by vol. It was found that, modified blends of J20 with *n*-butanol additives showed maximum in-cylinder pressure of 8–10.5° CA ATDC and increased accordingly with increasing speed. At 3000 rpm, the maximum in cylinder pressure of 86.95 bar and 86.07 bar was observed for J15B5 and J10B10 blends at 9.4° ATDC and 9.9° ATDC respectively. Decreasing pressures with the increasing of the percentage of *n*-butanol attributed to the lower calorific value of the *n*-butanol compared to diesel and biodiesels [187]. Retarded SOC of J15B5 was observed on -3.9°ATDC and for J10B10 it was on -3.5°ATDC, whereas for J15D5 and J10D10 it was found at -3.7°ATDC and -3.1°ATDC on average regarding the 1000, 2000 and 3000 rpm speeds respectively. Lower cetane number leads to SOC later with prolonged ignition delay [188, 189]. HRR at premixed combustion decreases for *n*-butanol additives however, at diffusion phase HRR was improved for additives blend compared to neat J20. They also reported that, maximum in-cylinder pressures for J15D5 and J10D10 were observed 86.92 and 86.10 bar respectively at 10.1° ATDC and 10.4° ATDC at 3000 rpm engine speed. Although DEE has larger cetane index, SOCs of DEE blends delayed because of its higher latent heat of evaporation [190], which also lowered the maximum in-cylinder pressures and the peak pressures for DEE blends, as combustion occurred in a lower temperature environment. It was also revealed that, 10% blends of the additives showed more delayed SOCs than 5% blends. HRR for DEE showed similar characteristics as *n*-butanol. Similar results were concluded by Imtenan et al. [191] for 15% of palm biodiesel with 5% ethanol, *n*-butanol, and diethyl ether additives. Sukjit et al. [192] studied the effect of addition of ethanol and butanol as additives in RME and found that, using EGR retarded the start of combustion as less air was used in the combustion process.

Hou et al. [193] studied the combustion characteristics of a turbocharged compression ignition engine fuelled with dimethyl ether with used frying oil as biodiesel in the blends. It was found the peak heat-release rate of Biodiesel, DME50, DME70 and DME100 is 241.9 J/° CA at 11.5°CA ATDC, 210.7J/° CA at 12.5° CA ATDC, 208.8 J/° CA at 17° CA ATDC and 186.9 J/°CA at 19°CA ATDC, respectively. They reported that, the peak in-cylinder temperature for Biodiesel, DME50 DME70 and DME100 is 2097 K, 1954 K, 1914 K and 1838 K with retarded phase of 26° CA, 30.5° CA, 32.5° CA and 39.5° CA.

Qi et al. [164] evaluated the effects of blending methanol as additive to Soybean biodiesel–diesel blends on combustion characteristics. They observed that, at low engine load (BMEP=0.177 MPa), both the blends showed similar peak cylinder pressure and peak ROPR but higher peak HRR than that of BD50 with low engine speed of 1500 rpm. But as the engine speed increased to 1800 rpm, the peak cylinder pressure and peak ROPR of additives blended fuels are lower but the HRR_{peak} was similar to that of BD50. At high engine load

(BMEP= 0.531 MPa), 5% methanol blends showed a little bit of higher HRR $_{peak}$ than 10% methanol blends and BD50 at engine speed of 1500 rpm whereas during 1800 rpm, it is almost identical for all fuels. HRR $_{peak}$ for BD50 showed earlier than methanol added blends. While Anand et al. [169] reported that 10% of methanol in neat karanja oil (100%) reduced the cylinder pressure, HRR with increased ID. Lower cetane number and higher viscosity is responsible for this. Yasin et al. [167] analyzed the combustion characteristics of diesel engine adding 5% methanol as fuel additives with B20 fuel blends. The main findings of the experimental work showed higher ROPR for B20 M5 than normal diesel. Higher mass of oxygen content of B20 M5 decreases the ignition timing with an earlier CD and higher maximum cylinder pressure. The maximum rate of heat release for B20 M5 was found 363.1 J/deg.CA at 13 CAD with B20 while for mineral diesel it was 358.7 J/deg.CA at 14 CAD. Higher mass of oxygen content in B20 M5 notably improved the diffusion combustion zone and reduced the combustion duration of 7.1% than normal diesel. The start of combustion for B20M5 has found delayed. Higher fuel consumption rate and maximum pressure may attributed to this [194].

Lü et al. [128] evaluated the combustion phenomenon of ethanol (5%, 10%, 15%, and 20% ethanol), DMC (10, 20, and 30%), and DMM (10 and 20%) mixed with the diesel. Results concluded that, the maximum heat release rate (HRR $_{max}$) reduced with the increased percentage of the ethanol and DMC at low engine loads while increased with the increase of the DMC and ethanol in blends at high loads. The ignition delay of all kinds of fuel blend was found delayed at increase proportion of ethanol, DMC, and DMM volumes at lower engine loads with oxygenated fuels in excess of 15% by volume. The combustion duration decreased with the increase of ethanol, DMC, and DMM additives percentage in diesel blend fuels at the same engine load. This is mainly due to increase the ignition delay, which leads to prepare more homogeneous air-fuel mixtures and burned faster at premixed combustion stage.

Vallinayagam et al. [138] investigated the impact of 1.5% IAN (Iso-amyl nitrate) and 1.5% DTBP (di-tertiary butyl peroxide) as ignition promoting additives on diesel engine combustion characteristics fuelled by pine oil-diesel blend. The fuel burning rate in premixed combustion stage reduced to 34.5% and 33.1% from 40.4% of diesel-biodiesel blends for both additives respectively. The ignition delay was reduced by 2°CA for IAN and 3°CA for DTBP compared to diesel-biodiesel blends. This is because IAN ($C_5H_{11}NO_2$) added to the pine oil ($C_{10}H_{18}O + C_{10}H_{16}$) and diesel ($C_{14}H_{28}$) generate free alkoxy radicals whereas DTBP in same blends generates two alkoxy radicals, hence improved the ignition attributes [195].

Chen et al. [158] studied the combustion behavior of a diesel engine fuelled with 30% by vol. 2,5-dimethylfuran, n-butanol and gasoline with diesel. The main findings of the experimental results showed that, D30 has prolonged ignition delay due to lower cetane index, that leads to increase the pressure rise rate with quicker mass burning rate. Heat transfer losses also decrease with retarded CA50 as the $ROPR_{max}$ decreased with this. D30 showed the shortest combustion duration and bulk mean gas temperature than B30, G30 and neat diesel. The $ROPR_{max}$ of D30 is obviously higher than that of diesel fuel, which will exceed 10 bar/° CA when CA 50 is advanced beyond 6° CA ATDC which leads to create higher combustion noise and mechanical load. Increase of EGR rate also lengthen the ignition delay than B30, G30 and neat diesel.

Vedharaj et al. [168] studied the effect of 1, 4-Dioxane with kapok biodiesel on combustion characteristics of diesel engine. It was concluded that, the ignition quality of fuel blends increased with the increase of additives that’s lowered the ignition delay. The amount of fuel combusted in premixed combustion stage was reduced to 24.86% for B25-10 ml from 31.2% for B25. Early start of combustion was found while additives introduced in biodiesel that restricts the mixture accumulation and reduced the peak heat release rate.

Details of the effects of additives on combustion parameters are described in tabular form in **Table 6** below.

Table 6: Effect of additives on combustion.

Engine specification	Operating Condition	Fuel used	% of Additives used	CGP	PP	HRR_{max}	ROPR	ID	CD	SOC	FBR	Ref.
4s,1-cylinder, WC, NA, DI, CR:17.5:1, RS: 1500 rpm, RP: 5.2 Kw IP:220 bar IT: 23° INS: Pump in line nozzle injection system	Load: 25%, 50%, 75% and full load corresponding to BMEP. Speed: 1500 rpm IP:228 bar IT: 23°-25.5° CA BTDC	Waste cooking palm oil biodiesel	$FeCl_3$ as a Fuel Borne Catalyst (FBC) 5-50 μ-mol	CGP ↑ With FBC and ↓ without FBC	PP ↑ with ↑ BMEP, in presence of FBC	HRR_{max} ↑ with adding FBC	-	ID↓ with ↑ IP But as IT ↑ also ID↑.	↑ BMEP ↓ CD, with FBC	Earlier SOC	-	98
In line, 4-cylinder, IDI, NA, TC, CR: 21:1, RS: 4200 rpm, RP: 65 Kw	Torque: 80 N-m constant. Speed: 1000-3000 rpm.	Jatropha biodiesel –diesel blend.	5–10% n-butanol and Diethyl Ether (DEE).	↑ % of n-butanol & Diethyl Ether (DEE)	↑ % n-butanol ↓ PP.	HRR at PC ↓ for both additives, but ↑ at DC	-	↑ % of n-butanol & Diethyl Ether	-	↑ % of n-butanol & Diethyl Ether	-	165

IP: 157 bar IT: ° CA BTDC INS: Distributor type injection pump.	IT: 29° CA BTDC.			in the blend ↓ **C**GP.				(DEE) ↑ ID.		(DEE) ↑ **SOC.**		
4s,1-cylinder, WC, NA, DI, CR:17.5:1, RS: 1500 rpm, RP: 5.2 Kw IP:220 bar IT: 23° INS: Pump in line nozzle injection system	Load: Full load. Speed: 1200-1600 rpm	Jatropha & Palm biodiesel –diesel blend.	*5% by vol. of n*-butanol, diethyl ether and ethanol	-	PP ↓ for both additives	HRR peak at PC ↓**,** but ↑ at DC.	**-**	ID ↑ with ↑ % of additives	**-**	SOC Delayed	**-**	191

In line, 4-cylinder, WC, DI, TC, CR:18.75:1, RS: 3600 rpm, RP: 75 Kw INS: Common rail injection system.	Load: 10%, 50% and 100% of BMEP. Speed: 2400 rpm. IT: 2°, 3° and 5° CA for each load	Waste cooking oil	Ethanol (5%, 10% and 20% (vol. %)	Without advanced IT, Peak cylinder pressure ↑ with ↑ % ethanol at ↓ load, While With advanced IT, ↑ % ethanol ↑ the Peak cylinder pressure.	-	Without advanced IT, HRR ↑ as load ↑ and HRR ↓ as load ↓. Whereas, With advanced IT, HRR ↑ at all load.	-	With advanced IT, ↑ %Ethanol ↑ ID at low load, but ↓ ID at high load. With advanced IT and low load, ID ↑.	-	SOC Delayed as load ↓ without advanced IT.	-	181

In line, 4-cylinder, DI, NA, CR:19:1, RS: 1800 rpm, RP:110 Kw IT: 8° CA BTDC INS: Common rail injection system	Load: BMEP- 0.09, 0.35 and 0.70 MPa. Torque: 30, 60, 120, 200 and 240 N-m.	Ultra Low Sulfur Diesel (ULSD) & Biodiesel (waste cooking oil)	Ethanol (5%, 10%, and 20% by vol.)	**↓ Load** ↓ the peak in-cylinder pressures, **Medium Load** ↑ the peak in-cylinder pressure, **High Load:** no variation	-	**↓ Load** HRR↑. At Medium Load HRR ↑. At High Load HRR $_{peak}$ ↑ than that of biodiesel but ↓ than that of ULSD.	-	ID ↑ with ↑ % ethanol.	CD ↓ as % ethanol ↑.	↑ Ethanol delayed the SOC.	↑ethanol in DBE blends has little influence on the diffusion fuel mass.	159
4s, 6-cylinder, DI, NA, WC,TC, CR:16.8:1,	Load: BMEP- 0.7 MPa. IP: 160 MPa.	Diesel	2, 5 di-methylfuran, n-butanol and	D30 showed ↑ cylinder pressure	-	D30 showed ↑ HRR.	D30 showed ↑ ROPR $_{max}$	ID for D30 ↑ than B30, G30.	CD for D30 ↓ than B30,	-	Faster mass burning rate	158

RS: 2200 rpm, INS: Common rail fuel injection system.	Speed: 1330 rpm.		gasoline (30% by vol.)						G30, diesel.			
4-cylinder, DI, NA, CR:17.5:1, RS: 2800 rpm, RP $_{max}$: 59 Kw	Load: BMEP-0.46 MPa, 0.58 MPa. Speed: 1800 rpm.	Rapeseed oil methyl ester-diesel blends	Ethanol (10%, 20%, and 30% by volume)	-	PP ↑ with % of ethanol fraction ↑.	HRR $_{max}$ ↑ with % of ethanol fraction ↑.	-	ID ↑ with % of ethanol fraction ↑.	Ethanol shortens combustion duration.	-	-	44
3-cylinder, WC, NA, DI, CR: 18:1, RS: 1500 rpm, RP: 27.9 Kw IP: 500 bar	Load: BMEP- 0.1-0.6 MPa. Speed: 1200, 1600 rpm.	Jatropha biodiesel –diesel blend	Ethanol (20%, 30%, 40% by vol.)	Peak cylinder pressure ↓.	-	HRR $_{max}$ ↑ with % of ethanol fraction ↑.	-	ID ↑ with % of ethanol fraction ↑.	-	SOC is delayed	-	160

IT: 13° CA BTDC,	IT: 13°, 18°, 21° CA BTDC											
4s,1-cylinder, WC, NA, HSDI, CR:19.8:1, RS: 1000-4500 rpm. Injection advance (at pump spill): 0–40°CA	Load: BMEP-1.40, 2.57 and 5.37 bar. Speed: 2000 rpm. IT: 29° CA BTDC	Neat cottonseed oil and its neat bio-diesel	20% by vol. of n-butanol or diethyl ether (DEE)	CP↓ for both n-butanol & DEE at high load.	-	HRR ↓ for both n-butanol & DEE**.**	-	ID ↑ for both n-butanol and Diethyl Ether (DEE).	-	SOC occur later for both the n-butanol and DEE blend .	-	190
4s, 1-cylinder, DI, NA, CI, WC, CR: 5:1-20:1, RS: 1500 rpm,	Load: BMEP-0–0.55 MPa which is from 0% to	Diesterol (diesel–biodiesel–ethanol) blends. Castor oil	Cerium Oxide Nanoparticles (CON) and	CGP ↑ for both (CON) & (CNT).	PP ↑ for both (CON) & (CNT).	The HRR ↑ For both (CON) & (CNT).	-	ID ↓ for both (CON) & (CNT).	-	SOC occur earlier.	-	112

RP: 3.7 Kw FIP: 20 MPa IT: 23° CA BTDC	100% load conditions. CR: 19:1 Speed : 1500 rpm	biodiesel was used.	Carbon Nanotubes(CNT)									
4s, 1-cylinder, DI, NA, CI, WC, CR: 16.5:1, RS: 2000 rpm, RP: 11.03 Kw FIP: 180 bar IT: 22° CA BTDC.	Load: BMEP-0.177MPa, 0.531MPa. Speed: 1500, 1800 rpm.	Soybean biodiesel –diesel blends	Methanol was added by volume percent of 5% and 10%.	↑ Load ↑ % of methanol ↑ peak cylinder pressure.	-	↓ Load ↑ HRR, but at medium load HRR is similar to biodiesel, and as load ↑ HRR ↑ for both blends.	↓ Load showed similar ROPR to biodiesel, but at medium load ROPR ↓, and as load ↑ ROPR ↑ for both blends.	ID ↑ at low load, but with ↑ load ID ↓.	-	SOC for both blends is later ↓ Load, but is almost identical at high engine loads.	-	164

4s, 1-cylinder, DI, NA, CI, AC, CR: 17.5:1, RS: 1500 rpm, RP: 4.4 Kw FIP: 180 bar IT: 23.4° CA BTDC	Load: 25%, 50%, 75% and full load corresponding to BMEP. Speed: 1500 rpm.	Diesel-soybean biodiesel ethanol blends.	Alumina as Nano additive.	Addition of Alumina as Nano additive ↑ CGP.	PP ↑ for D80SBD15E4S1+ alumina fuel blends at all the loads Respectively.	Heat release rate ↑ with addition of Alumina as Nano additive	-	ID ↑ at no load, but as load ↑, the ignition delay ↓.	-		-	162
4s,6-cylinder, WC, NA, DI, TC, CR:18.1:1, RS: 2200 rpm, RP: 184 kw	Load: BMEP-1.52 MPa. Speed: 1400 rpm	Used fried oil (UFO)	Dimethyl ether (DME) (50%, 70%, 100%)	↑ DME ↓ peak in-cylinder pressure	-	↑ DME ↓ HRR	↑ DME ↓ ROPR	↑ DME ↓ ID	-	SOC occur earlier.	-	193

4s, 4-cylinder, in-line, WC, NA, DI, TC, CR:17.5:1, RS: rpm, RP: 70 Kw (max) IT: 12° CA BTDC	IT: 12° CA BTDC	Karanji oil (B100)	10% Methanol	Peak cylinder pressure ↓ with addition of Methanol.	-	Peak HRR ↓ with addition of Methanol.	Addition of methanol ↑ the ROPR$_{max}$.	Addition of methanol ↑ ID.	Addition of methanol ↓ CD.	SOC delayed.	-	169
4s, 4-cylinder, in-line, WC, NA, IDI, CR: RS: 1500-3500 rpm.	Load: BMEP- (0.05 MPa). Speed: 2500 rpm.	Biodiesel (B20)	Methanol (5% by volume)	↑ methanol slightly ↑ the in-cylinder pressure	-	HRR ↑ with methanol addition	Methanol addition ↑ ROPR$_{max}$.	ID ↓ with methanol addition	Methanol addition ↓ CD.	Delayed SOC	-	167
1-cylinder, WC, NA, DI, CR: 17.5:1 RS: 1500 rpm RP: 5.2 kw	Load: five engine load. Speed: 1500 Rpm.	Cottonseed oil biodiesel	Ethanol (5%, 10%, and 15% by volume).	↑ Ethanol ↑ the in cylinder pressure	-	↑ Ethanol ↑ HRR.	-	ID ↑ with ↑ethanol	↑ Ethanol ↓ CD	SOC was retarded.	-	166

IT: 21° CA BTDC	Torque $_{max}$: 170 N-m.											
4s, 4-cylinder, WC, NA, DI, HS, CR: 18.5:1 RS: 3400 rpm RP: 58.5 kw INS: Pump line nozzle system	Speed: 3400 rpm.	Diesel	Ethanol, Dimethyl carbonate (DMC) and Di-methoxy methane (DMM)	-	-	HRR $_{max}$ ↓ with ↑ % of ethanol and DMC at low load. HRR $_{max}$ ↑ with ↑ % of DMC and ethanol at high load.	-	ID ↑ with ↑ % of DMC and ethanol.	CD ↓ with ↑ % of DMC and ethanol.	-	-	128
4s, 1-cylinder, WC, NA, DI, CR: 17.5:1 RS: 1500 rpm RP: 5.2 kw IP: 220 bar	Load: 20% to 100% in increments of 20% corresponding to BMEP.	Pine oil-diesel blend.	IAN–1.5%, DTBP–1.5%	-	-	HRR $_{peak}$ ↓ for adding both IAN and DTBP.	-	ID ↓ for adding both IAN and DTBP.	-	Both IAN and DTBP have prompted early SOC	FBR ↓ in PC for both IAN and	138

IT: 23°CA BTDC INS:Mechanical pump-nozzle injection.	Speed: 1500 rpm.										DTBP	
4s, 1-cylinder, WC, NA, DI, HS, CR: 15.6:1 RS: 1500 rpm RP: 5.9 kw IT: 26°CA BTDC	Speed: 1200 rpm. IT: 12.6° CA BTDC Torque: 0, 4, 8, 12, 16, 20 and 24 N-m.	Jatropha-diesel blends	Ethanol (5% by vol.)	Higher % of JME with 5% ethanol, ↓ the peak pressure.	-	HRR_{peak} ↑ with adding ethanol	-	Higher % of JME with 5% ethanol, ↑ ID.	↑ % JME with 5% ethanol, ↑ CD.	↓ % JME with 5% ethanol, advanced the SOC.	-	157
1-cylinder, WC, NA, DI, CR: 15.5:1 RS: 2500 rpm RP_{max}: 8.6 kw INS: Mechanical	Load: IMEP-3 bar EGR: 0%, 10 and 20%. Speed: 1500 rpm	Rapeseed oil methyl ester (15%) and Ultra low sulfur	Ethanol (10%) and butanol (16%).	-	-	With addition of both ethanol and butanol ↑ HRR_{peak}.	-	-	ID ↑ with addition of both ethanol and butanol.	SOC delayed with addition of both ethanol and butanol.	-	192

injection system.		diesel (ULSD).										
4s,1-cylinder, NA, DI, CR: 16.5:1 RS: 1500 rpm RP: 3.5 kw INS: three hole nozzle injection system.	Speed: 1500 rpm	Neem oil methyl ester	Diethyl ether (5%, 10% and 15% by vol.)	↑ % DEE ↓ cylinder pressure	-	↑ % DEE ↓ HRR $_{max}$	-	↑ % DEE ↓ ID	-	-	-	20
4s, In line, 4-cylinder, DI, NA, WC, CR:16:1, RS: 2200 rpm, RP: 60 Kw IT: 25° CA BTDC.	Speed: 1400, 1800, 2200 rpm. AFR: Air–fuel ratios of $\lambda = 5.5$, 3.0 and 1.5.	Ethanol (5%, 10%, and 15% by volume) & diesel.	Rapeseed oil methyl ester (5%)	In cylinder pressure ↑ with RME & Ethanol.	-	HRR $_{max}$ ↑ with RME & Ethanol.	-	ID ↑ with RME & Ethanol.	-	SOC occur earlier.	-	161

4s,1-cylinder, NA, DI, CI, CR: 17.5:1 RS: 1500 rpm RP: 5.2 kw IP: 220 bar IT: 23° CA BTDC INS:Mechanical pump-nozzle injection	Load: Varied in steps of 20% from 20% to 100%, corresponding to torque. Speed: 1500 rpm	Kapok methyl ester with diesel. B25(25% KME and 75% diesel)	1, 4-Dioxane (0.5%, 1.0%)	-	-	↑ % 1, 4-Dioxane ↓ HRR_{peak}	-	↑ % 1, 4-Dioxane ID ↓	-	SOC occur earlier.	FBR ↓ in PC and ↑ in DC.	168

4s=Four stroke, NA=Natural Aspirated, WC=Water Cooled, AC=Air Cooled, DI=Direct Injection, IDI=Indirect Injection, CI=Compression Ignition, CR=Compression Ratio, RS=Rated Speed, RP=Rated Power, IP=Injection Pressure, FIP=Fuel Injection Pressure, IT=Injection Timing, INS=Injection System, HS=High Speed, AFR=Air Fuel Ratio, IAN=Iso-amyl Nitrate, DTBP=Di-tertiary butyl Peroxide, FBC =Fuel Bourne Catalyst, DME=Dimethyl ether, DEE=Diethyl ether, DMC=Dimethyl Carbonate, DMM=Dimethoxy methane, DMF=Dimethyl-furan, CON=Cerium Oxide Nanoparticles, CNT=Carbon Nanotubes.

7. Summary

- Metal based additives like $FeCl_3$, CON, CNT, Alumina nanoparticles showed an increased in HRR, CGP & PP with earlier SOC and decreased ID. Presence of oxygen content, better fuel mixing, increased oxidation of hydrocarbons and improved combustion rate in both combustion zone are mainly attributed to this. Introducing metal based additives provide more oxygen to prompts the combustion.
- Increase proportion of n-butanol, DEE in biodiesel decreases the CGP & PP whereas HRR decreased at premixed combustion (PC) and increased in diffusion combustion (DC) increased the ID with delayed SOC. Higher latent heat of evaporation, lower dynamic injection timing leads to delayed SOC, although DEE has increase cetane number. More perfect fuel atomization and vaporization were found. But there was an exception in case of DEE with Neem biodiesel was found decreased ID with increasing proportion of DEE in the blends. This is because of less air-fuel mixture formation during ID period, higher cetane number and lower cylinder pressure.
- Increase in ethanol percentage in the blends increases the cylinder pressure but decreases with high ethanol content in the blends due to cooling effect of higher blends. The PP, HRR_{max} and ID also increases with increases ethanol in the blends. Lower calorific value, lower cetane number, higher latent heat of vaporization, faster rate of evaporation of ethanol attributed this matters. Increase the residual gas temperature and cylinder wall temperature with increasing engine load, leads to elevated charge temperature before injection and shortening the ignition delays. The higher latent heat of vaporization of ethanol leads lower in-cylinder temperature and consequently an increment in ignition delay was found. Higher oxygen content of the blends with ethanol indicates improved diffusion combustion with high heat release rate that leads to lower the combustion duration. Addition of high ethanol content lower the viscosity

and gives better air-fuel mixture that helps to burned higher amount of fuel in the premixed combustion stage.

- Addition of methanol proportion in the blends increased the cylinder pressure, HRR, ROPR with decreased ID, CD and SOC delayed. While 10% of methanol in neat karanja oil (100%) reduced the cylinder pressure, HRR with increased ID. Lower cetane number and higher viscosity is responsible for this.
- DME and 1, 4- dioxane in biodiesel decreased the cylinder pressure, HRR, ROPR, ID with earlier SOC. DME showed a slight modulus of elasticity with high compressibility. Whereas 1, 4- dioxane showed decreased FBR in PC and increased FBR in DC, increased oxygen content, improved fuel properties prompts the diffusion combustion and increased the heat release.
- Ignition promoter IAN & DTBP in biodiesel decreased HRR peak, ID with earlier SOC and reduced FBR in PC with bringing an efficient combustion. Both IAN and DTBP in diesel-biodiesel blends improved the density of biodiesel than diesel accelerate the diffusion combustion and upgraded fuel characteristics of biodiesel, bringing about an efficient combustion. The combustion phasing using ignition promoter are further to be investigated.
- 2,5- DMF, Ethanol, DMC & DMM additives also used in diesel fuel and found an increases in the cylinder pressure, HRR, ROPR, ID, FBR with decreased CD. Increase the ignition delay leads to prepare more homogeneous air-fuel mixtures and burned faster at premixed combustion stage.

8. Conclusion

The principle objectives of this review was to find out the optimum condition of combustion from previous work that's performed with various proportion of additives with diesel, biodiesel and their blends and correlates them to reach an optimum operating level keeping other conditions reasonable. Addition of additives in diesel, biodiesel and their blends has a great effects on fuel properties like viscosity, flash point, fire point, pour point, calorific value etc. which in-turns influences on the combustion parameters. Most of the oxygenated additives showed improved combustion phases, decrease in in-cylinder temperature due to high latent heat of evaporation. Multifunctional fuel additives in fuel blends decreases the ignition delay, improved premixed combustion duration and combustion stability. Ignition promoter additives improved the ignition attributes and the conditions should be further be investigated. Various types of antioxidants and cold flow improver additives will also need to be studied to ensure the better combustion attributes. Combustion parameters like ignition delay, heat release rate, rate of fuel burn, combustion phases will critically need to be analyzed with several potential additives like five carbon structure oxygenated additives, metal based additives, cetane improver additives etc. Fuel properties of various proportion of additives used in diesel and biodiesel to produce blends must be investigated intensively to make up the existing problems after using additives.

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Nomenclature

ATDC	After Top Dead Centre
BTDC	Before Top Dead Centre
BSFC	Break Specific Fuel Consumption
BTE	Break Thermal Efficiency
BSEC	Break Specific Energy Consumption
BMEP	Break Mean Effective Pressure
CA	Crank Angle
CAD	Crank Angle Degree
CD	Combustion Duration
CGP	Cylinder Gas Pressure
CN	Cetane Number
CO	Carbon Monoxide
DC	Diffusion Combustion
FBR	Fuel Burning Rate
HC	Hydro Carbon
HRR	Heat Release Rate
HRR_{max}	Maximum Heat Release Rate
HRR_{peak}	Peak Heat Release Rate
ID	Ignition Delay

NOx	Oxides of Nitrogen
PM	Particulate Matter
PC	Premixed Combustion
PP	Peak Pressure
ROPR	Rate of Pressure Rise
SOC	Start of Combustion
SOI	Start of Injection
TDC	Top Dead Center
THC	Total Hydrocarbon
WCO	Waste cooking oil