Chapter 7
Recent Development for Use of Alcohol-Based Renewable Fuels in Compression Ignition Engine

Nikhil Sharma

7.1 Introduction

Energy crisis and growing environmental concerns have given importance to renewable fuels. Beyond the problems of energy crises, renewable fuel provides advantage to overcome harmful emissions with fossil fuels. Petroleum reserves are limited and may vanish in future if they are consumed continuously. Due to limited fossil fuel availability, dependence of the global transportation sector (94%) is estimated to decrease to 89% by 2030 (Petroleum 2012). Securities of energy supply and climate change are the principal factors encouraging use of alternative fuels in transport sector. Due to limited resources and increasing demand for energy, numerous alternative transport fuels are being considered. Alternative fuel candidates, which are expected to displace petroleum fuels in the transport sector, have to perform nearly similar to conventional fuels. Cost competitiveness, infrastructure development, toxicity, emissions, and contribution to greenhouse gas (GHG) emissions could be fair criteria to judge those alternative fuel candidates. Fuels other than diesel and gasoline are considered as alternative fuels. These comprise electricity, liquefied petroleum gas (LPG), unconventional fossil oils, natural gas, hydrogen, Fischer–Tropsch liquids, ethers, alcohols, biodiesels, gasohol, etc. Market developments and government policies for implementation of appropriate alternative fuels will play a significant role in their implementation and acceptance. The aim in near future should be to diversify energy resources portfolio in order to meet future transport sector demands. Dr Rudolf Diesel demonstrated that a fuel–air mixture in engine combustion chamber can be ignited by compression ignition. The engine was successfully operated in

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compression ignition mode in 1897 (Debnath et al. 2013). Since 1897, compression ignition engine is preferred to be used in applications of power generation, transportation, agriculture, offshore drilling, military, marine, telecommunication, and generator. With growing population, energy security is becoming an important concern for government worldwide. Due to this reason, scientists are exploring for renewable environmentally friendly fuels which can be blended with conventional gasoline or diesel fuel to reduce carbon footprint.

In general, alcohols are usually considered as a spark-ignition engine fuel. Few decades back, in 1970 and 1980, it was emphasized and shown that it is likely to use alcohols as diesel engine fuel with addition of fuel additive and ignition aids. Sometimes, tertiary butyl alcohol (TBA) is considered as an additive, extender, and co-solvent when mixing methanol and ethanol. Dimethyl ether (DME) is considered as a clean fuel because of no carbon bound present in DME structure and therefore produces less emission and is excellent fuel to be used with diesel. However, DME has limitation in terms of production, handling of fuel, and availability. Therefore, alcohols are considered as a fuel because it has combustion properties similar to diesel and gasoline. Alcohols have relatively lower energy density; they produce formaldehyde and acetaldehyde combustion by-products.

Fuel properties: Alcohols consist of hydroxyl groups fixed to a carbon atom. Molecular structures of primary alcohols vis-à-vis gasoline are shown in Table 7.1.

Alcohols are oxygenated fuel and when blended with diesel results in complete combustion due to inherent oxygen content of fuel. Figure 7.1 shows various oxygenates as a replacement for conventional fuel. Figure 7.2 shows diesel engine emission and its cause. Figure 7.3 shows possible emission reduction techniques once the emission is formed in tail pipe. Once they are formed in the tail pipe, diesohol results in efficient combustion efficiency and reduces the engine-out gaseous and particulate emissions. The most popular oxygenated fuels are methanol, ethanol, and butanol, and the physical and chemical properties allow them to be used in compression ignition engine. Pentanols are less used as a commercial fuel because of high cost of production. There are two popular methodologies of alcohol diesel

Table 7.1 Molecular structures of primary alcohols vis-à-vis gasoline

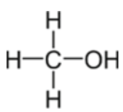
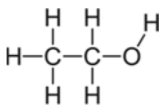
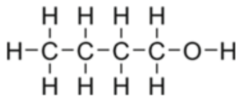
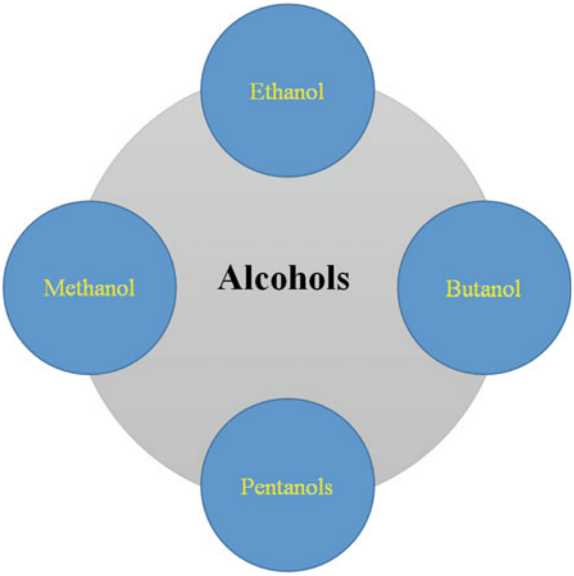
Test fuel	Molecular structure
Methanol	
Ethanol	
Butanol	

Fig. 7.1 Flowchart of oxygenates as an additive for automotive application



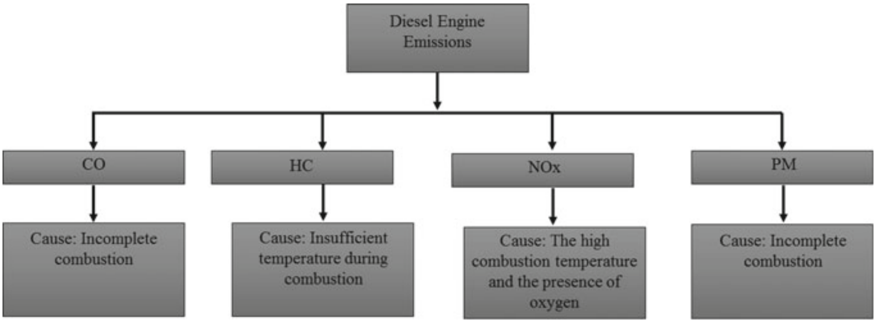
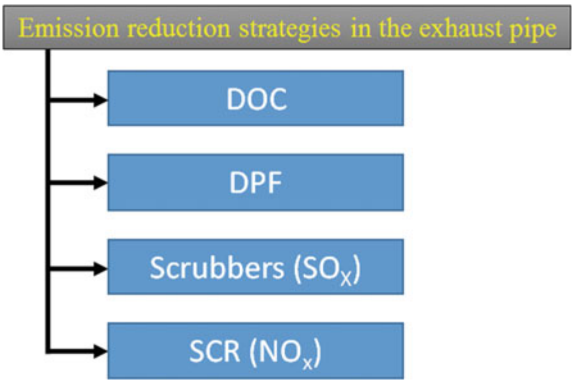


Fig. 7.2 Diesel engine emission and cause

Fig. 7.3 Diesel engine after-treatment emission reduction strategies



combustion in automotive sector among many other available alternatives. The first method is the use of diesel–alcohol-blended externally for direct injection combustion. In the second method, mineral diesel is injected in cylinder as high-reactivity fuel (HRF), and alcohol is injected in port as low-reactivity fuel (LRF). This is called reactivity-controlled compression ignition (RCCI) combustion. Blending relatively higher percentage of alcohol with diesel sometimes does not offer an ignition in an un-modified engine with compression and therefore is a major issue. Therefore, a high cetane number and low auto-ignition temperature are possible compression ignition engine fuel. This is possible in dual-fuel engine. Liao et al. (2007) and Zhang et al. (2008) investigated the laminar flame speed for mixtures of methanol and air at relatively elevated temperatures. Authors stated that laminar burning velocity was related to initial temperature and equivalence ratio. A notably large size of research has been published on using alcohol with diesel in a compression ignition engine. The present chapter reviews these to provide insightful views. This chapter addresses several critical areas and future research scope.

7.2 Economic Aspect

It is important to discuss economic aspect of fuel because people's decision to buy biofuel is based on price. People will buy cars with biofuels if price of biofuel is attractive and competitive compared to other biofuels and conventional fuels such as diesel and gasoline. Some of the biofuels are being mass produced, and the technology has been developed over the past few decades. Nevertheless, some of the biofuels are still in laboratory scale because of the higher price compared to conventional fuels. Cost of biofuel varies from country to country because of variation in feedstock prices. Government in different countries also encourages the industries to produce biofuels and provide subsidy from year to year. This subsidy stimulates industries to establish themself in due course of time and makes the price competitive in marketplace and develop infrastructure. Another aspect is taxes implemented by government on fuels which makes a lot of difference in end user price.

Figure 7.4 shows the projected price of ethanol and butanol. Different biofuels have different costs. For example, butanol is extensively investigated by researchers, but the production of butanol is still limited to laboratory scale. The innovative biotechnological production of biofuels from non-edible feedstocks results in decrease of prices, and limited petroleum reserves may encourage people to use biofuels.

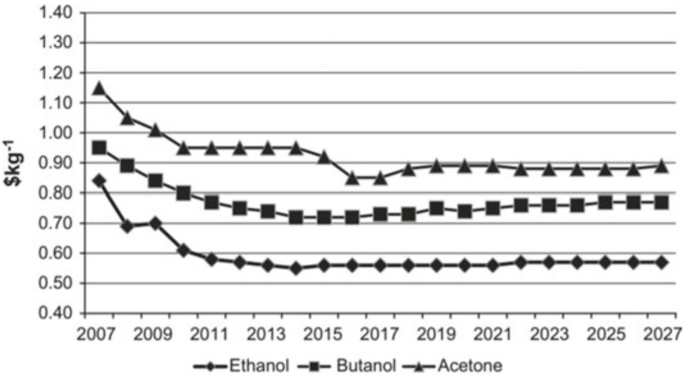
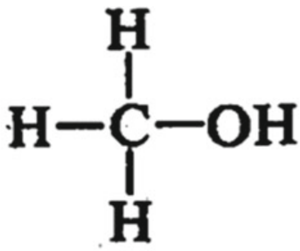


Fig. 7.4 Projected prices of ethanol, butanol, and acetone (Pfromm et al. 2010)

7.3 Properties of Alcohol Relevant to Engines and Its Material Compatibility

As discussed earlier, alcohols are fuels of the family of oxygenate, and generally speaking, all alcohols can combust. Figure 7.5 shows structure of monohydric alcohols. In organic compounds, one hydroxyl (−OH) group is replaced for one hydrogen atom. Thus, methane becomes methyl alcohol, CH_30H; ethane becomes ethyl alcohol, C_2H0H (ethanol). As of today, only ethanol and methanol are economically suitable as fuels for internal combustion engines. Biobutanol is also gaining an interest, and process is being found out by scientists to make it an economical fuel for internal combustion engine. Alcohols have relatively higher flame speeds and slightly longer flammability limits compared to its counterpart hydrocarbons. A limitation of oxygenated fuel is that it reduces the heating value of the fuel when compared to hydrocarbon fuels. Methanol has relatively higher oxygen present in it compared to butanol and can be commercially produced. As an internal combustion engine fuel, methanol has physical and chemical fuel properties similar to ethanol. Also,

Fig. 7.5 Structure of monohydric alcohols



$$C_nH_{2n+1}OH$$

Table 7.2 Properties of alcohol fuels (Awad et al. 2017; Campos-Fernández et al. 2012; Chen et al. 2010; Chen et al. 2013; Chen et al. 2014; Giakoumis et al. 2013; Kumar and Saravanan 2016; Kumar et al. 2013; Shahir et al. 2014; Zhang et al. 2006)

Property	Diesel	Gasoline	Methanol	Ethanol	Propanol	Butanol
Boiling point (°C)	180–370	27–225	65	78	97.1	117–118
RON	20–30	80–99	136	129	112	96
CN	40–55	0–10	3.8	5–8	12	25
Low heating value (MJ/kg)	42.5	42.7	20.1	26.9	30.6	33.1
Heat of vaporization (kJ/kg)	243	349	1162.64	918.42	727.88	585.40
Flashpoint (°C)	65–88	−13 to 45	12	13	22	35
Auto ignition temperature (°C) (Kumar and Saravanan 2016)	~300	257	463	420	350	345
Stoichiometric air/fuel ratio (Lapuerta et al. 2010)	14.3	14.7	6.47	9.01	10.35	11.19

methanol has relatively lower risk of flammability compared to gasoline. Ethanol is a colorless and renewable fuel in nature because it is made from biomass by distillation fermentation. Ethanol can be produced from many different feedstokes but tend to have same chemical formula irrespective to its production methodology. Octane number of ethanol is relatively higher and therefore gives a premium blending properties. Propanol is relatively expensive and difficult to produce and therefore is a less researched fuel among scientists. The energy content of propanol is nearly similar to ethanol, and therefore, ethanol is preferred because of less cost of production. Butanol is another promising renewable internal combustion fuel. Butanol has relatively higher heat of evaporation than its counterpart ethanol and results in reduced combustion temperature and therefore results in reduced formation of NO_x (Cucchi and Samuel 2015). Table 7.2 shows properties of alcohols adapted from the literature for different investigations.

In the next section, alcohol-based fuel compatibility issues in IC engine will be discussed. Thereafter, effect of specific alcohol on material compatibility issues in IC engine will be discussed. Figure 7.6 shows alcohol-based material compatibility issues.

Friction, wear, corrosion, and lubricant issues are related to fuel physical and chemical properties. Viscosity, density, and oxidation stability are the fuel properties among many others which cause such issues. High value of viscosity results in poor atomization. Biodiesel has three OH groups attached on the glycerol molecules that are esterified with the same fatty acid. Therefore, it is called simple triglyceride. Figure 7.7 shows a simple triglyceride molecule structure.

- **Wear and friction**: Wear is common in internal combustion engine because of the several rotating parts such as crankshaft, piston, and connecting rod and valves. In addition to rotating parts, wear also depends on engine load, engine rpm, temperature of the engine, type of lubricant used, and additives present in lubricant. This

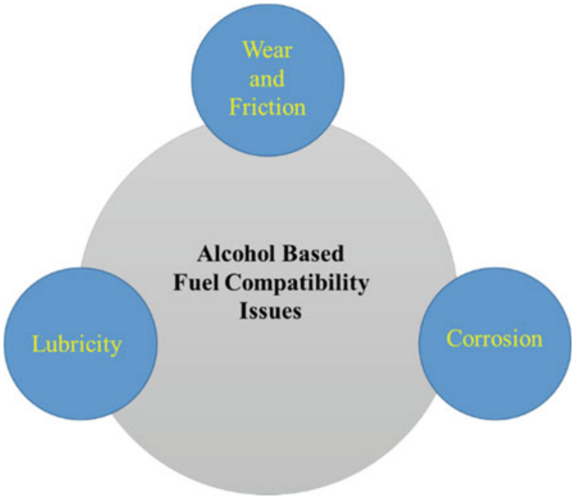


Fig. 7.6 Compatibility of alcohol fuels for IC engine

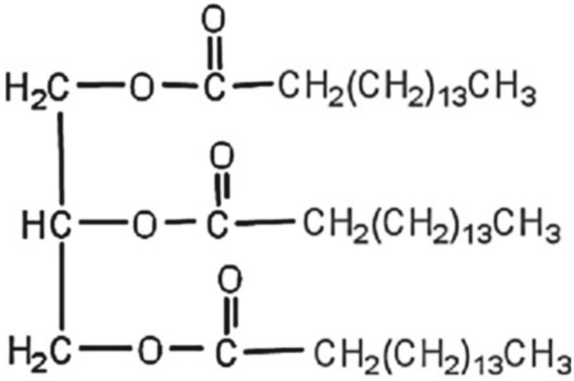


Fig. 7.7 Simple triglyceride molecule

wear due to rotating parts is dependent on lubricating property of fuel as well and reduces the life engine components.

- **Corrosion**: Engine parts/components can become corrosive with time if fueled with oxygenated fuel or if conventional fuel is blended with oxygenated fuel. This is because alcohols may absorb water and in turn accelerates the rate of corrosion. Corrosive rate of biofuels is also dependent on method of preparation and from bacterial contamination during the fermentation process. Corrosion is undesirable because it damages the metal surface of engine, in particular fuel injection system. It is believed that anti-corrosion components added in fuel may reduce the corrosion rate but with a plenty of new and more harmful emissions products. Each alcohol fuel (ethanol, methanol, butanol, or propanol) has different responses to corrosion because of its inherent properties.

- **Lubricity**: Lubricity of fuel is vital property because it reduces wear and friction of fuel injection component (injection pumps and fuel injectors) and other engine rotating component. Lurbicating oil changes its property with time because it gets contaminated from soot, metals, water, and other hydrocarbons produced with combustion of fuel.

Apart from the above three alcohol-based fuel compatibility issues in IC engine, different alcohols also have specific effect on material of IC engine. In the next section, material compatibility issues by the use of specific alcohol fuel will be discussed.

- **Methanol**: Among alcohols, methanol is more violent in terms of materials compatibility, and it can affect both metals and elastomers. Magnesium has poor reaction when it comes in contact with metals. Therefore, the use of magnesium is usually probated. Moreover, aluminum is also corroded when it comes in contact with methanol, but the reactions in comparison with magnesium are slow. Once corrosion of methanol occurs with aluminum, aluminum hydroxide and gelatinous precipitates are produced. These can plug filters and generally result in wear of fuel injectors and results in increase of engine wear. Normal carbon steel and stainless steel do not result in aggressive corrosion and are relatively less affected by methanol in dry form. The reason is that it does not have large amount of dissolved water and therefore has less foreign impurities. On the other hand, metals such as brass, bronze, and die cast zinc can corrode quickly when methanol is blended with gasoline. Fuel hoses are more prone to damage (crack upon hardening), and the life span of hoses is also less if they come in contact with methanol. Therefore, hoses made of cross-linked polyethylene are compatible methanol fuel material
- **Ethanol**: Compared to methanol, ethanol is relatively less violent in terms of materials compatibility toward both metals and elastomers. A corrosion potential is water present in methanol which results from art effect of production. The amount of water is more compared to methanol and therefore more prone to corrosion. Carbon steel, stainless steel, and bronze are the metals which can be considered when using ethanol as a fuel. Metals such as magnesium, zinc, cast iron, brass, and copper are not recommended. Aluminum is coated with cadmium, hard chromium, nickel, or anodized aluminum to make them compatible. Ethanol is less violent to elastomers compared to methanol. Buna-N, Viton, Teflon fluorosilicones, neoprene, and natural rubber are some of the compatible elastomers.

7.4 Cold Start

A cold start is a condition attained in vehicle when a vehicle is at low temperature, relative to its normal operating temperature due to cold weather condition. Cold-start emissions are unavoidable while driving a vehicle. In colder countries, low ambient temperature results in increase in oil viscosity and also reduces the in-cylinder gas temperature up to few initial seconds of start of engine (An et al. 2016; Armas et al. 2012). This low in-cylinder gas temperature makes the fuel droplets difficult to atomize. Since droplets are less atomized, they evaporate relatively less, and they mix lesser with the air. An ambient temperature of 20 degree C was considered to be cold-start condition by Armas et al. (2012) investigate the effect of different alcohol engine characteristics. In addition, cetane number of the blends during cold start was adjusted so that blended fuel acts as an ignition improver in the existing un-modified diesel engine. Moreover, alcohol may result in increase in emission at cold-start conditions. In a study (Zhang et al. 2016), hot- and cold-start particulate emissions were investigated by author. They found that cold start (120 s of idling) resulted in increase in nucleation mode particles significantly compared to hot-start emission. Another investigation (Iodice and Senatore 2014) found that higher blends of ethanol with gasoline resulted in relatively higher engine-out emission in cold-start condition.

7.5 Combustion Characteristics

Ning et al. investigated diesel fuel and its blend with methanol, ethanol, and butanol for combustion characteristics. Figure 7.8 shows combustion characteristics of diesel with alcohol.

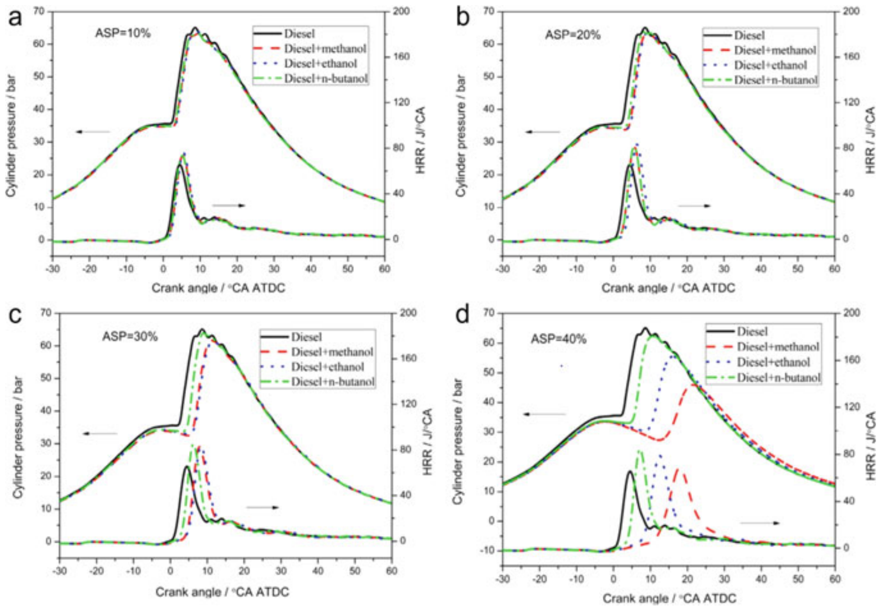


Fig. 7.8 Effects of alcohol additions on cylinder pressure (Ning et al. 2020)

In this experimental investigation, a relative study of the consequences of addition of alcohols such as methanol, ethanol, and n-butanol on the combustion characteristics was achieved. P_{max} in case of alcohol was found to be lower in comparison with diesel. As seen in the figure, diesel and the n-butanol/diesel mixture resulted in relatively higher P_{max} value. Similarly, HRR_{max} was relatively higher for alcohol fuels.

Yusri et al. (2019) investigated the effect of different fuel properties on combustion characteristics. In this experimental investigation, n-butanol was blended with diesel in volumes of 5, 10, and 15% in diesel fuel, and engine was operated at an engine speed of 2500 rpm with load of 15 Nm. Figure 7.9 shows distribution of the maximum engine in-cylinder pressure (P_{max}) at 15 Nm load for an average of 1000 consecutive engine cycles. It was observed that the P_{max} decreases with more butanol in the diesel-blended fuels. Authors plotted the graph with the help of wavelet transform analysis. By this innovative technique, the frequency of cyclic variation can be investigated with the help of time series and frequency. As seen in the above graph, the engine cycle-to-cycle distribution has significant effects on P_{max}.

Similar to the above authors, Jamrozik et al. (2018) investigated the effect of addition of alcohol fuel to diesel fuel in a compression ignition engine. Their experimental investigation explores the results of blending alcohol to diesel fuel on the basis of same energy content of fuel injected per cycle. Figure 7.10a represents the blending of diesel fuel with ethanol, Fig. 7.10b represents blending of diesel fuel with ethanol, Fig. 7.10c represents the blending of diesel fuel with 2-propanol, and the last Fig. 7.10d represents blending of diesel fuel with 1-butanol.

In this paper, authors made a comparison based on the same energy content of the diesel fuel replaced by different types of alcohol fuels. As seen in figure above, 15, 30, 45, 55, and 70% of total energy supplied with diesel fuel to the combustion chamber was replaced by alcohol. The results were compared with reference fuel diesel.

Consider the last case in Fig. 7.10 wherein 70% energy was provided by alcohol fuel. The aim was to achieve 1100 J/cycle of energy by different test fuels. It can be seen that in order to reach the goal of 1100 J/cycle, nearly 8 mg of diesel fuel and 39 mg of methanol, 30 mg of ethanol, 27 mg of 2-propanol, or 23 mg of 1-butanol were needed to reach required energy content of fuel. It can be inferred from the experiments that increasing percentage of alcohols in diesel fuel increase oxygen content in the fuel–air mixture. This in turn affects stoichiometric fuel–air ratio and thus changes the individual phases of the combustion process during a cycle.

Many researchers have blended kerosene with diesel to investigate emission characteristics. In a similar experiment by Agarwal et al. (2019), authors experimentally investigated diesel fuel blended with kerosene and gasoline. Authors implemented advanced endoscopy visualization technique to find out soot distribution in the images of combustion of compression ignition engine. Authors made a comparative analysis K20 (20% kerosene (v/v) blended with mineral diesel) and G20 (20% gasoline (v/v) blended with mineral diesel) with diesel.

Figure 7.11 shows combustion images acquired from endoscope and its spatial soot distribution with respect to in-cylinder pressure and HRR curve. As seen in the

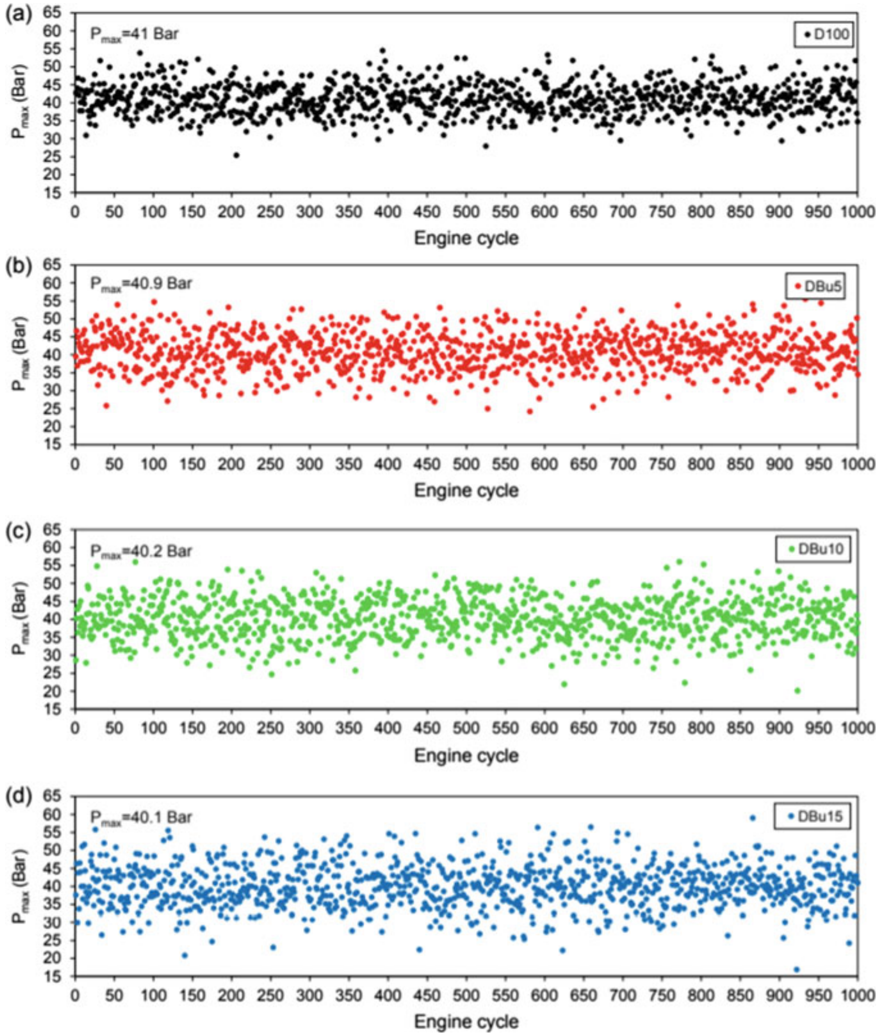


Fig. 7.9 Pmax for different tested fuels (Yusri et al. 2019)

images, authors have attempted to correlate the results from combustion images to in-cylinder data. The pressure crank angle curve showed superior combustion characteristics compared to diesel and K20. In the results from pressure transducer data, G20 exhibited better combustion characteristics when compared with diesel and K20. As expected, Pmax, Rmax, and combustion duration were more for G20 test fuel. As far as endoscopy images are concerned, G20 and K20 exhibited relatively lowest R intensity values for G20 test fuel. This designated lower soot concentration for G20 test fuel. Overall, authors made an experimental investigation using endoscopy

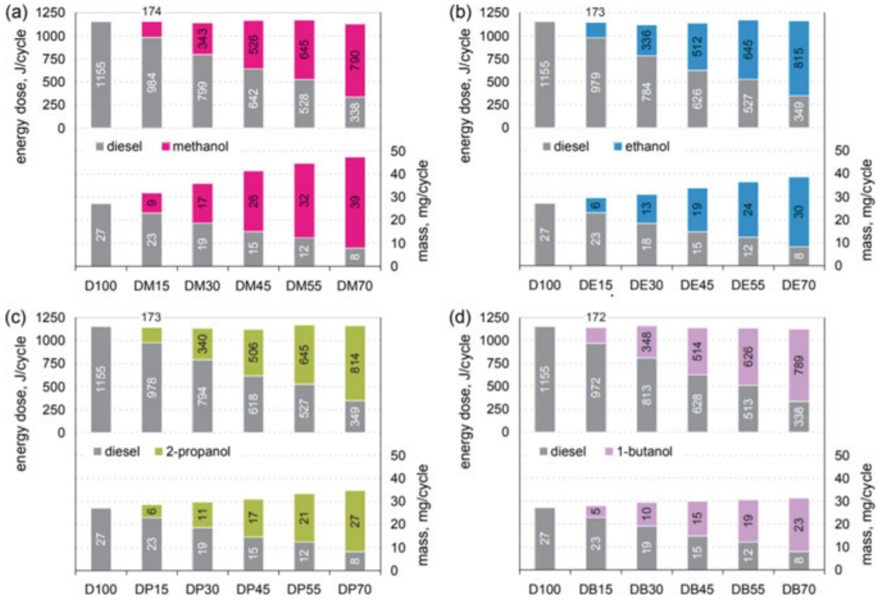
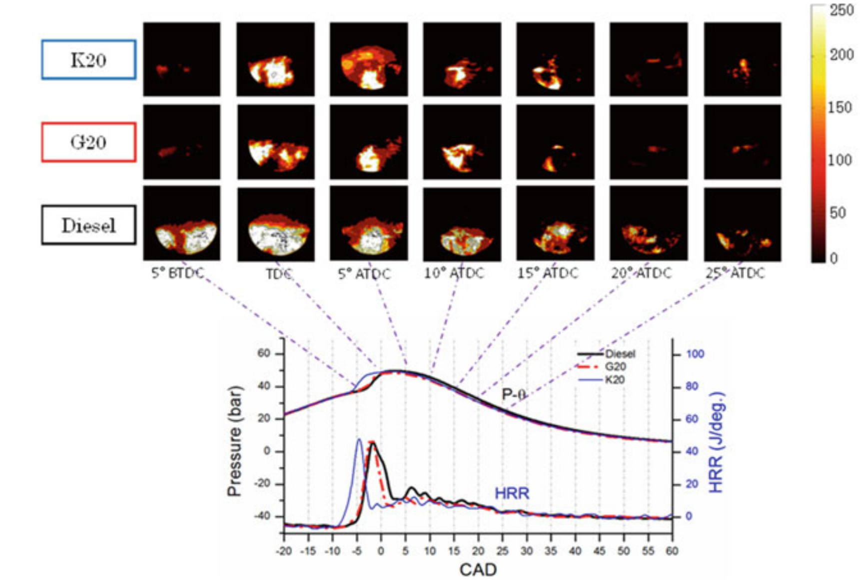


Fig. 7.10 Effect of the addition of alcohol to diesel (Jamrozik et al. 2018)

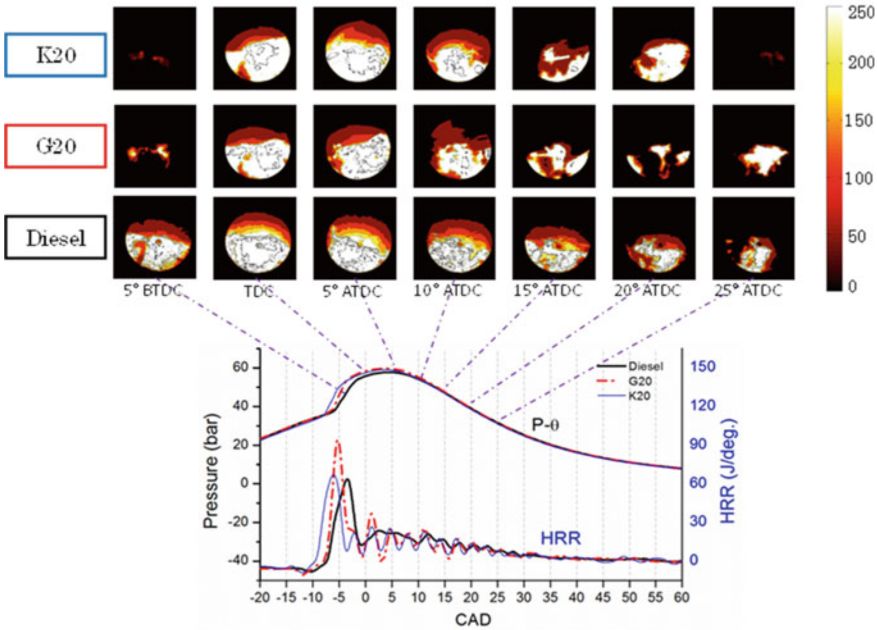
technique and showed that it is a useful technique for characterization of in-cylinder combustion process and detect soot distribution.

7.6 Conclusions, Outlook, and Recommendations

The literature review shows that blending of diesel with alcohol fuels can increase combustion efficiency of engine. As expected from the calorific value, brake power is relatively lower of alcohol-blended diesel fuel. Brake power also depends on cetane number of blended fuel. Properties such as lower density, viscosity, and calorific value of the alcohol fuels compared to mineral diesel result in increasing fuel consumption. Many research laboratories are working on application of methanol, ethanol, propanol, and butanol in the compression ignition engine like dual fuel, RCCI, and PCCI because of the potential to decrease emissions. Higher vaporization and higher oxygen content of fuel result in complete combustion and reduced emission. The present review shows that alcohol is a promising fuel to be blended with diesel; however, material compatibility and combustion process have to be optimized to take the advantage of oxygen present in fuel to reduce emission.



(a) No load



(b) 3.0 kW

Fig. 7.11 Soot contours, cylinder pressure, and HRR (Agarwal et al. 2019)

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