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Alcohols as a Sustainable Alternative Fuel for Combustion Engines: A Review

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A R T I C L E I N F O

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A B S T R A C T

In recent decades, alcohols have emerged as an important alternative fuel for internal combustion (IC) engines. Because of its suitability for storage, ease of production, good vaporization characteristics, transportation, and other factors, alcohols have gained popularity as are liable fuel among other liquid alternatives of gasoline and mineral diesel. In this review, fuel properties of methanol, ethanol, and but anol have been discussed in the context of their use as are placement for gasoline/diesel. Alcohols can be produced using either non-renewable or renewable sources of biomass. Furthermore, the production methodologies of various alcohols have been discussed and presented here. The review goes on to discuss the use of alcohols in both spark ignition (SI) and compression ignition (CI) engines separately. The effect of alcohols on combustion, performance, and emission parameters has been thoroughly discussed for SI and CI engines. SI engines are known to be able to use a higher alcohol blend (up to 85 percent v/v). This review shows that the alcohols can be used in CI engines up to a 15% blend v/v without requiring major engine modifications.

1. Introduction

Petroleum products like natural gas, gasoline, mineral diesel, kerosene etc. have become popular from the start of industrial age. For the mobility in the modern world, availability of liquid fuels is one of the most important factors in the development of society. India imports a large fraction of its crude oil requirement (~83%) from other petroleum rich countries which results in exchange of foreign reserve [1]. Alternative fuels like biodiesel, alcohols etc. can play a major role in partial replacement of mineral fuels. Biodiesel are being used for a long time since 1980s fuel crisis [2], however its limited supply and some issues with its physico-chemical properties such as higher viscosity and density restricted its wider application in automobiles. On the other hand, alcohols (mainly, methanol and ethanol) are being used in gasoline vehicles for a long time as blends upto85% v/v [3]. Alcohols are also popular in compression ignition (CI) engine but mostly limited to laboratory research as alcohol blending in diesel reduces the overall cetane number (CN). Ethanol and methanol are popular alcohols which can be produced from many edible and non-edible organicre sources and waste products.

Specific to the utilization of alcohols in transportation sector, seve ral researchers have investigated combustion, performance and emission parameters in various types of gasoline and diesel vehicles. Gharehghani A. (2019) [4] has observed that ethanol and methanol is favorable for low load, low intake air temperature (IAT) and lean mixture. Hansen et al. (2005) [5] found that, particulate matter emissions reduced by blending ethanol in diesel engine and its magnitude of reduction depends upon the operating condition and blend ratio. Mishra et al. (2020) [6] have investigated methanol blends with gasoline and tested it for varying engine speeds at constant torque. They observed reduced emission and knocking for methanol blended fuel compared to pure gasoline. Also, emission of oxides of nitrogen (NOx) was observed higher atricher fuel conditions than leaner fuel conditions [6]. Methanol/hydrogen, ethanol/hydrogen and methane/hydrogen blends analyzed for combustion & emission performance in high compression ratio engine by Zhenetal. (2020)[7]. They observed that combustion duration and ignition delay (ID) has been extended due to hydrogen addition for all three blends in which methane/hydrogen has longest under the same ratio of hydrogenation. They concluded that methanol/hydrogen provides better engine break power (BP) and break specific fuel consumption (BSFC) than the other two blends [7]. Wakaleetal. (2018) [8] blended n-butanol with diesel (5%, 10% and 20%; v/v) and performed experiments with varying start of injection (SOI), they observed in-cylinder pressure (ICP), peak heat releaserate (HRR) decreases significantly and NOx emission was decreased by 30-40%. Saraswat and Chauhan (2019) [9] concluded that butanol-gasoline and algae oil-gasoline blends showed lowerbreak thermal

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efficiency (BTE), exhaust gas temperature (EGT) and carbon monoxide (CO) emissions compared to pure gasoline. They observed that higher NOx emission possibly due toin herent oxygen (available in butanol and algaeoil) which led higher degree of complete combustion and elevated in-cylinder temperature [9]. Mourad and Mahmoud (2019)[10] performed experiments with ethanol & butanol blends; they observed the reduction in CO by13.2% and hydrocarbons (HC) by 25.2%.

In this work, an attempt has been made to study the properties of various alcohols and their blends with respect to it sutilization in internal compression (IC) engines. Prospects of alcohol utilization in gasoline and diesel vehicles have also been discussed. Methanol, ethanol and butanol are primarily reviewed fortheir performance, combustion and emissions characteristics.

2. Properties and Production of Alcohols

Mineral diesel and gasoline are largely accepted fuels because of their several advantages such as high energy density, easy to transport, easy to store, combustion convenience compared to gaseous and solid fuels etc. Alcohols like methanol, ethanol, butanol etc. are also liquid fuels but with different fuel properties. As an alternative fuel, alcohols have many advantages like lower emission levels, can be renewably produced. However, alcohols show disadvantages like lower calorific value (CV), higher ignition temperature, storage issues as it can absorb atmospheric moisture. The current section is divided in two sub-sections; first sub section deals with the explanation of various properties while the later subsection explains important production technology of alcohols.

2.1 Properties of Alcohols

Alcohols are a group of compounds which contain a single hydroxyl group (-OH) attached with alkane group of *n*-carbon number. Figure1 show the chemical structures of some of the important alcohols. It is desirable to know the chemical properties of alcohol in relation to the commercial conventional fuels in order to utilize it for trans portation. Some of the important properties include Carbon-Hydrogen-Oxygen content, CV, density, kinematic viscosity, auto-ignition temperature, flashpoint, CN and octane number (ON) etc.

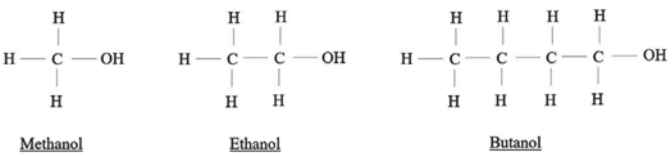

Figure 1: Schematic diagram and chemical structure of methanol, ethanol, butanol (reproduced and adapted from [11],[12])

Composition (C, H, O) (mass %) – It is the percentage of the mass of an element in the mass of agiven molecule. Diesel and gasoline poses no oxygen while alcohols constitute a significant fraction of oxygen. Different fraction of oxygen in alcohols may result in varying ignition timing, combustion efficiency, emissions etc. Table 2 shows the percentage mass fraction of oxygen in some common alcohols.

Calorific value - The energy value of a fuel, is for a specific mass the amount of heat released during the combustion [16]. Alcohols has lower CV and higher auto-ignition temperature compared to diesel fuel, which restrict their operation in current days IC engine.

Auto-ignition Temperature- The lowest temperature of a fuel at which it spontaneously ignites without any external source of ignition[17]. In diesel engineit matters more due to the requirement of high compression ratio for alcohols to burnin comparison with diesel.

Latent heat of vaporization-The enthalpy of vaporization or heat of evaporation, is the amount of energy required to a fuel, to transform an amount of that fuel into a gas [18]. Alcohols has higher heat of vaporization than gasoline and diesel, it mitigates knock and improves combustion efficiency, it also decreases NOx formation marginally.

Density - Mass per unit volume of a substance is called density [19]. Current generation injectors that feed fuel to combustion chamber, controls fuel volume, not mass, thus if one fuel has a greater density than another, it implies that considerably additional mass is entering the combustion chamber for the same volume of fuel.Hence density can effectively influence injection timing and injection spray pattern.

Viscosity - The viscosity of a fuel is a measure of its resistance to flow at a given rate [20]. Viscosity affects atomization of the fuel and fuel delivery rate during injection. Density and viscosity of alcohols (methanol, ethanol and butanol) lies between gasoline and diesel, which is very helpful for researcher to use ethanol in IC engine.

Table 1: Thermal, physical and chemical properties o f diesel, gasoline, methanol, ethanol and butanol [13-15]

Properties	Diesel	Gasoline	Methanol	Ethanol	n-Butanol
Molecular formula	$C_{10.8}H_{18.7}$	C_4-C_{12}	CH_3OH	C_2H_5OH	C_4H_9OH
Molecular weight	148.3	100-110	32	46	74.12
Calorific value(MJ/Kg)	44	42.7	19.9	26.8	32.7
Boiling Point (°C)	180-330	25–215	64.5	78	118
Cetane Number	45	-	5	5-8	25
Motoroctane number	-	80–88	88.6	90	78
Flashpoint (°C)	78	-45to-38	11	21.1	28
Auto-ignition Temperature(°C)	235	∼300	465	420	343
Density(kg/m^{3}at20 °C)	840	720–780	792	790	810
Kinematic Viscosity (cP at 20°C)	3.3	0.60	0.59	1.08	2.54
Stoichiometric air-fuel Ratio	14.4	14.7	6.4	9.0	11.2
Composition(C, H, O)(mass %)	87.4, 12.6, 0	86, 14, 0	37.5, 12.5, 50	52, 13, 35	65, 13.5, 21.5
Latent heat of vaporization (kJ/kg)	280	380–500	1178	904	716

Table2: Oxygen massfraction in alcohols

CH3OH	C2H5OH	C3H7OH	C4H9OH
50.00	34.78	26.67	21.62

Stoichiometric air-fuel Ratio - Stoichiometry measures the quantitative relationships between the components of air and fuel for the state of completion of chemical reactions, this means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Methanol has lowers toichiometric ratio than other considered fuels. Many researchers using this alcoholas additives to obtain arange of stoic hiometric ratio to reduce emission parameters.

2.2 Production of Alcohols

Switching from diesel and gasoline to alcohols and other fuels and systems would be worthless before sustain able energy sources are created. The Government of India's 2018 National Policyon Biofuels puts a focus on the use of biomass, agri-residues, and wastes in the production of "drop-in" renewable fuels [21]. From here, potential alcohol alternatives production methods are described.

2.2.1 Methanol

Methanol is produced in industrial scale by catalytic conversion of synthesis gas (CO and hydrogen mixture) in which CO is hydrogenated. Synthesis gas is largely produced from methane and carbondioxide (CO_2) which can be obtained using renewable or nonrenewable resources. Process flow diagram of methanol production is shown in figure 2.

i) Non renewable resources – Conventional resources for the production of synthesis gas includes coal, mineral oil and petroleum products (residual oil, shale, peat, tar, sands and waste). The seresources are being used for the production of methane using dry reforming and steam reforming, subsequently to producesyn gas. These processes have draw backs of high energy consumption and unfavorable H2/COratio [22]. Reactions are as follows;

$$3CH_4 + 2H_2O + CO_2 \rightarrow 8H2 + 4CO \quad \text{(i)}$$

$$8H_2 + 4CO \rightarrow 4CH_3OH \quad \text{(ii) [23]}$$

ii) Renewable resources–Biomass, animal fats and vegetable oils come under this category of raw materials for methanol production. Heating of biomass leads to evaporation of water and partial oxidation of vapors followed by subsequent heating, produces synthesis gas [24].

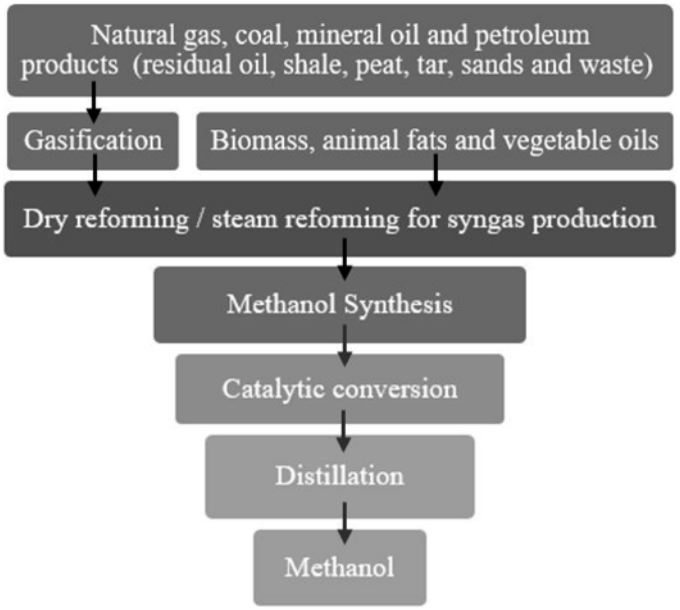

Figure 2: Process flow diagram of methanol production

The produced synthesis gas can be extracted and further processed for the production of methanol using catalytic conversion method. Normally, alumina pallets with coated catalysts used as catalytic mediato produce methanol from synthesis gas at high temperature (475-575K) and pressure (5-10MPa) in fixed bed intercooled reactor [25]. Reactor effluent can be distilled later in distillation units. Reactions involved in this process are;

$$CO+2H_2 \rightarrow CH_3OH \quad \text{(iii)}$$

$$CO_2+3H_2 \rightarrow CH_3OH+H_2O \quad \text{(iv)}$$

$$CO+H_2O \rightarrow CO_2+H_2 \quad \text{(v)}$$

Several other ways i.e. catalytic partial oxidation of natural gas (CH4) and biomass, methanotrophic strains,CO_2 hydrogenation etc. of methanol productional so explored by the researchers [26-31]. However, low yield and economic aspects of the other methods limits the production of methanol in most cases.

2.2.2 Ethanol

Ethanol can be produced by either chemical or biological methods. There are mainly three methods for the production of ethanol named as synthesis, fermentation and biological method [32-34]. Asia has a strong potential for producing ethanol fromrice and rice paddy straw, with India having the large strice cultivation region (44 million hectares), followed by China (30.8 million hectares), Indonesia (11.8 million hectares), and Bangladesh (11.6 million hectares) as on 2021 [35].

i) Synthesis method – This method includes the hydration of ethylene double bond in presence ofsulfuric acid (as catalyst) results in ethanol and some of the toxic byproducts. Here ethylene was produced by steam cracking of petroleum products. Therefore, this method is not suitable forethanol production until the purification is performed. This method contributes about 7% of world ethanol production. Reactions for ethylene to ethanol are;

$$C_2H_4+H_2O \rightarrow C_2H_5OH \quad \text{(vi)}$$

ii) Fermentation method –In this method, microbial fermentation produces aqueous solution with upto 15% of ethanol. Hemp, sugarcane, potato, cassava, rice and corn are the main crop for ethanol production having better well to wheel ratio. Mostly yeast e.g. *saccharomyces cerevisiae* etc. is used for fermentation. For industry level production of ethanol, certain factors are very important to consider like availability of raw materials, logistics, large scale production facility, demand driven etc. Following is the chemical reaction of fermentation process is;

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + \text{heat} \quad \text{(vii)}$$

Typically, distillation of fermented mash results in hydrous ethanol which needs dehydration forutilization in various medicinal and chemical processes and to blend it in gasoline/mineral diesel. This process results in some ofthe byproducts such as acetic acid and glycols[36].

iii) Biological method–Complex natural polymers made from sugars (xylose, mannose, galactose etc.) present in biomass waste are not digested by yeast. Biomass waste (rice hulls, bagasse, cornstalks, forestry waste etc.) are converted to ethanol by genetically engineered *E-coli* bacteria like KO1 [37-39].

Process flow diagram of the ethanol production is shown in figure 3. In other way ethanol can be produced from algae directly and can be removed many times in the single life cycle of algae. Algae can produce approximately 56000 L/ha of ethanol in compare with the 3700 L/ha of thecorn. Also, ethanol can be produced from coal, acetylene, natural gas etc. [35].

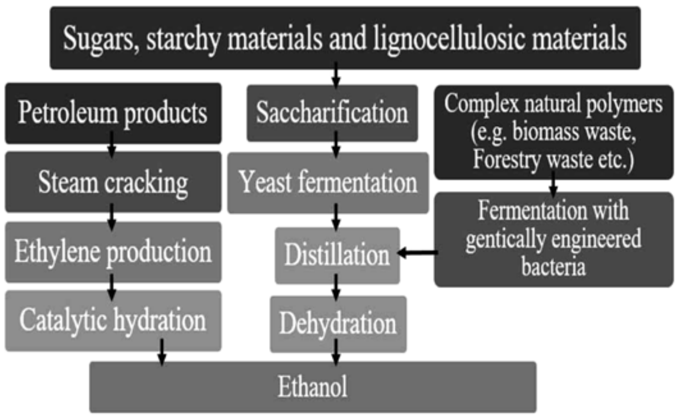

Figure 3: Process flow diagram of ethanol production by fermentation

2.2.3 Butanol

Butanol is mainly produced by three type of methods; oxo method, fermentation method and aldol method. In figure 4, process flow diagram for butanol production is presented.

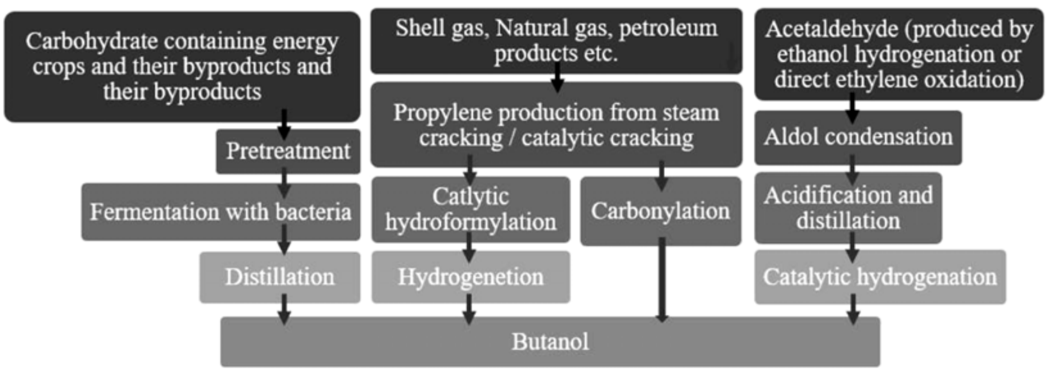

Figure 4: Process flow diagram of butanol production

i) Oxo method – Butanol is primarily manufactured from propylene. Propylene hydro formylation with cobalt and rhodium-based catalysts selectively produces mixture of nandiso butyral dehydes. This is referred as the oxo synthesis and the reactions are;

$$CH_3CH{=}CH_2{+}H_2{+}CO \rightarrow CH_3CH_2CH_2CHO \quad \text{(viii)}$$

$$CH_3CH{=}CH_2{+}H_2{+}CO \rightarrow (CH_3)_2CHCHO \quad \text{(viii)}$$

Hydrogenation of butyraldehyde results in the formation of butanol [23, 40]. Butanol is also generated during the carbonylation of propylene with CO and water as shown in chemical reaction below;

$$CH_3CH{=}CH_2 + H_2O + 2CO \rightarrow CH_3CH_2CH_2CH_2OH{+}CO_2 \quad \text{(viii)}$$

ii) Fermentation method–Butanol can be produced by bacteria such as *Clostridium acetobutylicum* and *Clostridium beijerinckii* fermenting carbohydrate containing biomass (i.e. sugarcane, maize, grains, sugar beets, cassava, switchgrass corn etc.) and their by products (rice straw, corn stalks etc.). This method is called acetone, ethanol and butanol (ABE) method. Butanol is produced in a reactor using biomass, water and dietary supplements of bacteria. After pretreatment, the broth comprising ethanol, acetone, and butanol is extracted and distilled in columns to obtain the final items [41, 42].

iii) Aldolmethod-When acetalde hydeistreated with a base at low temperatures between 5-25°C, the compound acetaldol is formed through aldol condensation. Then acidifying and distilling the solution, the acetaldolis dehydrated to crotonaldehyde. Catalytic hydrogenation of this unsaturated aldehyde produces butanol.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO \quad \text{(viii)}$$

$$CH_3CH{=}CHCHO{+}2H_2 \rightarrow CH_3CH_2CH_2CH_2OH \quad \text{(viii) [23]}$$

Other than above three methods, butanol can also be produced by biosynthesis with the help of genetically engineered micro organism like Cyanobacteria, Escherichiacoli, Bacillus subtilis etc.

2.2.4 Propanol and other alcohols

Propanol is generated in a fewer quantities with fermentation processes and is primarily used as are sin solvent in the pharmaceutical industry. Other than that, N-propanolis manufactured industrially by hydroformylation of ethylene. Isopropanol can be manufactured chemically by reducing acetone in the presence of surplus hydrogen or by hydration of propylene over an acid catalyst. As far as fuel properties are concerned, this is one of the higher-octane fuels. However, the cost and complexity of propanol production has made it unviable for automotive industry. The same reason will also apply for other higher order alcohols [43, 44].

3. Alcohols as an alternative fuelin IC engines

Number of automobiles are increasing drastically in developed and developing countries both during the last fourde cades. Fluctuation in the crudeoil price affects the import, economic growth, transportation etc. Pollution from automotive engines are causing harmful effects in human being like eye irritation, skin & nose problems, asthmaetc. [45]. Due to the string entemission norms and higher energy demand in recent decades, it is important to adopt various preventive methods and technologies such as after treatment devices, inclusion of advanced enginec ombustion techniques, use of suitable alternative fuels etc. [46]. Although, electric vehicles have gained popularity in recent years due to its certain advantages in terms of emissions, these vehicles are still struggling with large scale implementation due to technology complications. For example, electric vehicles need battery charging time, lack the battery efficiency at cruising, battery disposal and cost of batteries [47]. In this context, the current engine technology may be continued for the couple of decades before the full-fledge implementation of electric vehicles. This may be even difficult for heavy duty diesel vehicles which are mostly used for goods transportation. One of the better options is to utilize the alternative fuels with the existing engine technologies in order to improve the performance and reduce emissions. Bio diesel and alcohols are two important liquid fuels which have lot of potential to fully or partial replace the conventional fuels i.e. gasoline and mineral diesel. Higher octane ratings of alcohols, like – ethanol, methanol and butanol make them us able in IC engine [13].

3.1 Utilization of alcohols in CI engines

The heavy-duty diesel engines in global economies are saddled with the increasing price and problematic emissions. Nevertheless, OEMs are learning that due to the heightened public awareness and increasingly restrictive emissions regulations, it's necessary to explore alternatives like biodiesel, fuel cells, and spark ignition (SI). Although these innovations would have shown promise in some product categories, the efficiency and liquid-fueled simplicity of diesel engines are essential in other areas. Wakale et al. (2018) [8] investigated the impact of n-butanol blending in diesel fuel on engine output using a single cylinder common rail direct injection (CRDI) engine. They found that the increased NOx pollution associated with increased fuel injection pressure (FIP; 300, 500, and 800 bar) can be mitigated by applying n-butanol to diesel, implementing split injection techniques, and delaying fuel injection timings. According to their chemical sensitivity study [8], n-butanol delayed the OH-induced hot injection peak by 2°CA. The observed decline in flame temperatures results in a roughly 20% reductionin NOx pollution for B20 fuel. Additionally, a 35% decrease in NOx pollution was reported when a B20 blend was used with split injection (20% fuel in the pre-injection pulse). By blending n-butanol, the peak ICP is decreased while the peak HRR is increased [8]. Use of 100% alcohols in CI engines needs engine modifications, due to their thermal and physico-chemical properties, such as a higher auto ignition temperature and a lower heating value [48]. Following that, the research to overcome the limitations of alcohols and their full-fledged uses in automotive was discussed in detail. It is essential to understand the influence of operating temperature on all investigated parameters of a CI engine. The ambient temperature, especially in countries like India, varies significantly and has a direct effect on the engine's heat transfer rate. At elevated temperatures, pure ethanol and diesel fuelmixes very well. However, as the atmospheric temperature decreases, the solubility decreases dramatically, subsequently resulting in phase separation of the anhydrous ethanol/diesel system,as shownin figure 5 [49].

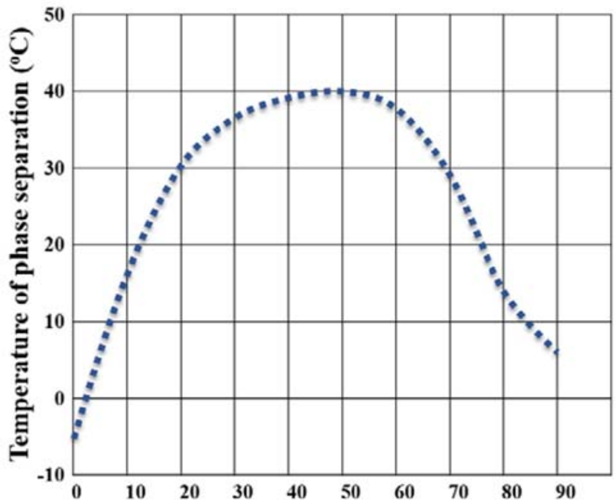

Figure 5: Temperature of natural phase separation of anhydrous-ethanol diesel blends (reproduced and adapted from [49])

Absolute ethanol/diesel mixtures are totally miscible only at atmospheric temperatures above around 40 degrees Celsius, regardless of the proportion of ethanolin the blend. It makes sense to explain that as temperature increases, thermal motion becomes more aggressive, which is beneficial to molecule diffusion and dispersion [49]. CRDI diesel engine fueled with diesel and ethanol/hydrous-ethanol through manifold injection was studied by EL-Seesy et al. (2020)[50]. Results obtained by them showed that therising water level in the aqueousethanol solution increased ID time, NOx and smoke emissions as compared to absolute ethanol [50]. Sayin C. (2010) [51] added dodecanal to stabilize the diesel-alcohol blends (M5, M10, E5, E10; v/v) (performed in a DI diesel engine) and used mixer in the fuel tank to avoid phase separation. M10 showed highest BSFC and lowest BTE among the tested fuels. Smoke opacity, CO and total HC decreased and NOx increased by addition of alcohols in allover conditions [51].

It has become critical that notonly biofuel production is sufficient to achieve these goals, but that engine design and functionality are extensively tested prior to wide spread use of such fuels. Emission and combustion parameters of DICI engine was recorded by Lietal. (2005)[52] with ethanol/diesel blends (D, E5, E10, E15, E20; v/v). They observed that BSFC increased significantly for low loads with ethanol/diesel blends and BTE increased (1-2 % for E15 blends). Smoke concentration decreased with higher ethanol inclusion like E15 and E20. However, total HC increased up to 40% for all tested blends at variable engine loads at variable engine speeds compared to diesel. For ethanol/diesel blends, at low and medium loads CO increased and decrease at higher loads. Similarly, for higher loads NOx increased and vice versa [52]. The effect of IAT and commonrail pressure on a DICI engine operating with pure ethanol had been retraced by Woo et al. (2016) [53] as presented in figure 6. With ethanol's 36 percent lower calorific content than diesel, applying the combination of a higher IAT (80°C) and a higher commonrail pressure (50 MPa) resulted in 50% increase in fuel conversion efficiency and 5% decrease in brake specific fuel consumption (BSFC). It may be noted that IAT lead to reduced volumetric efficiency, however, CI combustion is normally leaner combustion and possibly, IAT does not really reducing opportunity of fuel-air interaction with slightly reduced air density [53]. Higher IAT reduced CO & unburned HC due to extenuated wall wetting. Due to the existence of soot radiative heat transfer, the lower air density produced a slight rise in smoke, which in turn reduced NOx by 27%[53].

Low temperature combustion is a technique used to keep the combustion temperature below the temperature above which NOx and soot particles develop in combustion chamber. Yu (2019) [54] examined spray penetration properties and the development of induced shock waves for ethanol/diesel blends (5%, 10%, 15%; v/v; E5, E10, E15). This experiment was conducted in CIengines using a high-speed camera and schlieren technology with injection pressure between 200-350 MPa. Hequested that increased ethanol inclusion indiesel at same injection pressure createda more rounded supersonic jet and bow shaped shock waves (increased shock wave angles withlesser number of shock waves) because of ethanol's low kinematic viscosity and surface tension [54]. The aerodynamic force may thus induce distortion of the spray and create a more spherical spray tip. The fuel spray jets attained the greater penetration velocity (along spread thin body) under higher injection pressure or lower ethanol volume fraction. Fuel spray jet and induced shock waves for E15. E15 blend demonstrated much longer mean wavelength of shock waves at same injection pressure than other tested blends [54]. Improved atomization performance is possible due to smaller droplet size as a result of shock waves. Thus, better atomization of fuel result in complete combustion and lower particulate matter (PM) emission.

Belgiorno et al. (2018) [55] tested a single cylinder CI engine two fuel blends of diesel, gasoline, and ethanol (DGE) with different compositions (DGE1 (68:17:15) and DGE2 (56:14:30); v/v). DGE blends were found to have a net efficiency of around 51 percent, whereas diesel had a net efficiency of about 47 percent at 8 bar of break mean effective pressure (BMEP). While changing diesel to the DGE2, NO_X was reduced when a single injection method is used for lower loads, whereas NO_X emissions rose by about 1.5 g/kW h for the double injection method at 13 bar BMEP. Soot mass in diesel combustion (0.46 g/kW h) was almost four times higher than that of the DGE blends (0.1 g/kW h), while taking particle size distribution into account, mean diameter and number of particles are both higher than DGE fuel combustion. Although DGE fuels had lower cetane values, better combustion stability was detected [55]. Sahu et al. (2021) [56] investigated the ignition properties of diesel-ethanol mixtures in CI engines and concluded that higher ID and shorter CD are the typical features for ethanol blends [56]. Cetane number (CN) improver (0%, 0.2%, 0.4%; v/v) made by Akzo Nobel Surface Chemistry and Lubrizol Corporation had been mixed with ethanol/diesel blend (E15 – 15%; v/v) and tested in the four-cylinder, high speed, in-line, water cooled, DICI engine by Xing-caietal.(2004) [15]. This research (figure 7) revealed that the addition of CN improver results in reduced ID and increased burn duration for ethanol/diesel blends. At higher loads, the combustion characteristics of ethanol/diesel blends was re established inline to diesel using CN improver unlike the lower engine loads [15].

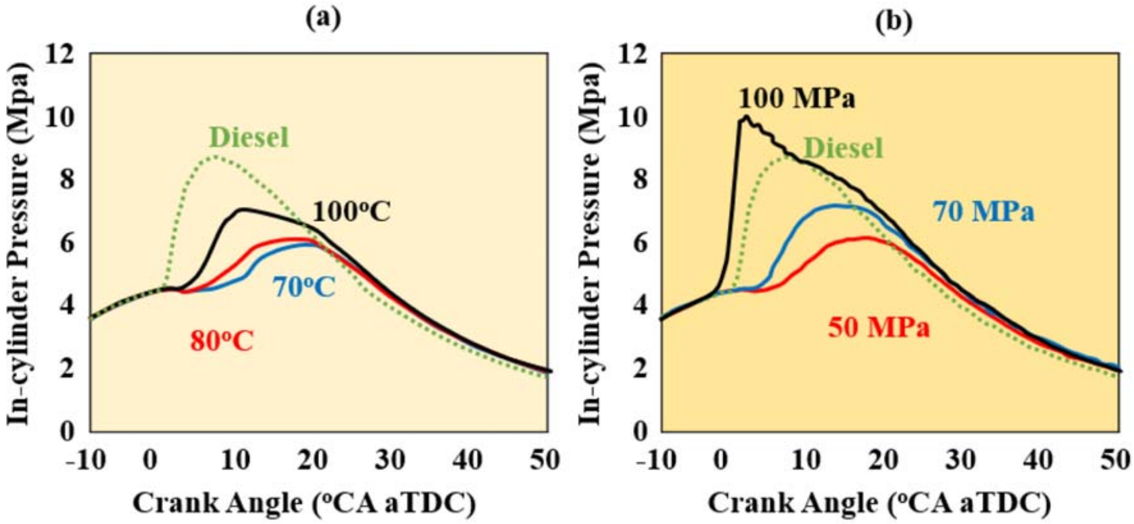

Figure 6: ICP variations due to alterations in (a) IAT and (b) common rail pressure for n-ethanolfuel (reproduced and adapted from[53])

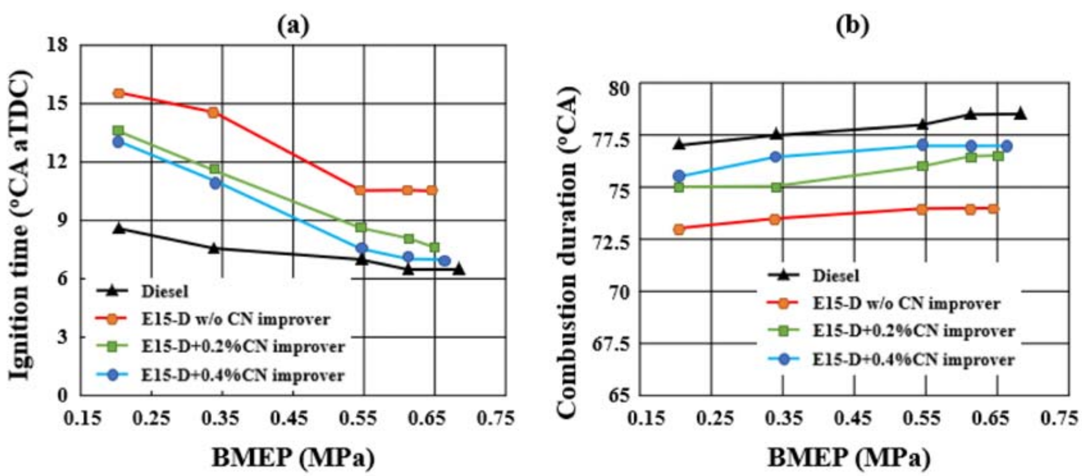

Figure 7: Effectoftested fuels on (a) ignition time and (b) combustion duration at 3400 rpm (reproduced and adapted from [15])

Diesel CI engines are more durable and efficient at high temperatures than gasoline SI engines. However, owing to the auto-ignition of heterogeneous mixtures, diesel engines produce elevated amounts of NOx and PM. These environmental challenges can be resolved by the dual-fuel combustion principle as shown in figure 8.

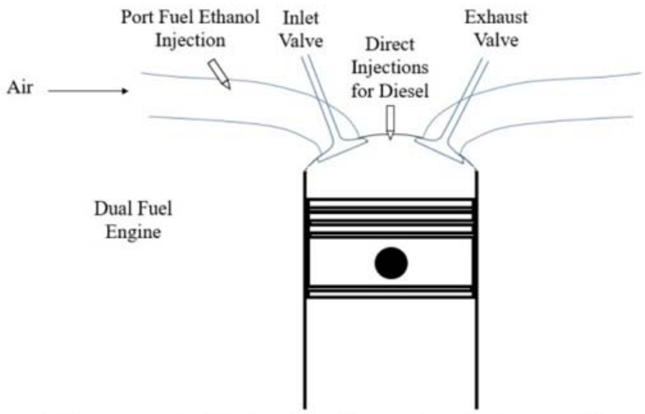

Figure 8: Schematic diagram of adual-fuel engine with DI of diesel and port fuel injection of ethanol ((reproduced and adapted from[57])

Dual fuel combustion is accomplished in the CI engine by injecting the primary fuel (diesel) directly and the secondary fuel through the air intake line. Two parameters are specified in dual fuel combustion to determine secondary fuel utilization: the alcohol substitution percent (ASP), replacement ratio (SR) and alcohol energy fraction (AEF), which are defined in equation (1), (2) and (3) respectively.

$$ASP=\frac{m_d-m_{dF}}{m_d}X100 \quad \text{......(ix)}$$

$$S_r=\frac{m_a}{m_d-m_{dF}} \quad \text{......(x)[58]}$$

$$AEF=\frac{m_a.LHV_a}{m_a.LHV_a+m_d.LHV_d} \quad \text{......(xi)[57]}$$

Here, md and mdf are the mass flow rates (g/s) of diesel in diesel only and dual fuel experiments and ma is mass flow rate of alcohol in dual fuel experiments. Also, LHVa is lower heating value of alcohol and LHV dis lower heating value of diesel indual fuel experiments. In theory, the value of SR is 2.21 considering the CVs of diesel and methanol are 44 and 19.9 MJ/kg, respectively. ASP is the highest achievable value for dual fuel combustion at each load stage. AEF was described asthe ratio of the alcohol's energy content to the total fuel energy supplied in the engine. Ma et al. (2020)[58] investigated the energy balance (load characteristics and energy flow conversion) of a methanol/diesel fueled dual fuel engine at 1660rpm with differing load. Although the methanol/diesel blend had little effect on the exhaust loss ratio in terms of overall out flow energy, it had a lower cooling loss on all loads. At medium-high load, the residual loss for dual fuel combustion was greater than for diesel combustion alone, and vice versa [58]. Additionally, they indicated that for increasing IATs from 35 °C to 65 °C, BTE enhanced and SR declined slightly, while residual and intercooler loss reduced significantly. Where as BTE stayed almost stagnant between 65 and 100 °C, SR declined as previously. By increasing the temperature of the cooling water, residual loss is minimized due to less in complete combustion and mechanical loss [58].

The implications of varying the ethanol replacement ratio (from 0 - 50% of input energy) on NOx and PM emissions in a heavy-duty single-cylinder diesel engine with dual fuel combustion (two direct injectors) were studied by Lee et al. (2018) [59] under fixed speed and variable load conditions. NOx and PM emissions decreased as ethanol content increased. This change was attributed to the improved conditions for 'lean' and 'premixed' mixtures. The mean size of the PM emissions decreased as shown in figure 9[59]. Ianniello et al. (2021)[60] concluded that ethanol blended diesel fuel produces greater combustion noise, total HC, and CO while consuming less fuel and emitting lower NOx than diesel fuel alone in their experiment conducted in a CI engine. They also noted that using dual-fuel mode, NOx, combustion noise, and coefficient of variation $(COV)_{IMEP}$ are equal, although there are negative consequences in terms of unburned HC and efficiency on comparing with conventional operation [60]. Low Temperature Combustion engines are capable of simultaneously reducing NOx and PM emissions. However, this combustion process usually results in increased HC and CO pollution. Hencefor dual-fuel combustion, modification of the combustion chamber design, such as the piston bowl and headshapeis desired.

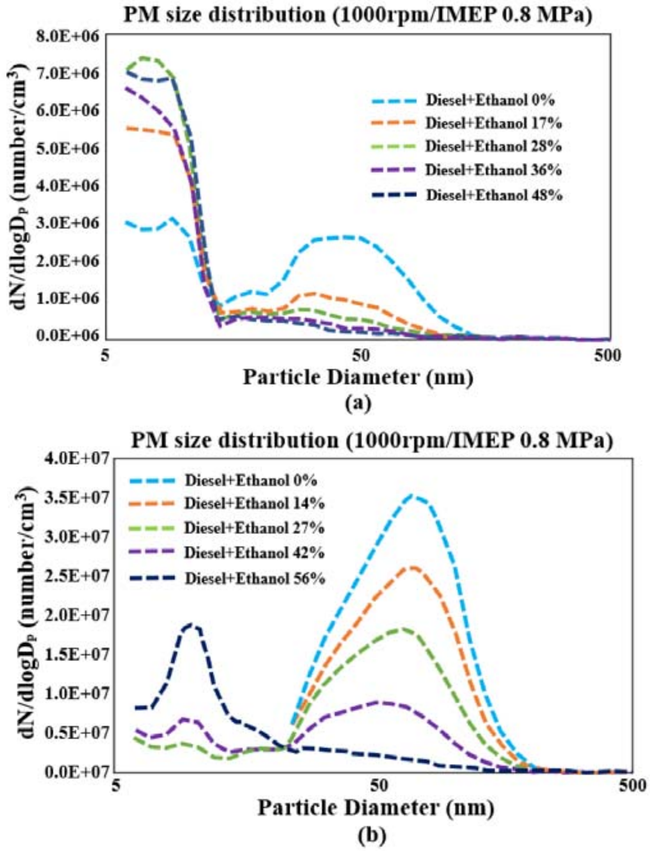

Figure 9: The particle number sized is tributions of particle emissions at IMEPs(a) 0.4 and (b) 0.8MPa at 1000 rpm (reproduced and adapted from[59])

In 1991, methanol was combusted in IC engine at17:1 compression ratio without the use of as park and other assistance with sonex combustion system (SCS) pistons [61]. In micro chamber of SCS piston shown above in figure 10 [61], intermediate (CH2O & H_2O_2) and radical (HO_2) species formed during earlier expansion stroke. They were formed through partial oxidation reaction at below auto-ignition limits and retained (inactive in frozen equilibrium) till the next compression stroke due to restricted inflow and outflow. This chemical kinetics was examined by Blank et al. (2001) [62] in a numerically simulated methanol combustion DIengine. This species (CH_2O, H_2O_2 and HO_2) altered oxidative chain initiation reducing ID time. Hence helpful inseeding, doping and fumigating of next in take charge. This chemical kinetics resulted in faster and low temperature (<100K–200K) combustion of methanolfuel with ultraclean exhaust [62].

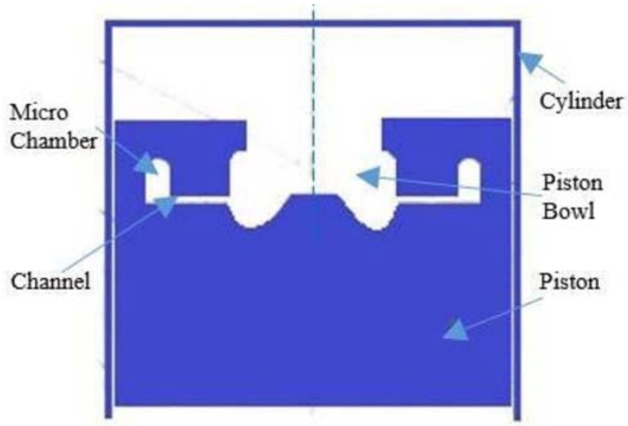

Figure 10: SCS pistons design (reproduced and adapted from[61])

Dual-fuel combustion and traditional diesel combustion studies are often conducted using various engine hardware con figurations, exhaust gas recirculation speeds, and intake and exhaust manifold pressures. These improvements are usually produced to reduce ICPriserates and achieve emission goals. Vancoillie et al. (2013) [63] modified a four-cylinder, high compression ratio (19.5:1), automotive CI engine by swapping the injector with a port fuel injection (PFI) manifold with a swirl ratio of 2 to improve engine turbulence. Stainless steel fuel supply ensures compliance with methanol, and avariable geometry turbocharger is fitted to maintain intake manifold inlet pressure. They run thisengine with methanol (M100) for wide open throttle condition with exhaust gas recirculation and achieved 42% BTE as shown below in figure 11.

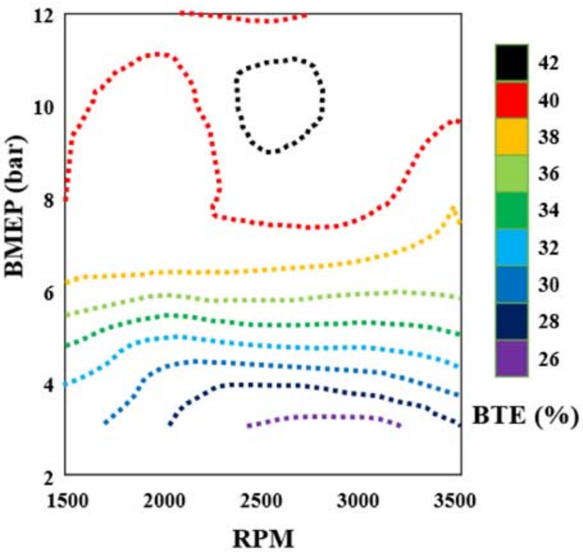

Figure 11: BTE(%) of modified engine running on M100 fuel for wide open throttle condition with exhaust gas recirculation as a function of engine speed and brake mean effective pressure(bar) (reproduced and adapted from [63])

Consequently, they gain a 20% improvement in relative efficiency at part load thanks to the elimination of throttling losses and the resulting advantages of lower in-cylinder temperatures. Due to the high levels of EGR dilution (upto 50%) at part loads, NOx emissions were also reduced to marginal levels [63].

In general, this modification resulted in methanol (M100) having diesel-like performance and gasoline-like emissions in a CI engine. The investigation of butanol fuel combustion and emission mechanisms (for example, comprehensive chemical reaction kinetics) is a critical scientific problem for the production of butanol engines. Physico chemical properties of diesel-butanol blends (2.5%, 5%, 7.5%, 10%; v/v) and its effect on injection & combustion in four cylinders in line, four stroke CI engine had been tested by Zoldy et al. (2010) [64]. After engine testing, they run a passenger vehicle (1.7 ltr, CRDI engine) with blend fuels for 500 km. They concluded that butanol blends (up to 5%) acted similarly to mineral diesel, with the exception ofthe stymied flash point. This blend achieved an equal amount of fuel consumption and cleaner injection than diesel, while still adhering to the CN limits [64]. Li et al. (2020) [65] explored the direct dual fuel stratification (DDFS) ignition method for methanol and diesel. They discovered that a short spray-included angle for diesel injectors is essential for complete oxidation of fuel, where as a medium spray-included angle for methanol injectors is necessary to prevent excess heat exchange loss. Owing to methanol's non-sooting nature, DDFS emits as little soot as reactivity-controlled compression ignition (RCCI) [65]. Maurya et al. (2014) [66] investigated the poisoning and surface characteristics of PM emissions into a modified homogeneous charge compression ignition (HCCI) engine (port injector attached) running on gasoline, ethanol, methanol, and butanol at 1200 and 2400 rpm. all of the test fuels, the Benzene Soluble organic fraction data demonstrated a reduction in the organic fraction of PM with increasing engine load. In a study performed by Maurya et al., (2014) [66], particulate samples were collected on quartz substrate and analyzed for trace metals (B, Ca, Fe, Cu, Mg Cr, Mn, and Zn) using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). B, Ca, Fe, Cu, Mg, and Zn concentrations were found relatively higher compared to Cr and Mn concentrations for tested conditions, and the mass specific concentration of all trace elements declined with increasing engine load for all test cases [66]. Agrawal et al. (2016) [67] discovered that no substantial changes were detected for sulphur dioxide, iso-butane, n-octane, n-pentane, formic acid, benzene, acetylene, and ethylene when utilising diesel-methanol blend (M5, 5%; v/v) [67]. Applying partially premixed combustion (PPC) technique with alcohol fuels takes soot emissions to very low level. Shamun et al. (2016) [68] determined the mass concentration, number concentration, and particle size distribution of soot while varying the intake oxygen concentration, intake air temperature, and common rail pressure for methanol ethanol and naphtha gasoline in PPC mode. Methanol never surpassed 1.6 mg/m^3, whereas gasoline never fell below 1.6 mg/m^3 soot mass concentrations [68].

Biodiesel fuels (such as jatropha biodiesel, karanja biodiesel, soapnut oil biodiesel, palm oil biodiesel etc.) blended with alcohols can provide and offer a viable alternative due to their abilityto be generated from a variety of plants and seeds. Killol et al. (2019) [69] blended n-butanol (5,10,15,20%;v/v) with karanja methylester (KME) and further added di ethylether (DEE;1,3,5%;v/v) ton-butanol/KME blend (15%; KB15). They tested the above blend sin a 4.4kW capacity, single cylinder, four-stroke, air cooled, DI diesel engine at 1500 rpm and compared them with diesel. Killol et al. (2019) [69] observed an expanded delay period of up to 4°C A for KME-butanol blends versus diesel at maximumload, compared to a 2°C Acontraction for pure KME. Additionally, the BTE of KBB20 and diesel was found to be 9% and 3.2% higher, respectively, then that of KME. They discovered that the presence of oxygen in higher order n-butanol blends reduced NO and CO emission, which was subsequently minimized by the insertion of DEE. With increasing load, blends decreased unburnt HC emission as load increased due to an expanded spray flame-out region during ID, however DEE inclusion had an adverse effecton UHC emission [69]. Various techniques were applied to CI engines to accommodate alcohol fuels and its effects on combustion, performance and emission have been discussed above in details. However, adoption of a sustainable technique for use of alcohol in mass has been long awaited.

3.2 Utilization of alcohols in SI engines

Parallel use of multiple alternative fuels can be advantageous from supply as well as engine efficiency stand point. Blends of these fuels can contribute to better evaporative and combustion efficiency and control i.e. methanol, ethanol, and gasoline in SI engines or butanol and mineral diesel in CI engines. Daniel R et al. (2012) [70] investigated the efficiency and emissions of a SI engine using dual fuel technology (gasoline in PFI and alcohols in DI). The tests were conducted at 1500 rpm with a variable load (4.5 -8.5 bar indicated mean effective pressure (IMEP) at 1 bar intervals). They observed a maximum spark advance of 11-12 CAD compared to PFI and a significant reduction in combustion duration of upto 5 CAD overgas olinedirect injection (GDI) by using dual injection technology. As per their results, GEDI and GMDI had a higher indicated efficiency at higher loads (>5.5 bar IMEP) than PFI and GDI. Until 7.5 bar IMEP, GEDI and GMDI had equal indicated efficiencies (37.6%, 2.3% higher than GDI), while at 8.5 bar IMEP, GEDI was 1% more efficient than GMDI and 2.8 percent more efficient than GDI. At 8.5 bar IMEP, GEDI and GMDI generated upto 14% more is NOx and 5% less is CO_2 than PFI and GDI, respectively, due to the higher combustion pressure and temperature. At low load, GEDI generated 2.9% less is CO_2 and 26.6% higher is HC than GMDI [70]. Higher ON of etha nol and methanol, allowing for a higher compression ratio and their molar expansion results in compression with no temperature rise, this are the two basic reasons for increased efficiency.

Iso-butanol, ethanol and methanol blended with gaso line (B5, B10, B15, B20, E10, M10; v/v) and experimented in a four-cylinder SI engine by Bata R. M. (1989) (figure 12) [71]. He reported that iso-butanol/gasoline blend B20 had a 6.5 % higher BSFC and a 2.5% lower BTE than gasoline fuel. Subsequently, B10 performed better thermally than E10 and M10 [71].

Alcohols with a higher-octanerating and a lower stoichiometric ratio improve santiknock properties. However, it is unlikely to vary the blend ratio ondem and in currently used SI engines. P opuri S.S. and Bata R.M. (1993) [23] explored the performance of a single cylinder SI engine with alcohol/gasoline blends (methanol, ethanol, iso-butanol; 5%, 10%, 15%, 20%; v/v). For engine experiments, the fuel flow rate, sparktiming, and compression ratio were varied at constant revolutions per minute. They

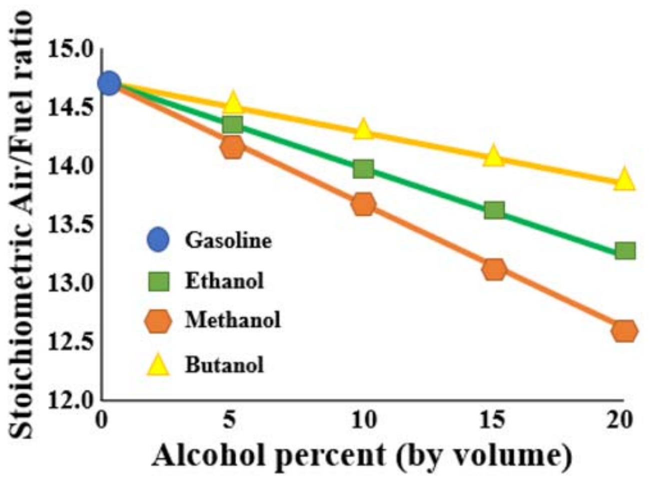

Figure 12: Stoichiometric Air/Fuel ratio of gasoline/alcohol blended fuels (reproduced and adapted from[71])

discovered that methanol, ethanol, and iso-butanol all possessed comparable antiknock properties. Within the range of fuel alcohol concentrations, thermal efficiency stayed relatively stable. Consequently, they discovered that iso-but anolout performed ethanol and methanol at all equivalence ratios and spark timings. However, gasoline surpassed any of the alcohol blends in terms of BSFC, power and efficiency [23]. Since alcohols have a higher - octanelevel, they can be used in GDI engines with comparatively higher compression ratios. However, the comparatively higher PM emissions from GDI engines continue to be a significant issue. Kalwaretal. (2020) [13] investigated the emission parameters of a dual fuel engine (alcohols in PFI and gasoline in DI) running on premixed ratios (15 and 30%; on energy basis) of methanol, ethanol, and butanol in gasoline under 22 Nm load, 2000 rpm engine speed, and comparable injection parameters.

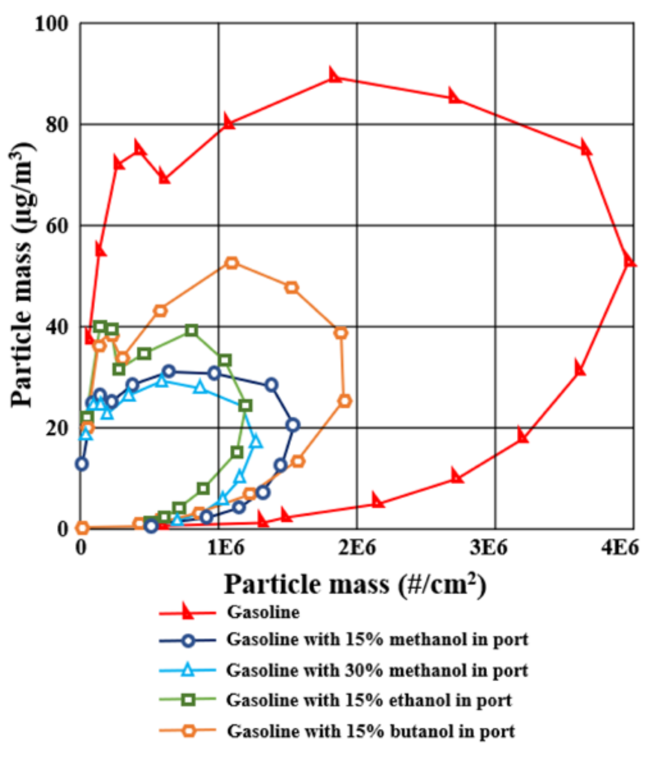

Figure 13: Effect of premixed ratios of port injected fuel on the particle number-mass correlations from the dual fuel engine (reproduced and adapted from [13])

They discovered that dual fuel engines emit less particulate matter than GDI engines. Due to the higher peak ICP and advanced combustion phasing, the methanol/gasoline combination was more efficient at lowering PM emissions (by number and by mass both) as compared to the ethanol/gasoline and butanol/gasoline dual fuel tests. Effect of premixed ratios of port injected fuel on the particle number-mass correlations from the dual fuel engine is presented in figure 13[13].

CO and NOxemissions were reduced, while HC emissions increased marginally in dual fuel engines. Prasadetal. (2020) [72] experimented with an equi-volume mix of methanol and gasoline (M50) at wide open throttle inavariable compression ratio (VCR) SI engine. They reported that a high fraction blend (M50) performs better when the compression ratio is increased. In their work, raising CR from 8 to 10 at 1600 rpm resulted in a 27.5% and 30% increase in peak ICP and net HRR, respectively. Additionally, they observed a 30-40% reduction in CO and HC pollution with M50 blends compared to gasoline fuel. However, NOx emissions increased as CR was increased. High compression ratio induced turbulence, enhanced fuel atomization and leads to increased CO2 with addition of methanol [72]. Pure methanol was experimented on modified engines by Vancoillie et al. (2013) [63]. They modified two engines for flex-fuel operation. A four-cylinder gasoline engine by installing higher flow injectors, a cold heat grade spark plug, and a stainless-steel fuel supply and a single-cylinder diesel engine by replacing the injector with a spark plug with making similar modifications as previous. This resulted in a nearly 10% increase in relative efficiency for methanol in total, as well as a 5-10 g/kWh NOx reduction and up to a 10% CO_2 reduction [63]. The key impediments to the application of low temperature combustion enginesare increased cyclic variation (misfire) at low engine loads and a rapid pressure rise rate (knock) at high engine loads. Thus, fuels with a high auto-ignition specification (lower ONs) are ideal for low load conditions, while fuels with a higher ON are expected for high load conditions.

Fu et al. (2014) [73] studied the dissociation of methanol through exhaust gas recovery heat in a SI engine model using GT Power software. In their study, they used a Rankine cycle in conjunction with a SI engine exhaust system to evaporate and dissociate methanol in the catalytic converter. They discovered that increasing methanol dissociation results in an increase in the heating value of the fuel and an improvement in the conversion efficiency of recovered exhaust gas energy. This method, on the other hand, has a larger negative impact on cylinder volumetric efficiency, which eventually affects maximum load capacity of the engine [73]. Alcohols are capable to reduce emissions and enhance engine performance in most of working engines practically. Even so the main contenders like methanol and ethanol, necessitate anti-corrosion precautions. Szwaja S. and Naber J.D. (2010) [74] investigated n-butanol/PON 87 gasoline blends (0, 20%, 60%, and 100%; v/v) in a single cylinder, variable compression ratio SI engine. They discovered that the addition of n-butanol resulted in less than optimal combustion phasing at constant spark timing due to the shorter early burn duration. They concluded that in order to attain the MBT, the optimal spark timing for the stoichio metric n-butanol-air mixture should be retarded before gasoline spark timing is achieved using an electronic control device. Furthermore, combustion stability of n-butanol is lower than gasoline at part load as determined by the COV of NIMEP in figure 14 [74].

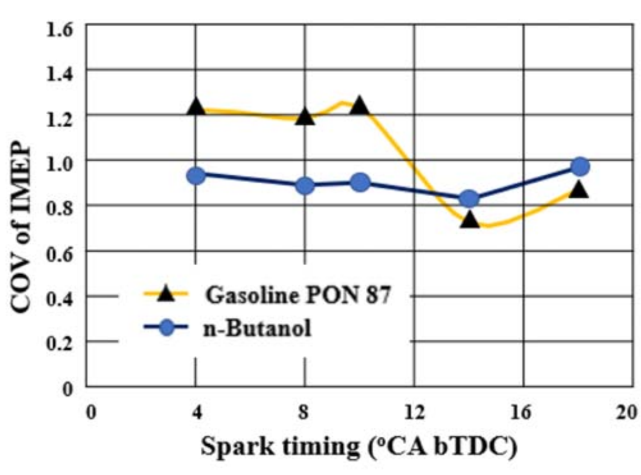

Figure 14: COV of NIMEP for n-butanol and gasoline with PON 87 vs. spark timing (reproduced and adapted from [74])

Butanol gasoline blends were found to be naturally beneficial to each other for the stabilization of combustion and the exothermic method. Similar to PON 87 gasoline fuel, n-butanol's knock tendency is highly susceptible to spark timing and compression ratio. On a carburetor-mounted single cylinder SI engine with CR9. 1 and modified spark timings, gasoline and its bio-butanol blends (B30, B35; v/v) were tested by yangetal. (2011) [75]. They showed that butanol is an extremely promising renewable fuel with significant potential for energy savings, as shown by a 14%, 48% and 22% decrease in BSEC, CO and HC emissions respectively on average for all engine speeds [75]. LiuK. etal. (2018) [14] tested n-butanol/gasoline blends (0, 30%, and 35%; v/v) in a high speed single cylinder, four stroke SI engine. They discovered that n-but anol's higher antiknock capability and oxygen content resulted in earlier ignition timing and increased combustion efficiency. Peak cylinder pressure and rate of heat release decreased as the butanol blend ratio increased [14]. Li et al. (2017) [76] adopted gasoline ABE blended fuels (ABE30 (361) and ABE30 (631)) in a single cylinder, SI engine operating at 1200 rpm and two load situations (3 and 5 bar BMEP). They discovered that changing load and equivalence ratios had no effect on ethyl benzene emissions, and that ABE 30 (361) produced the least amount of ethyl benzene under all circumstances. Benzene emissions decreased as engine load increased, owing to the increased reaction temperature. While toluene and xylene levels rose as engine load increased. Additionally, ABE 30 (631) resulted in a decrease in benzene emissions, while ABE 30 (361) resulted in a decrease in toluene and xylene emissions owing to its greater oxygen concentration and reduced aromatic compound concentration in blended fuels compared to gasoline [76]. Agarwal et al. (2015) [77] examine unregulated emissions in a SI engine operating on gasoline, ethanol, and methanol blends (5 and 15%; v/v, respectively). They discovered that formic acid, iso-butane, and iso-pentane were available in small concentrations inside the exhaust of alcohol-gasoline blends. In the test of E15, ethyl alcohol, formaldehyde, propane, and iso-butylene and for M15 test, methanol, formaldehyde, propane, n-pentane, and toluene were found in higher concentrations. Acetaldehyde was found only in ethanol blends [77]. Karavalakis et al. (2014) [78] examined the emissions of seven fuels with different ethanol and iso-butanol percentages in gasoline (E10, E15, E20, Bu16, Bu24, Bu32, and a combination E10/Bu8) in 2 passenger vehicles. The most abundant carbonyls in the exhaust of both cars were formaldehyde and acetaldehyde, trailed by butyraldehyde, benzaldehyde, crotonaldehyde, methacrolein, and propionaldehyde. The study's primary results include that NMHC, Formaldehyde, Acetaldehyde, and Benzene emissions seemed to be greater for E15 and E20 than for E10, while some decreases in non-methane hydrocarbons, Formaldehyde, Acetaldehyde, and Benzene emissions were seen for higher butanol blends than for Bu16. Additionally, it was discovered that using butanol compositions increased the production of butyraldehyde emissions [78]. Combustion, emission and performance of the SI engine discussed above, gives the overall picture of the growth in popularity of SI engines as alcohol contents in the gasoline increases.

4. Conclusions

This study summarizes current alcohol production methods as well as IC engine modifications and its impact for their vehicle applications. Alcohols are considered good-quality fuels that can be mixed with fossil-based gasoline and diesel for use in low as well as high compression ratio IC Engines due to their ability for production from renewable sources and their high-quality combustion characteristics. They have the potential to transform our transportation energy base and significantly minimize life-cycle CO_2 emissions. By review the literary work on alcohols following conclusions can be drawn;

1. The benefits of ethanol in terms of combustion and antiknock ability have long been recognized. Due to the formation of azeotropes, ethanol has an effect on other fuel properties especially the vapor pressure and distillation profile.
2. Methanol is now regarded as a sustainable green fuel for IC engines due to its nearly soot-free combustion, minimized NOx, and the potential of CO_2-neutral production. Unlike ethanol, methanol is extremely poisonous and unsafe for human use. Since methanol being incompatible with a range of materials, the fuel supply must use stainless steel tubing and Teflon gaskets.
3. Butanol is most preferable among possible alcohol substitutes to gasoline due to its lower affinity for water absorption, vapor pressure characteristics and comparatively higher CV than methanol and ethanol. Additionally, butanol may be used directly in place of gasoline in SI engines, either neat or mixed, from a combustion and energy density basis. For SI engine replacing alcohol with higher order was more significant than changing blend content for same alcohol. In same context, modifying engine parameters was much more significant forengine performance than changing for alcohol totally or blending.
4. Nonetheless, as opposed to diesel and gasoline, the total effect and danger to health and the environment with alcohols is lowered due to its environmental efficiency, low cost, and large number of feed stocks, including substantially decreased impact on water and soil from spills. Since alcohols have a lower energy density, larger fuel tanks are needed to prevent a reduction in range.

Stricter norms and regulations for use of biofuel will expedite the adoption of alcohol- diesel/gasoline blend commercially. The international cash exchange has been chiefly driven by the oil imports. Hence, consumption of alcohols as a fuel in IC engines simply implies a better control of crude oil prices and hegemony of oil rich countries in the international forum. Self-sufficient alcohols consumption is quite a game changer as a strategic point of view and may be the best reason to shift from gasoline and diesel to alternative bio-alcohols.

Acknowledgments

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Abbreviations

CI	Compressionignition
CN	Cetanenumber
IAT	Intakeairtemperature
NOx	OxidesofNitrogen
ID	Ignitiondelay
BP	Breakpower
BSFC	Breakspecificfuelconsumption
SOI	Startofinjection
ICP	In-cylinderpressure
HRR	Heatreleaserate
BTE	Breakthermal efficiency
EGT	Exhaustgastemperature
CO	Carbonmonoxide
HC	Hydrocarbons
ICE	Internalcombustion engine
CO2	Carbondioxide
FIP	Fuelinjectionpressure
CRDI	Commonraildirectinjection
SI	Sparkignition
OEM	Operationenginemanufacturer
MBT	Maximumbraketorque
ON	Octanenumber
PON	Performanceoctanenumber
DGE	Diesel, Gasoline, ethanol
BMEP	Break mean effective pressure
ASP	Alcohol substitution percent
SR	Replacement ratio
AEF	Alcohol energy fraction
CV	Calorific value
LHV	Lower heating value
IMEP	Indicated mean effective pressure
COV	Coefficient of variation
PM	Particulate matter
SCS	Sonexcombustionsystem
DI	Directinjection
DDFS	Direct dual fuel stratification
RCCI	Reactivity controlled compression ignition
HCCI	Homogeneous charge compression ignition
PPC	Partially premixed combustion
KME	Karanjamethylester
DEE	Diethylether
PFI	port fuel injection
VCR	Variablecompressionratio
NIMEP	Net indicated mean effective pressure
-OH	Hydroxyl Group

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