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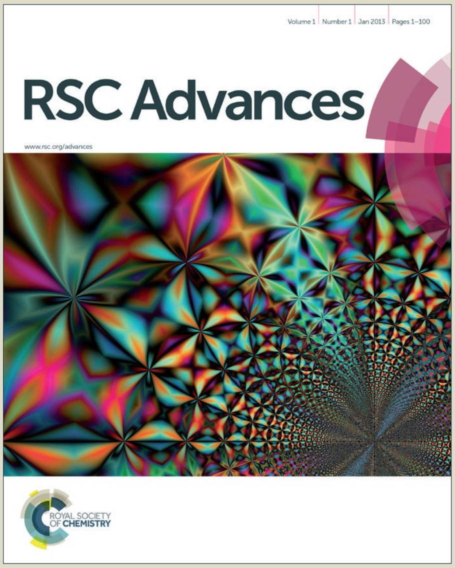

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# Feasibility of Bioethanol and Biobutanol as transportation fuel in Spark-Ignition Engine: A Review

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## ABSTRACT

Until this day, fossil fuels depletion becomes a globally main issue because it is well known for its function as transportation fuel. Furthermore, environmental issues including global warming and climate changes add up the problems that need to be dealt with immediately. Therefore, the biofuel (bio-based fuel), i.e. bio-alcohols (bioethanol and biobutanol) which is produced from the natural materials has emerged as a promising transportation fuel because of its sustainability and environmental benefits which can reduces the dependency on crude oil reserves. Today, bioethanol is widely used as an option for transportation fuel or additives to gasoline in spark ignition (SI) engine due to its attractive properties of its high octane numbers and able to reduce exhaust emissions. The next promising and competitive biofuel is biobutanol which has superior properties to be used in SI engine without engine modification. The aim of the present review is to highlight on the feasibility of the bioethanol and biobutanol as alternative transportation fuel in SI engine. The first section of this paper will be overview on bioethanol and biobutanol as gasoline alternate. On the next section, comparative physicochemical properties of gasoline, bioethanol and biobutanol and their potential sources of production are presented. The effect of bioethanol and biobutanol with

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gasoline blends on engine performances, combustion analysis, exhaust emissions, engine durability and their effect on lubricating oil are discussed in the next section. The review study acknowledges that the bioethanol and biobutanol are capable of improving engine performances, combustion and also reducing exhaust emissions. However, the addition of alcohols in fuel blends gives negative impacts to the engine durability and lubricating oil properties.

***Keywords:*** *bioethanol, biobutanol, gasoline engine, renewable energy, engine performance, engine emission*

## NOMENCLATURE

| | |
|---|---|
| SI | Spark ignition engine |
| CI | Compression ignition engine |
| IC | Internal combustion engine |
| GHG(s) | Greenhouse gases |
| RVP | Reid vapours pressure |
| RON | Research octane number |
| LHV | Lower heating value |
| HoV | Heat of vaporisation |
| T | Torque |
| BP | Break power |
| BSFC | Break specific fuel consumption |
| BTE | Break thermal efficiency |
| EGT | Exhaust gas temperature |
| ICP | In-cylinder pressure |
| HRR | Heat release rate |
| $CO_2$ | Carbon dioxide |
| $NO_x$ | Nitrogen oxides |
| HC | Hydrocarbon |

| | |
|---|---|
| CO | Carbon monoxide |
| PM | Particulate materials |
| $SO_2$ | Sulphur dioxide |
| EGR | Exhaust gas recirculation |
| -OH | Hydroxyl |
| E | Ethanol, Bioethanol |
| DAE | Denatured anhydrous ethanol |
| Bu | Butanol, Biobutanol |
| M | Methanol |
| Pr | Propanol |
| Pe | Pentanol |
| E0/Bu0 | Pure gasoline |
| E100 | Pure ethanol or 100 vol% ethanol |
| Bu100 | Pure butanol or 100 vol% butanol |
| MaxR | Maximum research octane number optimum blend |
| MaxH | Maximum heating value optimum blend |
| MaxD | Maximum petroleum displacement optimum blend |
| EFB | Palm empty fruit bunches |
| POME | Palm oil mill effluent |
| PKC | Palm kernel cake |

## 1. Introduction

The revolution of industrialization sector and high standard living need huge energy consumption. Currently, the most significant growth of energy consumption is taking place in China with the rate of 5.5% per year [1]. The energies are typically consumed for transportation, manufacturing process, industrial facilities, lighting, etc. Meanwhile, transportation and industrial sectors are the main energy usages in Malaysia with 40.3% and 38.6% respectively [2]. It is estimated that the total world energy consumption will be increased by 33.5% from 2010 to 2030 [3]. The existing amount of fossil fuel such as petroleum, coal and natural gas which is represented as the primary source of energy in the world is decreasing day by day and it is assumed to be completely diminished for the next 50 years. Fig. 1 shows that approximately 80% of fossil fuel from the total usage is more than 400 EJ per year.

**Fig. 1 Fuels contribution to total world energy consumption [3].**

The burning of fossil fuel tends to cause environmental pollutions as it releases the greenhouse gases (GHGs) i.e. $CO_2$ that aggravates global warming. The rising of global temperature caused by global warming could leads to extinction of millions natural species and also brings harmful to the ecosystem. It is shown that the emission of $CO_2$ has increased around 1.6 times in recent three decades [2]. The pollutants such as $CO_2$, NOx, CO and $SO_2$ are emitted and they are extremely harmful for humans around the world. Moreover, acid rain which is one of the air pollution is mostly occurred in industrial regions because of less awareness in controlling the fuel utilization. In spite of that, the government seeks into new policies to empower renewable energy to solve environmental issues. For example, Kyoto

Protocol (KP) 1997 has mandates any countries that involved in industrial activities must reduce by at least 5% pollutants below 1990 levels [2].

The limited sources of non-renewable energy i.e. fossil fuel will not be able to sustain the needs for the next generation, leads us to study and discover a new sustainable and renewable energy sources i.e., bio energy. The bio-energy concept is focused on various renewable energies due to massive exploitation on the fossil fuels since its discovery. Bio-energy is one of the renewable energy that uses natural resources for production of biofuels [4]. The potential contribution of bio-energy in the future global energy supply ranges from 100 EJ/year to 400 EJ/year in 2050 [5]. Malaysia's National Energy Policy of 1979 targets to have an efficient, safe, clean and environmental friendly of energy supply in the future [6, 7]. Therefore, biofuel is a promising alternative to reduce the reliance on petroleum from unstable regions indirectly improves the national energy security [8, 9]. This renewable energy source is produced from the natural materials (bio-based) as an alternative compared to conventional petroleum fuels. Therefore, biofuel creates a stronger demands on various feedstock while boosting agricultural economies and producers' incomes [10]. Biofuel production also encourages rural economies become stronger than before. This is because agricultural crops and wastes are being used as the feedstock [11]. Therefore, the production of biofuel is a very potential energy supply to reduce biomass containing waste and reduce its disposal area [3]. In addition, biofuel is available in different forms i.e. liquid or gas [12]. It consists of bioethanol, biodiesel, biogas, bio-methanol, bio-syngas (CO+$H_2$), bio-oil, etc. [4]. The production of global biofuel has increased three times from year 2000 to 2007 which is from 4.8 billion gallons to 16.0 billion gallons. However, it still accounts for less than 3% of transportation fuel supply [13].

The world has proposed the use of bioethanol and biodiesel as the additive sources in liquid transportation fuel [14, 15]. Currently, bioethanol is an alternative fuel for gasoline while biodiesel is an alternative fuel for diesel. They are able to reduce toxic emissions i.e. CO, HC, etc. and reduce smog pollution from the exhaust [8, 11, 13, 16]. Nonetheless, conventional gasoline engine needs major modifications to perform higher concentration of bioethanol, i.e. pure ethanol (E100) can be used in flex fuel (FFV) engine only [8]. Besides that, bioethanol is very difficult to handle and use relative to that of gasoline due to corrosive behaviour. The other option of liquid fuels that able to replace conventional gasoline in transportation is biobutanol, which can be produced from the same feedstock as bioethanol, i.e. waste biomass or non-agricultural products. Biobutanol is a very competitive biofuel to be used for IC engines because it has many promising physicochemical properties that enhances engine performance. It is also a good potential towards green energy consumption. Although the biotechnological production of biobutanol is much more complicated compared to bioethanol production, biobutanol has more advantages than bioethanol and gasoline. Nevertheless, the development on biofuel requires a big space to produce a huge amount of crops, and this aggravates serious environmental effects, i.e. soil corrosion, fertilizer run off, deforestation, eutrophication and salinity [8]. In addition, the biofuel production costs a lot of money and ineffective enough to reduce $CO_2$ emission if compared to other options [11].

The aim of the present work is to review the literature regarding the feasibility of alcohols-gasoline fuel blends on the spark ignition (SI) engine performances, combustion analysis and also exhaust emissions that related to their physicochemical properties. The biofuels that are considered in the present work are; (i) Bio-ethanol (ethanol) and (2) Bio-butanol (butanol). These biofuels are proposed as the potential biofuels regarding their production rate, availability and capability in engine performances and emissions. Numerous studies on ethanol and butanol addition on engine performances and combustion characteristics are discussed in details. The analysis on engine performances of SI engine will be focused on engine torque, break power, break specific fuel consumption, break thermal efficiency and also exhaust gas temperature. Meanwhile, the experimental findings on in-cylinder gas pressure and heat release rate of combustion will be further discussed in details. Then, the analysis is followed by the effect on exhaust emissions i.e. $CO_2$, $NO_x$, HC and CO with addition of alcohol-gasoline fuel blends. The standard way is used by comparing the physicochemical properties between the alcohols fuel blend with the gasoline as a reference to analyse the effect on engine performance, combustion and exhaust emissions. Therefore, the obtained experimental findings can be explained clearly and effectively.

## 2. Bioethanol and Biobutanol as transportation fuel

### 2.1 Bioethanol

Ethanol as a fuel is not a new concept as once before Samuel Morely had developed an engine that ran on ethanol in 1826. Besides that, Henry Ford's Model T ran on ethanol in 1908. However, demands on ethanol declined after World War I and then gasoline dominated the market in 1920s. In 1974, Solar Energy Research, Development, and Demonstration Act of 1974 promoted ethanol as gasoline alternate due to energy crisis. Ethanol is the most widely used biofuel in transportation due to rising oil price, tremendous risk of climate change, increasing on fuel vehicle demands, security of energy supply. Therefore, the government authorizes new policies to do researches, develop and deploy more energy sources. In United States, the Energy Policy Act of 2005 shows the most significant steps by mandate the use of ethanol through the Renewable Fuel Standard (RFS) [17]. Besides that, the initiation of National Alcohol Fuel Programme (ProAlcool) in Brazil aims to increase the production of bioethanol in order to substitute the high cost and inadequate petroleum-based products [14].

Generally, ethanol or ethyl alcohol can be divided into two types; bio-based ethanol (bioethanol) and synthetic ethanol. Bioethanol is produced from agricultural food and agricultural wastes i.e. corn, sugar cane, etc. fermenting sugars with yeast. The synthetic ethanol is produced via catalytic hydration of ethylene, a petroleum by-product. Bioethanol and synthetic ethanol are practically the same products as they have the same chemical formulae, $C_2H_5OH$. Bioethanol or synthetic ethanol is a colourless liquid, transparent, neutral, volatile, flammable, miscible in both water and non-polar solvents and oxygenated liquid hydrocarbon which has a pungent odour and sharp burning taste [18, 19].

The analytical studies towards global ethanol production showed that most of the ethanol is produced by fermentation process which contributes 97% while the other less than 5%, the ethanol is produced via catalytic hydration of ethylene [20-22]. Besides that, the largest plants of synthetic ethanol in Germany and Scotland can produce about 4.4 million gallons per year. There are a several multinational companies produce synthetic ethanol i.e. Sasol (in Europe and South Africa), SADAF of the Saudi Arabia, Shell of the UK and Netherlands, BP of the UK and also Equistar (in United States) [20, 23]. The production of synthetic ethanol is economically less attractive as compared to fermentation in USA due to the high cost of ethylene and abundance of raw materials of agricultural products as the feedstocks. Nevertheless, the production of synthetic ethanol is growing in Middle East countries especially in Iran.

In United States, more than 7.3 billion gallons of bioethanol were added to conventional gasoline in year 2009 to achieve biofuel requirements [24]. Fig. 2 shows the graph of world bioethanol fuel production as it reached 4.5 billion gallons in year 2000, then rose up to 22.7 billion gallons in year 2012 [25]. The bioethanol production increases steadily as the nations are now looking to reduce oil imports, improving air quality and boosting rural economies. In

2011, there are 31 countries in international level and 29 provinces mandate the use of gasoline-bioethanol blends [26].

**Fig. 2 Graph of world fuel ethanol production, 1975-2012 [25].**

Bioethanol-gasoline blends are often used in fuel injection engines of light duty vehicles as alternative to gasoline or acts as fuel additive due to its high octane number, faster flame speed, higher HoV and also broader flammability limits. These properties allow higher compression ratios and shorten combustion time, which give more advantages compared to pure gasoline [14]. The burning of bioethanol in SI engine also reduces the emission of HC, CO, NOx [11, 18]. The 10 vol% ethanol in gasoline (E10) is commercialized by the automakers in United States as conventional vehicles' fuel and it is widely known as gasohol by the public [24]. In addition, higher concentrations of fuel blends, i.e. 85 vol% ethanol in gasoline (E85) has been used for new FFVs. However, the 85 vol% ethanol blend (E85) cannot be used in normal gasoline engine. FFVs were launched since 2003 in Brazil's market. As record, almost 90% of the new cars which are sold today have flexible fuel engine and the gasoline sold contains 20-25% anhydrous ethanol and 100% hydrous ethanol (4-4.9% of water) [18, 27, 28]. The addition of anhydrous ethanol fuel blend [29-31] and hydrous ethanol blends [32, 33] on engine performances is widely studied by the researchers. Meanwhile, United States has nearly 8 million FFVs which can run 85 vol% ethanol blend (E85) on the road with various ranges of models such as sedans, pick-up trucks and minivans [34]. Table 1 below shows the usage of bioethanol-gasoline fuel blends in different countries.

**Table 1 Bioethanol-gasoline fuel blends used in different countries [8, 35].**

The other alternative and more competitive biofuel for the use in SI engine is butanol. Butanol was discovered by Wirtz in 1852 as a regular constituent of fusel oil [36]. Louise Pasteur then clarified the synthesis of biobutanol at laboratory scale after 10 years in 1861 [37]. The production of industrial acetone-butanol-ethanol (ABE) fermentation of molasses and cereal grains using Clostridium acetobutylicum was achieved in 1912-1916 by the chemist Chaim Weizmann, University of Manchester UK [38, 39]. The ABE fermentation continuously declined since 1950s, and butanol was produced via petrochemical process due to lower price of petrochemicals and higher food demands of sugar and starchy grains [36]. Because of the high cost, low-yield and slow fermentations process of butanol, it could not compete on commercial scale so it is only produced synthetically. However, there are many countries and big oil companies that look forward on butanol again during oil crisis in 1970s. The reason is because of the rising price of petroleum oil and the increasing amounts of GHGs in the atmosphere.

Butanol or butyl alcohol is non-poisonous, less corrosive, less prone to water contamination, easily biodegradable and has higher energy content than ethanol, but it has similar energy content with gasoline [40]. Butanol exists with different isomers with respect to location of –OH and carbon chain structure. They all have the same chemical properties consisting of 4 carbon atoms, 10 hydrogen atoms and 1 oxygen atom, but this four butyl alcohol can be distinguished by their structures as listed in Table 2 shown below. The physical properties of the butanol isomers are different in octane number, boiling point, viscosity, etc., but the main applications are quite similar for certain usages.

**Table 2 Molecular structure and main application of butanol isomers [36, 41, 42].**

Biobutanol becomes an alternative to bioethanol and gasoline as transportation fuels in spark ignition engine due to its advantages in terms of physicochemical properties. Currently, bio-based n-butanol and isobutanol are considered as gasoline components to be blended with in higher concentrations without any modification on conventional gasoline engine [42]. However, new automobiles FFVs that use 85 vol% ethanol blend (E85) cost a lot of money and quite unaffordable for most buyers. Therefore, butanol fuel blends are able to replace conventional gasoline in existing cars without modifying the engine's specifications. Szulczyk [43] explained that butanol can be blended with gasoline in any percentage up to 100 vol% of biobutanol in conventional SI engine. In addition, Ramey [44] successfully demonstrated by moving across America in 2005 and South Dakota in 2007 with pure butanol (Bu100) with unmodified SI engine. Besides that, biobutanol is less corrosive fuel so it can be easily distributed via existing pipelines or distribution stations as compared to bioethanol. The lower amount of HoV and higher flash point of biobutanol compared to bioethanol is likely to indicate safer handling and usage. Moreover, biobutanol doubles the amount of carbon of bioethanol and contains 25% more energy. This results on better fuel consumption of biobutanol rather than bioethanol [36]. Biobutanol also reduces exhaust emissions i.e. 95% of HC, 0.01% of CO and 37% of NOx over gasoline [44].

There are a few attempts to commercialize the biobutanol as an alternative fuel in transportation sectors by Ramey [44] with Department of Energy (DOE) from 1998 to 2003. However, it was not clarified as an alternative to gasoline by DOE or National Renewable Energy Laboratory. The International Clostridia Group strives to acknowledge on butanol fermentation for 25 years but it is ignored by the producers as they are only concern on bioethanol. In Europe, Fuel Quality Directive 2009/30/EC have allowed a maximum of 15 vol% of butanol in gasoline [45].

## 2.3 Potential feedstocks for bioethanol & biobutanol production

Several raw materials from biomass are still being studied to discover various available alternatives for biofuel production. On fundamental basis, the various sources of the feedstocks can be classified into two main categories; (i) first generation biofuel and (ii) second generation biofuel [18, 46].

The first generation of biofuel feedstock consists of sucrose (i.e. sugar cane, sugar beet, sweet sorghum) and starch rich crops (i.e. corn, milo, wheat, rice, cassava, potatoes, barley). The production of the first generation biofuel is widely commercialized with approximately 50 billion litres produced annually [47]. Today, bioethanol from agricultural food crops i.e. corns are used commercially for the blend component in transportation fuel. However, the feedstock of the first generation appears unsustainable due to the increasing demands of biofuel production. Thus this event causes the rising of food prices and shortage of these edible materials [47].

As alternative, the secondary generation of biofuel is recommended as an efficient fuel production. The second generation of the biofuel feedstock consists of non-food materials such as lignocellulosic biomass. The lignocellulosic materials consist of crop residues, corn stover, grasses, sawdust, woodchips, etc. It includes seaweed, pineapple leaf, banana peel, jatropha waste, oil palm frond, sugar cane bagasse and other major agro residues. The cheese whey can be fermented to produce biobutanol only and cannot be utilised for bioethanol production [43, 48, 49]. The feedstocks are environmentally friendly and have the potential to give novel biofuels, as this feedstock is non-edible, cheap raw materials and abundant plant waste biomass. In addition, the feedstocks can improve the energy balance of ethanol because of the less usage of fossil fuel energy to yield bioethanol. The cellulosic ethanol contributes to significant reduction of life cycle of the GHG emissions i.e. $CO_2$ as these energy crops are nearly carbon neutral [46]. For example, the switch grass can store more carbon in the soil than the agricultural food feedstocks, thus reducing the total GHGs emissions. The un-harvested roots of the grass creates soil organic carbon as the carbon negative [50]. Besides that, United State Department of Energy's Centre for Transportation Research studied that the cellulosic ethanol offers highest reduction of GHG emissions compared to corns-derived bioethanol as illustrated in Fig. 3 [50]. However, the cost for cellulosic ethanol production is not very effective due to the technical barriers and the challenges that need to be solved before their potential could be even realize. The comparison of the petroleum refinery products, first and second generation of the biofuels production is illustrated in Fig. 4.

**Fig. 3 Reduction of Greenhouse Gas (GHG) emissions from cellulosic bioethanol and corns-derived bioethanol blends [50].**

**Fig. 4 Comparison of the petroleum refinery products, first and second generation of the biofuels production [47].**

In addition, Asia continent is reported as the largest potential producer of the biofuel from crop residues and waste crops due to higher biomass availability [51]. Table 3 represents the biomass feedstocks and their potential ethanol yield [46, 47]. United Kingdom (UK) has almost 148,000 hectares of sugar beet in year 2005 and produces nearly 1.25 million tonnes of sugar which means that it could yield around 6.5 million tonnes of bioethanol. There are also about 1.9 million hectares of wheat grown which produces almost 15 million tonnes of wheat grain and this could yield 4.3 million tonnes of bioethanol. However, the cost for raw materials is highly volatile, which can highly affect the total production cost. The price of the raw materials varies from different studies with the range of US$21-US$61 per metric ton dry matter [52]. Besides that, the raw materials cost contributes 60-75% of the total bioethanol production cost.

**Table 3 Biomass feedstocks and their potential ethanol yield [46, 47].**

Malaysia is one of the biggest producers of the palm oil as it has become the most important commodity crop. This situation results on great amount of wastes production. Palm oil has been listed as the second most used oil in the world since 1985 just below soybean oil [6]. The bioethanol and biobutanol are potentially produced from palm oil industrial wastes, i.e. palm empty fruit bunches (EFB), oil palm trunks, oil palm fronds and palm oil mill effluent (POME) as raw materials. Although the country is one of the main producers of biodiesel, they are encouraged to discover and commercialize the bioethanol and biobutanol from the palm oil waste due to their inexpensive lignocellulosic feedstock and renewable mass sources. In addition, Noomtin & Cheirsilp [53] studied the production of biobutanol from EFB that hydrolysed by Clostridium acetobutylicum. Shukor et al. [54] also studied on the production of butanol from palm kernel cake (PKC) via ABE fermentation by Clostridium saccharoperbutylacetonicum N1-4 using an empirical model. The PKC contains lignocellulose that composed of 11.6% of cellulose and 61.5% of hemicellulose, including 3.7% of xylan and 57.8% of mannan [54, 55].

Other than that, banana is also one of the potential energy resources for bioethanol as it is the second largest produced fruit, contributing about 16.26% of the world’s total fruit production in 2007 [56]. In 2001, the total planted area of banana in Malaysia is around 33,704.2 hectares.

Tock et al. [57] studied the maximum amount of potential power generation by banana biomass feedstock is 949.65W, which is about 4.6% of Malaysia's total available capacity, 20789MW in 2007. Therefore, Malaysia able to achieve this target if the banana is successfully used for energy feedstock as required in Fifth Fuel Policy (Eight Malaysia Plan 2001-2005) with the target of 5% of the total energy consumption. Banana has a huge of waste generated from its peels. It may contribute bad effects to the environment. This is because commonly the banana peel is improperly disposed. The waste may produce hazardous gases to the environment such as hydrogen sulphide, ammonia, etc. during decomposition. Thus, bioethanol production from the agriculture waste from banana peel can overcome environmental issues. The banana peel produces higher LHV and can be considered as the best raw material to be utilized for fuel in the utility plant. Amylaceous and lignocellulosic materials which are found in the fruit and the organic residue are feedstock that can be used to produce ethanol via hydrolysis, fermentation and distillation [58].

## 2.4 Production of Bioethanol and Biobutanol

Bioethanol is produced via different routes from several raw materials of the feedstocks as shown in Table 4. The first generation feedstocks i.e. sucrose-rich materials and starch-rich materials can be produced from alcoholic fermentation [18, 59]. The starch rich crops consist of long chain polymer of glucose need additional process. The process is by mixing and ground it with water to break down into simpler glucose before it is fermented by yeast into bioethanol as shown in equations (2.1) and (2.2). The corns-derived bioethanol production is obtained by dry milling and wet milling process [47]. In dry mill process, the starch from the corns is fermented into simple sugar before it is distilled into bioethanol. High value chemicals i.e. fragrances, flavouring agents, food related product are removed during fermentations. Prior to bioethanol production, two economic valuable ethanol co-products are produced including distiller grains which is used for nutritious livestock feed and also carbon dioxide which is sold for industrial needs. Besides that, there are three selective species of micro-organisms that can be used in fermentation for ethanol production; yeast (saccharomyces species), bacteria (zymomonas species) and mold (mycelium) [47]. Abundance of researches has been done to discover a supreme micro-organism to produce ethanol from different feedstocks. Practically, about 40%-48% of glucose is converted into bioethanol, equivalent to 1000 kg of fermentable sugar produces 583 litre of pure ethanol (sp. gravity at 20°C = 0.789) [47, 60].

**Table 4 Bioethanol routes from different raw material of feedstocks [14].**

$$\underset{\text{Starch}}{n(C_6H_{10}O_5)} + \underset{\text{Water}}{nH_2O} \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6} \qquad (2.1)$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{yeast}} \underset{\text{Bioethanol}}{2C_2H_5OH} + \underset{\text{Carbon dioxide}}{2CO_2} \qquad (2.2)$$

The lignocellulosic biomass consists of cellulose, hemicellulose and lignin as its main components. The biochemical production of lignocellulosic bioethanol has four major steps; (i) pre-treatment, (ii) hydrolysis- enzymatic and acid [45], (iii) fermentation and (iv) distillation and evaporation as shown in Fig. 5. The production of lignocellulosic ethanol much more complicated as the pre-treatment process of hemicellulose is needed to increase the hydrolysis yield before it is hydrolysed and fermented into bioethanol. Hamelinck et al.[61] reported that the hydrolysis with pre-treatment yields over 90% while the hydrolysis without pre-treatment yield less than 20%. The common method of dilute or concentrated acid hydrolysis is used to convert lignocellulose into fermentable sugars, and then the hydrolysate is fermented into bioethanol.

**Fig. 5 Production process for bioethanol from lignocellulosic biomass [52].**

Furthermore, bioethanol can be produced with other alternatives which is thermochemical conversion [3]. The biomass can be converted into bioethanol via two ways either thermochemical or biological process. Presently, the lignocellulosic materials are thermo-chemically gasified and the product of synthesis gas is fermented into bioethanol under specific conditions [14, 62].

The estimated production cost of bioethanol from lignocellulosic feedstocks is discussed in previous studies [52, 63-65] and in more advanced techno-economic evaluations [66]. The cost for enzymatic hydrolysis process is also a major contributor [52]. The researchers are going to improve the enzymatic hydrolysis with efficient enzymes reducing enzyme production cost. In addition, the economical production of lignocellulosic bioethanol shows reliable estimated cost in laboratory scales, and endorsed in pilot and demonstration plants. Developers such as Iogen Corps and Abengoa Bioenergy are currently operating with the demo-scale plants to yield lignocellulosic bioethanol [52]. Table 5 shows the estimation cost of the bioethanol production from different feedstocks.

**Table 5 Estimation costs of the bioethanol production from different feedstocks (exclusive of taxes)** [14, 67]**.**

Similar with bioethanol, biobutanol can be produced from same feedstock i.e. sugar crops, starch crops and lignocellulosic biomass. The biological production of biobutanol has been invented decades ago but the process is quite expensive compared to petrochemicals hydration process i.e. oxo-synthesis and aldol concentration. Therefore, almost modern butanol is produced from petroleum known as petrobutanol. However, due to the depletion of fossil-fuel reserves and environmental issues, the interest on sustainable vehicle fuels especially from non-edible materials encourages the technological development in biobutanol fermentation.

Biobutanol can be produced via ABE fermentation. This alcoholic fermentation is called as ABE fermentation as the acetone, butanol and ethanol are the main products. The total concentration of solvents in ABE fermentation stock is 20 g/L with butanol which is around 13 g/L (ratio of butanol, acetone and ethanol is 6:3:1) [68-70]. Previously, the cereal grains and sugar feedstocks were utilized for industrial scale by the ABE fermentation process. The study of butanol production by Qureshi & Blaschek [71] pointed that the butanol can be produced at US$0.34/kg based on the corn price at US$79.23/ton with the ABE yield of 0.42 and the assumption of the co-products of $CO_2$ gas will be captured, compressed, and sold. However, the utilization of these food crops into biobutanol was condemned because of food shortage. Therefore, the researchers focus on the secondary generation biobutanol due to abundant cheaper raw materials as the feedstocks. The process to produce biobutanol from the lignocellulosic feedstocks is illustrated in Fig. 6 [72, 73].

**Fig. 6 Production process for biobutanol from lignocellulosic feedstocks [72, 73].**

ABE fermentation was the second largest industrial fermentation process after bioethanol by yeast fermentation [70]. This is basically because of the economic importance of acetone and butanol as the petrochemical solvents. The substrates of the feedstocks can be fermented with different strains such i.e. *C. acetobutylicum, C. beijerinckii, C. sacharoperbutyl acetonicum and C. saccharobutylicum* are being used to utilize cellulolytic activities [72]. ABE fermentation of biobutanol production can be done via different modes i.e. batch fermentation , fed-batch fermentation and continuous fermentation processes; free cell continuous fermentation , immobilized cells continuous fermentation and cells recycling and bleeding . Table 6 shows the comparison of the biomass feedstocks via different fermentation process and their potential butanol yield/ productivity. The challenges such as lower butanol titer and product inhibition are being resolved with the strain improvement by mutation and genetic engineering. Other than that, it can be resolved with metabolic activities of the organism in acid producing and solvent producing pathways and also effective continuous fermentation process with promising recovery techniques i.e. gas stripping, distillation, liquid-liquid extraction, etc. [40, 70]. Presently, the developers i.e. Butamax Advanced Biofuels LLC, Swiss Butalco GmbH, American Gevo Inc., ButylFuel LLC and Advanced Biofuels LLC are developing their own fermentation process towards an economical synthesis of biobutanol [45].

**Table 6 Comparison of biomass feedstocks and their potential biobutanol yield/ productivity via different fermentation process [40, 70].**

# 3. Physicochemicals properties of Gasoline, Bioethanol and Biobutanol

The physicochemical properties indicate the quality of fuel to be combusted in SI engine [18]. Table 7 summarizes the comparison of physical and chemical properties of respective gasoline, bioethanol and biobutanol.

**Table 7 Physicochemical properties of gasoline, bioethanol and biobutanol.**

## 3.1 Oxygen content

The oxygenated fuel i.e. alcohol fuel has higher oxygen content i.e. biobutanol has 21.59% oxygen and bioethanol has 34.73% oxygen promotes higher complete combustion and lower exhaust emissions [40, 43].

## 3.2 Octane number

Bioethanol has higher octane number compared to biobutanol and gasoline [43]. High-octane fuel prevents the premature ignition that causes knocking which can damage the engine. The higher octane rating gives bioethanol advantages in improving the thermal efficiency. However, it emits 2-4 times higher of acetaldehydes than gasoline hence it is highly corrosive [16].

## 3.3 Reid vapour pressure

Alcohol fuels, i.e. bioethanol and biobutanol have lower RVP as compared to gasoline, thus they bring problems when starting cold engine especially during cold weather [8, 10, 32]. However, bioethanol is easier to evaporate relative to biobutanol. It means that it emits more volatile organic compound into atmosphere as pollution especially during summer hot day. This volatile organic compound along with $NO_x$ gases is converted by ultraviolet radiation into ground ozone pollution [43]. Thus, lower vapour pressure of biofuel brings both beneficial and consequences to the performances.

## 3.4 Lower heating value

Carbon, C and hydrogen, H are liable to raise the heating value when the oxygen is declining during combustion. The energy content of biobutanol is approximately 82% of gasoline energy, while bioethanol has 65% of gasoline energy. Therefore, these biofuels give higher fuel consumption as compared to gasoline.

## 3.5 Density

Density of bioethanol and biobutanol are 794 $Kg/m^3$ and 809 $Kg/m^3$ respectively which are higher than gasoline, results in enhancing the volumetric fuel economy fairly.

## 3.6 Boiling point

As the carbon chain length increases, the boiling point of alcohols increases. The boiling point of biobutanol and bioethanol are 117.7 $^oC$ and 78.3 $^oC$ respectively. The boiling point of each alcohol influences their evaporative behaviour.

### 3.7 Heat of vaporization

HoV of bioethanol and biobutanol are quite higher than gasoline, thus reducing the air-fuel mixture temperature during intake stroke. Higher HoV improves knock resistance and achieves better volumetric efficiency of the engine. However, higher HoV of bioethanol and biobutanol leads to problems when engine start-up including when running cold engine especially during cold weather due to the cooling effect of the air-fuel mixture at ambient temperature [40, 89]. Besides that, higher latent HoV promotes higher emissions of organic gases [90].

### 3.8 Viscosity

Viscosity of biobutanol and bioethanol is higher than gasoline. These properties may attribute the fuel injection system due to higher flow resistance at lower temperature [40].

## 4. Effect of bio-based alcohols-gasoline fuel blends on SI engine

### 4.1 Engine performance

The performance of an engine can be defined as the maximum power or the maximum torque available at each speed within the engine operating ranges [91]. Many studies have been carried out on SI engines vehicles using various alcohols-gasoline fuel blends to determine engine performances i.e. torque, break power, break specific fuel consumption (BSFC), break thermal efficiency (BTE) and exhaust gas temperature (EGT). In this review, the effects of addition of ethanol and butanol in fuel blends on the SI engine performances are the main focus and will be discussed in details.

### 4.1.1 Torque and break power

By definition, torque, T is a turning force produced by the pressure from crankshaft of the piston. It depends on length of the engine stroke, charge condition and average effective cylinder pressure [92]. Meanwhile for brake power, BP is the power output produced by the engine without the power loss caused by the gear, transmission, friction, etc. This power output is called as break power because the break is used to slow down the shaft inside the dynamometer. The break power can be expressed as in equation 4.1;

$$\text{Break power, BP (kW)} = 2\pi NT \tag{4.1}$$

Where N= Engine speed (rpm)

T= Torque (N/m)

A lot of literatures acknowledge that the addition of ethanol in gasoline fuel blend increases the torque as compared with pure gasoline in SI engine. The oxygenated fuel like ethanol in gasoline fuel blend produces leaning mixture to increase the air-fuel equivalence ratio (λ) so that it promotes a better combustion and consequently produce a higher torque output [31, 93-96]. It is revealed by the fundamental studied done by Hsieh et al. [93], who determined the torque output yield by SI engine at 1000 - 4000 rpm of engine speed and full throttle condition is caused by leaning mixture created by ethanol in gasoline fuel blends. As is evident, the 5 vol% up to 30 vol% ethanol in gasoline (E5-E30) gives higher torque output especially at higher speed of 4000 rpm and lower throttle valve opening at 20%. A typical result was reported by Wu et al. [96], found that the lambda, λ could be reached leaner condition as ethanol content are increased without changing the throttle opening and injection strategy. In support to this finding, the higher ethanol content gasoline fuel blend, i.e. 30 vol% of ethanol in gasoline (E30) gives highest torque at 4000 rpm of engine speed and 0.95 of λ. The same results were achieved by Masum et al. [94], who investigated the torque performance of different volume denatured anhydrous ethanol (DAE)-gasoline blends; 10%, 20%, 30% and 50% by volume with gasoline. The higher oxygen content of DAE blend gives better complete combustion, thereby gives higher engine torque. Furthermore, the addition of ethanol promotes high break power, caused by the faster flame speed. The brake power slightly increases by addition of DAE in gasoline fuel blends especially at high speed. However, it was observed that there is no significant change in brake power for the low engine speed with respective fuel changes.

The ethanol content in gasoline fuel blend increases the torque due to high latent heat of vaporization (HoV) of ethanol [31, 92, 94, 97]. This provides lower temperature intake manifold and volumetric efficiency. As the HoV of ethanol increases, the charge temperature is lowered than the ethanol evaporates. A comprehensive study was done by Saridemir [98], discovered the torque and break power increase as the ethanol content increases because the ethanol has triple times of evaporation rate value higher than that of gasoline and better combustion performance.

In addition, the higher octane number of ethanol leads to higher torque of engine as it revealed by Masum et al. [92]. The experiment showed that the engine torque produced by 15 vol% ethanol in gasoline (E15) is the highest among the all blends of maximum octane number (MaxR), maximum petroleum displacement (MaxD), maximum heating value (MaxH) though the ethanol has lowest LHV. The enhanced octane number of 15 vol% ethanol blend (E15) improves the torque performance. The number of octane aggravates the ignition delay that decelerates energy release rate and reduces the heat loss from the engine [99].

However, there is contradiction on the torque and break power performances as Yuksel et al. [100] observed the reduction of engine torque and power output while using ethanol-gasoline blend at various engine speeds ranged from 1538 rpm to 3845 rpm at different throttle opening position. The torque and power output of the engine decrease due to lower calorific values of ethanol-gasoline blend over pure unleaded gasoline (22.771 MJ/kg for ethanol, 44.001 MJ/kg for gasoline) [84, 100].

Limited studies were carried out on another potential gasoline alternate which is biobutanol on SI engine [101]. The researchers concluded that the biobutanol promotes a standard level performance compared with the gasoline in SI engine and diesel in CI engine. It is examined by Xialong et al. [102] as the torque of 30 %vol butanol in diesel is comparable to the regular leaded gasoline at a low speed. However, the torque obviously drops at the higher speed. The torque reduction at high speed was attributed to higher volumetric efficiency of biobutanol and much longer combustion delay due to its greater latent HoV. Similar case applies if the biobutanol is used as an alternative fuel to diesel in a single cylinder compression ignition (CI) engine as revealed by Al-Hasan & Al-Momany [103]. The break power reduces with the respective isobutanol-diesel fuel blends because the higher HoV of the isobutanol. The combustion temperature decreases as the air-fuel mixture temperature at the beginning of the combustion stroke is lower.

### 4.1.2 Break Specific Fuel Consumption

Break specific fuel consumption (BSFC) is simply a measure for the fuel efficiency of any reciprocating engine which indicates the usage of fuel during operating engine. In other words, BSFC is the ratio of the rate of fuel consumption to the brake power with the unit of g/kWH. A lot of manufacturers tried to determine a fixed engine with the least fuel consumption while still producing higher power. Obviously, lower amount of BSFC is desirable. The typical best value of brake specific fuel consumption for SI engine is about 75 x $10^{-6}$ g/J = 270 g/kWH [91].

The researchers revealed that the addition of ethanol in gasoline fuel blends gives negative feedbacks in terms of fuel consumption. The BSFC of the ethanol is increasing due to lower LHV of ethanol as compared to gasoline. As referred to Table 3, the LHV of the ethanol and gasoline are 28.9 MJ/kg and 44.4 MJ/kg respectively. The experimental done by Koc et al. [31], who observed that the BSFC of 50 vol% and 80 vol% ethanol blends (E50 and E80) are much higher than gasoline. The increment of BSFC is mainly caused by the percentage of ethanol in gasoline. Energy content of the ethanol is approximately 35% less than gasoline, thus more fuel blends are needed to produce same amount of engine power [104]. In addition, Saridemir [98] justified the energy content of ethanol is approximately 25% lesser than the gasoline. As the ethanol content in gasoline fuel blend increases, the energy content decreases. Therefore, more blends of fuel are needed to produce same power output at the similar operating conditions. The typical studies on the effect of ethanol addition on BSFC were found by other researchers [87, 105-107]. Some of researchers highlighted the increment of BSFC of the alcohols that leads to higher density of alcohol, but it is not briefly explained [92, 94, 108]. Furthermore, Dhaundiyal [109] reported BSFC increases with the increasing of volumetric percentage of ethanol due to bigger volumetric percentage of water and solubility with higher pressure, thereby enhances the formation of azeotropes.

Interestingly, there is a contradiction revealed by Al-Hasan [29], who found the BSFC of ethanol-gasoline blends were decreasing as the ethanol content increased up to 20 vol% ethanol blend (E20). The significant reduction of BSFC as the addition of ethanol as fuel additive to that gasoline was caused by engine break thermal efficiency behaviour.

The addition of biobutanol in gasoline fuel blends also promotes higher BSFC as compared with pure gasoline. The increment of BSFC from biobutanol fuel blend is caused by its lower calorific value. Biobutanol has greater LHV value than bioethanol but quite comparable with gasoline. As is evidence, Varol et al. [110] found the BSFC of 10 vol% of butanol, 10 vol% of ethanol and 10 vol% of methanol in gasoline (Bu10, E10 and M10) are higher than gasoline due to its lower energy content. Therefore, it is clearly stated that greater amount of alcohol-gasoline fuel is required to achieve an equivalent energy and more fuel injection quantity is used to maintain the torque. Similar results are reported by Pukalskas et al. [111] and Dernotte et al. [83] as the BSFC of biobutanol was higher with the increasing of biobutanol content in fuel blend, thereby more fuel is needed. The same case applies if different types of alcohols are used as reported by Masum et al. [108], who concluded that the alcohols with higher carbon numbers, i.e. butanol has greater LHV because LHV increases with carbon number, thus less fuel blends are needed to yield same engine power.

### 4.1.3 Break Thermal Efficiency

Break thermal efficiency is a measure of the efficiency or completeness of the engine to produce brake power from the thermal input over the fuel amount supplied. The BTE of the engine is calculated as following Eq. 4.2 [112].

$$BTE = \frac{Brake\ power\ (BP)}{Fuel\ consumption\ rate(\dot{m})\cdot LHV} \tag{4.2}$$

Numerous studies have showed the effects of ethanol addition in spark ignition engine on break thermal efficiency. The BTE can be improved with the oxygen content of the fuel and heat of vaporisation (HoV) [113]. In fact, the alcohol-gasoline with low carbon number, i.e.

methanol and ethanol has greater oxygen content than those blends with high carbon number, i.e. butanol and pentanol. Thus, the BTE value for low carbon number is greater than high carbon number of alcohols. The higher oxygen content of the fuel enhances the complete combustion; therefore the BTE is improved [99]. The ethanol-gasoline blend was proven to produce higher BTE than butanol-gasoline blend and pure gasoline as studied by Masum et al. [108].

Interestingly, Yacoub et al. [87] reported that ethanol-gasoline blend gives higher thermal efficiency BTE relative to gasoline but with higher carbon alcohols, i.e. butanol-gasoline blend degrades the thermal efficiency relative to gasoline. Similar trend of BTE has been proven by Ansari et al. [114], who determined the BTE of ethanol fuel blends enhances the thermal efficiency due to better combustion efficiency. The BTE gradually increases at high brake power and decreased at low break power with the low percentages of ethanol. In other contrast, Varol et al. [110] concluded that the BTE for all alcohol-fuel blends are lower than pure gasoline. It was recorded that the BTE of 10 vol% of methanol and 10 vol% of ethanol in gasoline (M10 and E10) are 4.5-6.8% lower and 10 vol% of butanol in gasoline (Bu10) is 2.8% lower than pure gasoline. In spite of that, all the fuel blends give same BTE at lower speeds.

In fact, the fuel continues to vaporize in compression stroke at high latent heat of vaporisation (HoV). During vaporization, the fuel absorbs the heat from the cylinder and the air-fuel mixture will be compressed easily hence improving BTE. The pressure and temperature decreases at the beginning of combustion as the ethanol content increases. This tends to increase the indicated work, i.e. increase the indicated efficiency. Al-Hasan [29] found that the thermal efficiency is improved as the increasing of ethanol content in gasoline blends up to 20 vol% ethanol blend (E20) for all engine speeds. The typical finding was reached by

Khieralla et al. [115] who determined the highest thermal efficiency is achieved by 15 %vol ethanol blend (E15) compared to gasoline.

### 4.1.4 Exhaust Gas Temperature (EGT)

Exhaust gas temperature (EGT) is a significant indicator of the cylinder temperature. EGT is also used to analyse the exhaust emission. In other words, EGT is the function of combustion temperature. The combustion temperature is also closely related to the heating value of the fuel (LHV). In addition, the formation of oxides of nitrogen, $NO_x$ basically depends on combustion temperature [116]. Therefore, the effect of alcohol content in fuel blends on EGT is fairly important due to tempting properties of the alcohols. The alcohol like ethanol which contains lower LHV yields lower combustion temperature that causes reduction of EGT. Ansari & Verma [114] had clearly observed reduction of EGT with the increment of ethanol percentage. The heating value of ethanol is less than the gasoline thereby reduces the combustion temperature and EGT.

Besides that, the reduction of EGT is caused by the oxygen content of alcohol in gasoline fuel blends. The oxygenated alcohol like ethanol gives more advanced combustion hence reducing exhaust temperature. Saridemir [98] observed the increment of oxygenated ratio in fuel blends, i.e. ethanol that truncated the EGT. Topgul et al. [117] conceived the greater amount of ethanol in fuel blend may reduce the exhaust temperature due to more efficient conversion process of heat to work. As evidence, the 60 vol% of ethanol in gasoline (E60) showed lower exhaust temperature than pure gasoline. Moreover, higher latent heat of vaporisation (HoV) of ethanol than gasoline causes the reduction of exhaust temperature. More heat is absorbed by ethanol from the cylinder when it is vaporised. Therefore, the adiabatic flame temperature will decrease [118]. The typical result was found by Elfasakhany [119] who identified the improvement of EGT as the percentage of ethanol in fuel blend increases due to higher latent heat of vaporization of ethanol than the gasoline.

The effect of EGT for addition of butanol in fuel blends shows an insignificant reduction in comparison to gasoline. More temperature drops are taking place in the cylinder charge at the intake valve closure since butanol has higher HoV value than gasoline. Thus, it promotes reduction exhaust gas temperature at the end of the combustion. Singh et al. [120] reported the high concentration butanol-gasoline blends reduces more exhaust temperature than pure gasoline. Interestingly, a contradict finding was revealed by Varol et al. [110] as the 10 vol% of butanol in gasoline (Bu10) gives higher EGT due to its high heating value and lower HoV that contributes high temperature of combustion . Table 8 summarizes the results of the effects of ethanol and butanol addition into gasoline blends on T, BP, BSFC, BTE and EGT from different researchers.

**Table 8 Effects of ethanol and butanol addition into gasoline blends on T, BP, BSFC, BTE and EGT**

## 4.2 Combustion analysis

In a spark ignition (SI) engine, the combination of air and fuel flow past the valve into the combustion chamber and cylinder during intake stroke. Then the air-fuel mixture is compressed during compression stroke. After that, the combustion is initiated by an electric discharged of spark plug at the end of compression stroke under normal operating condition. The spark ignited flame moves steadily across the premixes air-fuel mixture until it reaches combustion chamber walls before it is extinguished through exhaust. Consequently, the combustion analysis is an important characteristic to be considered. Better combustion characteristics of the fuel are acquired to gives higher torque and power. The characteristics of combustion, i.e. mass fraction burned, heat release rate and combustion duration were calculated from the in-cylinder pressure curve data.

### 4.2.1 In-cylinder pressure

Combustion analysis is the basic analysis for pressure and volume of the system. The in-cylinder pressure (ICP) versus crank angle is a significant characteristic of combustion analysis of an IC engine. The ICP varies with crank angle based on the results from the cylinder volume changes, combustion, heat transfer to the chamber walls, flow in and out of crevice regions and leakages [91]. Numerous studies showed that the addition of ethanol gives variations on maximum in-cylinder pressure. The studied done by Melo et al. [28], who determined high ratio blends of hydrous ethanol-gasoline promotes maximum ICP due to higher octane number of ethanol that promotes higher spark timing angle especially for bigger load and high speed operating conditions. Similar result as reported by Balki et al. [113] as the two different alcohols; methanol and ethanol were added separately into gasoline. Both alcohols have higher octane number and laminar flame speed than gasoline. Therefore, shorter period of time is taken for the combustion. In addition, higher latent heat of vaporisation of the alcohol fuels gives higher volumetric efficiency and BTE, thereby reflects higher ICP. The combination of advanced combustion and higher laminar flame velocity of 0 to100 vol% ethanol fuel blends cause faster combustion and reduce combustion initiation duration and also enhances the ICP (and therefore temperature) [121]. Moreover, a combination study of simulation and experiment analysis that was conducted by Deng et al. [122] with butanol-gasoline fuel blends. The addition of oxygenated fuel likes butanol yields faster burning velocity so it gives higher peak of ICP for all engine speeds.

### 4.2.2 Heat release rate

Heat release rate (HRR) is the rate at which heat is generated during combustion. Heat release rate is calculated from the first law of thermodynamics during a cycle. The effect of alcohol addition in gasoline on HRR was studied by Siwale et al. [123], who determined the increament in heat release rate with further spark timing. Faster burning rate in alcohols-gasoline blends attributes to higher rate of heat release. The result obtained is similar as reported by Masum et al. [92] as the HRR starts to increase earlier for all alcohol-gasoline fuel blends due to its faster flame speed of alcohols therby the duration for the combustion is shortened. The combustion duration is decreasing as the ethanol ratio in fuel blend increases. This is mainly because of the presence of oxygen within the ethanol molecule that contributes to faster flame speed as revealed by Turner et al. [121]. Oxygenated alcohol likes ethanol enhances the combustion initiation and stability, thus increases the HRR.

The effect of biobutanol addition into gasoline fuel blend on the heat release analysis was reported by Deng et al. [124] as the efficent combustion process was achieved at the optimal operating parameters with increasing butanol fuel blend ratio. The oxygen content and leaner fuel-air mixture of biobutanol give more complete combustion thus improve its combustion efficiency and HRR. Table 9 summarizes the results of the effects of ethanol and butanol addition into gasoline blends on ICP and HRR from different researchers.

**Table 9 Effects of ethanol and butanol addition into gasoline blends on in cylinder gas pressure ICP and HRR.**

## 4.3 Exhaust emission

Exhaust emission is an undesirable foreign substance i.e. flue gas that emitted and discharged into the air as a result of fuel combustion in the internal combustion engine. Excessive release of the undesirable foreign substances into the air will aggravate the air quality, which can causes acid rain, health problem to human and also cause damages to the ecosystem. Caiazzo et al. [125] observed that road transportation contributes up to 53,000 premature deaths per year in the United States due to the exhaust emissions. In United Kingdom, the pollution experts from MIT, Massachusetts have observed almost 5000 premature deaths per year is caused by the exhaust emission from the vehicle which is more than twice than traffic accidents [126].

The combustion gases consist of non-toxic gases, i.e. nitrogen ($N_2$), water vapour ($H_20$) and also carbon dioxide ($CO_2$) that contributes to global warming. The other little parts of unpleasant gases which are toxic and very harmful such as carbon monoxide (CO) discharged from incomplete combustion, hydrocarbon (HC) exhibits from unburned fuel, nitrogen oxides, $NO_x$ reveals from extra combustion temperatures, ozone ($O_3$) and also particulate matters (PMs), i.e. soot. Fig. 7 depicts the proportion data of emissions yield by SI engine [127]. In spite of that, the amounts of these emissions also depend on the engine design including operating condition.

**Fig. 7 The pie chart of exhaust emissions in SI engine [127].**

### 4.3.1 Carbon dioxide emission

In SI engine, the gases produced from the combustion of the fuel and air mixture are called exhaust gases. One of the largest amounts of exhaust gases is the carbon dioxide ($CO_2$). With sufficient air presence, the hydrocarbon will burn and generate heat to form $CO_2$ and water. $CO_2$ is a primary greenhouse gases emitted through human activities such as transportation. The $CO_2$ emission from motor vehicle is the main factor of anthropogenic influence that increases the $CO_2$ concentrations in the atmosphere. The effect of excessive $CO_2$ in the atmosphere is the earth's temperature will be continuously rising, leads to climate changes and global warming. In spite of that, several efforts are being carried out by many agencies i.e. EPA and National Highway Traffic Safety Administration (NHTSA) of United States in order to produce a new generation of clean motor vehicles to reduce gas house emissions. This is by improving the fuel usage for on-road vehicles and engines. Therefore, it is well known that an effective way to reduce $CO_2$ emission is by producing more energy from renewable sources. In addition, the lower carbon content of the fuel is implemented to the motor vehicle.

Studies on the effect of alcohols towards carbon dioxide have been conducted by many researchers. Research studies showed that the addition of ethanol in gasoline exaggerates the amount of carbon dioxide emission. This is because the ethanol-gasoline fuel blends combust better than pure gasoline and the amount of non-complete combustion products, i.e. CO can be reduced [128]. As result, 10 vol% ethanol blend (E10) shows an increment of $CO_2$ with 5-10% because of improved combustion. Similar result was revealed by Yuksel & Yuksel [100] who identified the higher ethanol content in gasoline fuel blend, i.e. 60 vol% ethanol blend (E60) produces greater amount of $CO_2$ emission due to improved combustion. In addition, the emission of $CO_2$ increases due to oxygen content from the alcohols. Farkade & Pathre [129] identified the emission of $CO_2$ is increasing with the addition of methanol, ethanol and butanol in SI engine. This is perhaps because of the alcohol blends with higher oxygen content of 7.5 wt.% produces more complete combustion of fuel, thereby increases the amount of $CO_2$ emission.

Meanwhile, there are also several contradicting studies that revealed the reduction of $CO_2$ emission with the addition of alcohols in gasoline fuel blends. Kumar et al. [107] identified the ethanol-gasoline fuel blends reduces more $CO_2$ concentration. Based on the study, 10 vol% ethanol blend (E10) can reduce 2.04% and 2.94% of $CO_2$ at the 3000 rpm and 4000 rpm as compared to pure gasoline. Srinivasan & Saravanan [130] showed the addition of 2 vol% of isoheptanol as fuel additive in 60 vol% ethanol in gasoline (E60) reduces up to 7.7% by volume of $CO_2$ at 2800 rpm of engine speed due its complete combustion. Besides that, the addition of butanol in gasoline also reduces the amount of $CO_2$ emission as yield by the engine. A comparison studied have been done by Singh et al. [131] studied two different alcohols fuel blends, 10 %vol of butanol and 10 vol% of ethanol in gasoline (Bu10 and E10). As results, 10 %vol butanol blend (Bu10) emits lower $CO_2$ emission level rather than pure gasoline and 10 vol% ethanol blend (E10). The reduction of $CO_2$ is because of faster flame speed but yet comparable of calorific values of butanol to gasoline.

### 4.3.2 Nitrogen oxide emission

The oxides of nitrogen, $NO_x$ consists of several compounds i.e. nitric oxide (NO), nitrogen dioxide ($NO_2$), nitrous oxide ($N_20$), dinitrogen trioxide ($N_20_3$), dinitrogen tetroxide ($N_2O_4$) and dinitrogen pentoxide ($N_20_5$) [18, 132]. However, only NO and $NO_2$ are the most prominent while the other oxides still exist with small quantities [133]. NO has no colour, odour or taste. Meanwhile, $NO_2$ is a reddish-brown gas with a pungent, toxic, corrosive and irritating odour. The $NO_x$ is naturally formed and produced by human activities such as burning of fossil fuels. When the combustion of fuel is taking place inside the cylinder, the endothermic reaction of nitrogen and oxygen gases occurred at high temperature will produce $NO_x$. In other words, nitrogen and oxygen gases do not react at ambient temperatures. Additionally, NOx is also an example of GHGs gas, which contributes to ozone depletion in the stratosphere. The composition of nitrogen oxides leads to harmful effect such as acid deposition or acid rain. The mechanism of NOx formation i.e. thermal, fuel, prompt NOx and NO from nitrous oxide, $N_2O$ were briefly studied by Masum et al. [18].

Immense investigations have been carried out on SI engines to study the effect of ethanol and butanol in gasoline fuel blend on $NO_x$ emission. Most of literatures concluded that the addition of ethanol and butanol with gasoline fuel blends degrades the amount of $NO_x$ emission. The formation of $NO_x$ is closely depends on combustion temperature, oxygen concentration and also the residence time inside the combustion chamber [97, 134-136]. The study was done by Lin et al. [137] showed that the $NO_x$ emission decreases as the ethanol content in the blended fuel increases. The reduction of $NO_x$ emission is due to low combustion temperature since excess oxygen is present in the ethanol. Based on the study, a significant reduction with the maximum of 86% of $NO_x$ is reduced with addition of 6 vol% of ethanol in gasoline (E6). In addition, Zervas et al. [138] observed similar findings as the reduction of $NO_x$ emission is caused by addition of oxygenated compounds like ethanol.

Moreover, the amount of $NO_x$ emission decreases due to higher latent HoV of ethanol as compared to pure gasoline. The temperature of ethanol blends decreases at the end of intake stroke thereby the combustion temperature will also decrease. Lin et al. [137] investigated ethanol addition in gasoline fuel blends results in significant reduction of $NO_x$ emission. This is because 9 %vol ethanol in gasoline (E9) reduces up to 77% of the mean average values of $NO_x$. This indicated results are typically similar as reported by Liu et al. [139] who tested methanol-gasoline blend and Zervas et al [138] who tested different fuel blends of eight hydrocarbons and four oxygenated compounds. Besides that, lower combustion temperature also caused by the higher latent heat and lower heating value of alcohol which reduces the amount of NOx emission. The study towards two different alcohol fuel blends, ethanol and methanol by Canakci et al. [135] showed decreasing tendency on NOx emission as the 10 vol% of ethanol and 5 vol% of methanol in gasoline (E10 and M5) give 15.5% and 9% maximum reduction of NOx. Furthermore, the NOx formation is caused by the increase of peak in-cylinder temperature [140]. The study of addition of ethanol in a single and split injection strategies by Turner et al. [121] showed lower amount of NOx emission as it is attributed by reduction of flame temperature. The addition of 30 vol% and 85 vol% of ethanol in gasoline (E30 and E85) cause lower flame temperature which leads to lower exhaust temperature thereby produces a lower amount of NOx emission.

Nonetheless, there are some inconsistencies when the amount of NOx emission increases with the addition of alcohols in gasoline fuel blends. A contradict result has revealed by Schifter et al. [141] as a small increment of $NO_x$ emission is produced by the addition of more oxygenated compounds with the usage of 9 vol% of ethanol in gasoline (E9). Zervas & Tazerout [142] identified the increment of NOx emission is also caused by higher percentage of volumetric efficiency. The rise in volumetric efficiency causes lean operation that leads to more complete combustion or near stoichiometric. This case results on increment of flame temperature, cylinder pressure and temperature [30].

Besides that, a significant increment amount of NOx emission is revealed by Turner et al. [121] with the usage of high ethanol content as the pure ethanol (E100) produces higher NOx that attributed by higher in-cylinder pressure and temperature due to advanced combustion. Singh et al. [131] indicated that the formation of NOx is caused by the reaction between the nitrogen and oxygen under high pressure and temperature in the cylinder engine. Based on the study, 10 vol% of ethanol in gasoline (E10) shows an increment of NOx formation because the ethanol leads to faster flame speed that gives quick combustion, thereby increases the temperature of the chamber. However, 10 vol% of butanol in gasoline (Bu10) shows lower NOx emission level compared to gasoline and it is slightly inferior to ethanol fuel blend due to comparable properties of butanol and gasoline in terms of density, laminar flame speed and also the flame temperature. A typical study was done by Gautam et al. [88] who observed the addition of different alcohols of methanol, ethanol, propanol, butanol and pentanol gives higher NOx emissions with 12-16% increment compared to gasoline. It is indicated by higher in-cylinder temperature for all alcohols addition.

### 4.3.3 Hydrocarbon emission

Hydrocarbon (HC) is a chemical compound consists entirely from carbon, C and hydrogen, H that induced from unburned mixture of the fuel molecules in the engine due to improper mixture and incomplete combustion. The formation of unburned HC leads to photochemical smog and ozone pollution [143]. There are approximately over 200 organic compounds that have been discovered in exhaust gas of SI engine. The typical HC composition in SI engine consists of paraffin, olefins and aromatic [91]. The unburned hydrocarbon emissions (HC) from the SI engine is widely cited by Lavoie & Blumberg [144] since 1980. The production of HC emission from the SI engine is quite different with the CI engine. The HC emission is produced at the surface of sprays by the fuel over-leaned and also at the nozzle sac via fuel effusing [145]. There are four mechanisms of HC formation in SI engine which have been studied.

1. The existence of propagating flame quenching layer at cold wall surfaces inside the combustion chamber [145-151].

2. The unburned mixture of air-fuel trapped in the piston top land and ring crevices [144, 145, 150, 152, 153].
3. Cyclic absorption or desorption processes of unburned fuel by lubricating cylinder oil films and deposits [144, 145, 148, 154-156].
4. Misfire and incomplete combustion of air/fuel mixture during engine cycles result to increment of HC emission formation [150].

Rigorous studies have been carried out by researchers to observe the effects of additional ethanol and butanol in gasoline fuel blends on HC emission. The progress study done by the researchers showed the significant reduction on HC emission with the addition of alcohols in fuel blends. The reduction of HC emission is caused by oxygen content in alcohol and leaning effect that enhances the combustion efficiency [31]. A massive reduction of HC emission with the addition of ethanol is revealed by Singh et al. [131] as higher oxygen content of 10 vol% ethanol in gasoline (E10) gives lower amount of HC emission compared to 10 vol% butanol in gasoline (Bu10) and gasoline. Similar study was conducted with higher ethanol content in gasoline fuel blends as the 60 vol% ethanol in gasoline (E60) emits higher reduction of HC emission level up to 16.45% [157] at 5000 rpm and 31.45% at 2000 rpm [117]. Faster flame speed of alcohol compared to gasoline coincidentally affects lower emissions of HC [158]. Therefore, it helps to improve complete combustion of alcohol fuel blends thereby reduces the amount of NOx emission level.

In addition, the amount of HC emission slightly decreases with higher engine load. A study by Yasar [159] found that higher alcohol content in fuel blends, i.e. 50 vol% of methanol and 50 vol% butanol in gasoline (M50 and Bu50) reduce the amount of HC emission at higher load of 2400 W compared to low engine load of 500 W. This result is much more consistent than Taylor et al. [160]. Other than that, HC emission is reduced at higher engine speeds compared to the slower one. The study done by Masum et al. [97] revealed that the addition of alcohols slightly reduces the HC emission level especially at high engine speed of 6000 rpm compared to low speed of 1000 rpm. This is due to air-fuel mixture that homogenises at high engine speed tends to raise in-cylinder temperature and enhances combustion efficiency.

Meanwhile, there is still a small increment of HC emission that has been reported by some researchers with the addition of ethanol. The formation of HC is affected by the large amount of cyclic variability that causes non-complete combustion which leads to increment of the HC emission. Ceviz & Yuksel [161] found that the addition of ethanol with greater than 10 vol% ethanol in gasoline exaggerates the formation of HC emission level. As result, the addition of 15 vol% and 20 vol% ethanol in gasoline (E15 and E20) induce greater level of NOx emission because of higher temperature at intake manifold and low volumetric efficiency.

### 4.3.4 Carbon monoxide emission

Carbon monoxide (CO) is a gas that consists of one carbon atom and one oxygen atom. Carbon monoxide is a toxic, odourless, tasteless and colourless gas. This poisoning pollutant is also formed during the burning of hydrocarbon fuels i.e. natural gas, petrol and diesel. Carbon monoxide, CO emission is one of the products from incomplete combustion of hydrocarbon fuels and also because of lack of air-fuel management [91, 162, 163]. The combustion is not complete due to insufficient amount of air in the air-fuel mixture. Another reason is because the time delay of the combustion cycle [164].

The production of CO emission is affected by the presence of oxygen in fuel blends to be run in the SI engine. It will enhance the leaning effect that leads to low CO emission level [135, 165, 166]. Oxygenated fuel blends i.e. ethanol-gasoline reduces CO emission. He et al. [167] found that

10 vol% and 30 vol% of ethanol in gasoline (E10 and E30) drastically lower the CO emission level. The presence of oxygen in ethanol is effectively improving the combustion in rich mixture. Besides that, Yasar [159] identified the methanol and butanol that contain oxygen ratio of 21.62 wt.% and 50 wt.% respectively promotes better complete combustion thereby lower the CO emission level. In addition, Feng et al. [146] observed the CO emission is reduced with the addition of butanol i.e. 30 vol% and 35 vol% of butanol in gasoline (Bu30 and Bu35) emit lower CO emission compared to gasoline due to oxygen content of butanol. Similar outcomes were reported by Rice et al. [168] and Gu et al. [169] as the CO emission is reduced with the addition of alcohol in gasoline. Besides that, the reduction of CO emission level is also caused by faster flame speed of ethanol that helps to contribute complete combustion [170, 171]. The higher LHV of the alcohol fuel blends accelerates the combustion that will lead to low CO emission. It is revealed by Masum et al. [97] that the MaxH (maximum heating value optimum fuel blend) reduces up to 12.4% CO emission compared to gasoline. Table 10 summarizes the results of the effects of ethanol and butanol addition into gasoline blends on exhaust emissions of $CO_2$, $NO_x$, HC, CO from different researchers.

**Table 10 Effect of ethanol and butanol addition into gasoline blends on exhaust emissions of CO2, NOx, HC, CO.**

### 4.3.5 Unregulated emissions

The unregulated emissions of aldehydes (HCO) i.e. formaldehyde, acetaldehyde, butyraldehyde, acrolein, propianaildehyde, methacrolein and benzaldehyde are released by alcohols are commonly formed in the exhaust gases from the vehicles. The aldehyde emissions can cause harmfull to human health. The study on the unregulated emissions showed that the formaldehyde and acetaldehyde emissions are richer in oxygen containing fuels than the gasoline [45]. The oxygenated fuel of ethanol fuel blend E85 shows highest emissions of acetaldehyde with 98mg/km and the formaldehyde emissions with 7mg/km. Similar result is achieved as the acetaldehyde emissions increase with increasing ethanol blend level due to oxidation [167, 173]. The emissions of formaldehyde, acetaldehyde and acetone from ethanol containing fuel are 5.12 to 13.8 times higher than neat gasoline [93, 174, 175]. However, the poly-nuclear aromatics from the burning of gasoline leads to worse environmental issues in spite of the aldehyde emissions will increase when ethanol is used as the fuel. Prior to that, higher composition of alcohol in the fuel blend gives a better air-quality than gasoline [168].

In different study, Wallner et al. [176] reported that the formaldehyde and acetaldehyde emissions increased with n-butanol and isobutanol compared to ethanol fuel blends. The amount of formaldehyde emissions is higher for isobutanol fuel blends comparred to ethanol fuel blends for most cases as illustrated in Fig. 8 [177]. The amount of acetaldehyde emissions of both ethanol and isobutanol fuel blends increases as shown in Fig. 9 [177].

**Fig. 8 Graph of formaldehyde emissions for isobutanol and ethanol fuel blends [177].**

**Fig. 9 Graph of acetaldehyde emissions for isobutanol and ethanol fuel blends [177].**

The formaldehyde emissions still remained in a large amount during both cold start and hot start engine operation due to lack of catalyst to oxidized the formaldehyde efficiently.

However, the acetaldehyde emissions are reduced during hot-start operation as it is achieved less than 0.3 mg/km [45].

Butyraldehyde emissions are generated by butanol fuel blends. The experiment done by Aakko-Saksa et.al [45] showed that the butyraldehyde emissions released by n-butanol are higher than iso-butanol blend fuels with (3-5 mg/km) and (0.5-1 mg/km) respectively . The butyraldehyde emissions are almost zero during hot-start engine operation for all fuel blends.

## 4.4 Effect on engine durability

Before the alcohol fuels i.e. ethanol is introduced to be used in existing vehicles, a range of studies have been carried out by researchers to investigate the effect of the alcohol fuel blend on the engine durability. A comprehensive study was done by Coordinating Research Council, Inc. (CRC) [178] of United States to investigate the effect of ethanol on engine durability for the current, on-road and non-FFVs models in response to US Energy Independence and Security Act, to mandate 36 billion gallons of renewable fuels for the upcoming year 2022. The study concluded that the engine operating on 15 vol% and 20 vol% of ethanol in gasoline (E15 and E20) will cause engine failure. The presence of ethanol fuel causes three main engine wear mechanism i.e. abrasive wear, adhesive wear and corrosion. The reduction of engine valve seat because of the wear mechanism causes poor sealing and high leakage, leads to loss of compression, cylinder misfires and also catalyst damage [178]. In addition, the ethanol fuels may degrade the metal, rubber and plastic parts of the fuel system because it is basically corrosive [179]. Therefore, anti-corrosion tanks, alcohol-tolerant rubber lines, seals and fuel pump diaphragms and plastic fuel system parts are needed to meet the standards.

A post-test teardown analysis was done by Hilbert [180] on internal parts of the Verado engine showed that the 15 vol% ethanol blend (E15) piston and connecting rod have higher amount of oil staining and carbon deposits than the pure gasoline (E0) engine parts as illustrated in Fig. 10 and Fig. 11. The visual inspection explained that the 15 vol% ethanol blend (E15) engine experience higher operating temperatures than pure gasoline. The wear pattern was observed on the 15 vol% ethanol blend (E15) exhaust cam lobe due to base circle contact as shown in Fig. 12.

**Fig. 10 Piston carbon deposit comparison for cylinder 2 [180].**

**Fig. 11 Connecting rod carbon deposit comparison for cylinder 2 [180].**

**Fig. 12 Exhaust cam lobes base circle details for cylinder 3 [180].**

However, the National Renewable Energy Laboratory (NREL) of United States denied the CRC's report because the 15 vol% and 20 vol% of ethanol in gasoline (E15 and E20) do not show the evidence of deterioration on engine durability [181]. The review on 43 studies with the usage of 15 vol% ethanol blend (E15) by NREL showed that there are no abnormal deterioration in engine condition i.e. metal corrosion or elastomer swell. Besides that, the effect of the ethanol-diesel fuel blends in CI engine on engine durability have been studied and discussed. The Archer Daniels Midland (ADM) of United States conducted a road test study on two trucks that use 15 vol% ethanol-diesel blend for over 400,000 km and the outcome is obtained with no abnormal deterioration on engine condition [182, 183]. Similar result is achieved by Chicago Transit Authority (CTA) of United States as 15 buses that running on

15 vol% ethanol-diesel blend for 434,500 km have not encounter any fuel related problems and abnormal maintenance [182, 183].

## 4.5 Effect on lubricating oil

The lubricant, engine oil or is known as lubricating oil is the oil that is typically used for lubrication of internal combustion engine. The role of the lubricating oil is to reduce the friction and cool the moving engine parts. The other function of lubricating oil is to prevent corrosion and wear, and also minimizing deposit formation. The lubricating oil circulates around the internal part of the engine and its quality decreases through times. The usage of alcohol as the alternative fuels is believed to affect the properties of lubricating oil. Jaroonjitsathian et al. [184] investigated the 4 stroke motorcycle engine that is running with 10 vol% ethanol blend (E10) for 100 hours high speed cycle or 100 hours composite cycle, results with higher lubrication oil degradation. The effect of ethanol fuels on engine oil physicochemical properties was studied by Cousseau et al. [185] as the ethanol fuelled engine give a lower oxidation level and less total acid number (TAN) than gasoline fuelled engine.

The usage of higher ethanol blends, i.e. 85 vol% ethanol blend (E85) as the fuel in SI engine enhances the formation of deposits compared to neat gasoline [186]. The deposits are formed due to the higher vaporization of ethanol at high temperature, engine lubricating oil flow, blow-by gases (positive crankcase ventilation) and combustion gases (EGR) [187]. The deposits such as gums are formed around the inlet valve, the injector tips of port injection engine and also combustion chamber [186]. The detergent additive is used to reduce the deposits formation. Besides that, the gum formation with associated rust or other particles inside the storage tanks can be dissolved and loosened by ethanol fuel [186]. Therefore, more filters are needed to be changed frequently as the abundant of particulates plug on the filters. In addition, an atomatic emission spectroscopy (AES) analysis on lubricating oil showed a significant dissimilarity on the amount of wear particles between ethanol and gasoline fuelled engine [185]. The rubbing of moving metal of the engine from the wear surfaces forms some microscopic particles, which circulate in the oil and move against the engine part that will lead to wear.

Furthermore, ethanol fuel is also miscible with water as compared to neat gasoline [188]. Boons et al. [189] reported that the usage of high ethanol content, i.e. 85 vol% of ethanol in gasoline (E85) causes higher water level in the lubricating oil rather than the usage of neat gasoline in the engine. The presence of water in the lubricants may degrades metal bearing fatigue life [190]. However, FFV engine fuelled with 85 vol% ethanol blend (E85) does not contribute the formation of valve train rust in lubricating oil [189]. Tomanik [191] also reported that the engine parts that operating with the 85 vol% ethanol blend (E85) are less lubricated due to ethanol low lubricity and water-fuel dilution of lubricating oil during the cold start conditions, leads to bearing corrosion and piston ring spalling.

The usage of ethanol fuel blends in the engine causes the tribological problems as the ethanol contaminated with the lubricating oil. The effects on friction and film formation of the engine oil was studied by Costa & Spikes [192] as it is related to the respective tribological problem. The viscosity for both based and formulated engine oil decreases with the addition of ethanol, therefore reduce the elastohydrodynamic film thickness and the friction. The ethanol in base oil reduces the friction with formation of a boundary layer at low speed. Besides that, the ethanol in formulated oil reduces friction at higher speed as the viscosity of the lubricant is decreased. However, at lower speed the ethanol reduces the boundary layer thus increasing the friction.

## 5. Conclusion

The demands of energy consumption, exaggerate depletion of fossil fuels energy sources and serious environmental issues are the main common problems to be debated currently. The ethanol is used as the commercial alternative substitution for conventional gasoline due to its stunning properties of higher octane number. A new promising biobutanol gives a great attraction to the researchers due to its competitive properties compared to gasoline. The production of biobutanol is almost identical with bioethanol as they are from same feedstocks, however the biobutanol production is high cost, low-yield and takes longer process which leads to difficulty to compete commercially.

The research and development on bioethanol and biobutanol as gasoline substitute are done with a vast number. The review indicates that the bioethanol and biobutanol are able to improve engine performances, combustion and also reduce exhaust emissions. The addition of alcohols blend gives higher T, BP, BSFC, BTE and lower EGT compare to gasoline especially biobutanol that contains higher carbon number than bioethanol thus it may improve the fuel properties i.e. RON, LHV, etc. Besides that, the higher flame speed of bioethanol and biobutanol gives higher ICP and HRR than gasoline. Bioethanol and biobutanol fuels are more environmental friendly than gasoline as the alcohol blends give higher reduction of CO and HC, notably bioethanol emits lowest CO amount. However, the alcohol blends emit more $CO_2$ and $NO_x$ than gasoline due to higher oxygen concentration. The biobutanol fuels also give higher amount of unregulated emissions as it emits higher formaldehyde emissions than those bioethanol and gasoline. The study also reviews that the addition of alcohols in the fuel blends gives negative influences to the engine durability and lubricating oil. The ethanol gives main problems to the engine such as corrosion on engine parts and contaminated lubricating oil that contributes engine failure.

By having these extremely impressive data, the further study on bioethanol and biobutanol especially from different agricultural wastes on spark ignition engine performance, combustion, exhaust emissions, engine durability and lubricating oil is authentically acceptable. Besides that, the extensive study on effect of alcohols fuels on engine durability and lubricating oil are to be done by researchers as the alcohols are significant as the gasoline alternate due to their outstanding properties.

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## References

1. R. Saidur, A. E. Atabani and S. Mekhilef, *Renewable and Sustainable Energy Reviews*, 2011, **15**, 2073-2086.
2. S. E. Hosseini and M. A. Wahid, *Renewable and Sustainable Energy Reviews*, 2013, **19**, 454-462.
3. R. Saidur, E. A. Abdelaziz, A. Demirbas, M. S. Hossain and S. Mekhilef, *Renewable and Sustainable Energy Reviews*, 2011, **15**, 2262-2289.
4. A. Gupta and J. P. Verma, *Renewable and Sustainable Energy Reviews*, 2015, **41**, 550-567.
5. G. Berndes, M. Hoogwijk and R. van den Broek, *Biomass and Bioenergy*, 2003, **25**, 1-28.
6. M. H. M. Ashnani, A. Johari, H. Hashim and E. Hasani, *Renewable and Sustainable Energy Reviews*, 2014, **35**, 244-257.
7. F. Sulaiman, N. Abdullah, H. Gerhauser and A. Shariff, *Biomass and Bioenergy*, 2011, **35**, 3775-3786.
8. P. Bajpai, *Journal*, 2013.
9. M. Kumar and K. Gayen, in *Biomass Conversion*, eds. C. Baskar, S. Baskar and R. S. Dhillon, Springer Berlin Heidelberg, 2012, DOI: 10.1007/978-3-642-28418-2_7, ch. 7, pp. 221-236.
10. K. R. Szulczyk, B. A. McCarl and G. Cornforth, *Renewable and Sustainable Energy Reviews*, 2010, **14**, 394-403.

11. D. Puppán, *Periodica Polytechnica, Social and Management Sciences*, 2002, **10**, 95-116.
12. A. Demirbas, *Applied Energy*, 2009, **86, Supplement 1**, S108-S117.
13. W. Coyle, *Amber Waves*, 2007, **5**, 24-29.
14. M. Balat and H. Balat, *Applied Energy*, 2009, **86**, 2273-2282.
15. M. F. Demirbas and M. Balat, *Energy Conversion and Management*, 2006, **47**, 2371-2381.
16. T. V. Rasskazchikova, V. M. Kapustin and S. A. Karpov, *Chemistry and Technology of Fuels and Oils*, 2004, **40**, 203-210.
17. B. D. McGuire, *Assessment of the bioenergy provisions in the 2008 farm bill*, Association of Fish and Wildlife Agencies, 2012.
18. B. M. Masum, H. H. Masjuki, M. A. Kalam, I. M. Rizwanul Fattah, S. M. Palash and M. J. Abedin, *Renewable and Sustainable Energy Reviews*, 2013, **24**, 209-222.
19. A. Ganguly, P. K. Chatterjee and A. Dey, *Renewable and Sustainable Energy Reviews*, 2012, **16**, 966-972.
20. B. Roozbehani, M. Mirdrikvand, S. I. Moqadam and A. C. Roshan, *Chemistry and Technology of Fuels and Oils*, 2013, **49**, 115-124.
21. C. R. Nelson, M. A. Taylor, D. D. Davidson and L. M. Peters, *Journal*, 1951.
22. Y. Maki, K. Sato, A. Isobe, N. Iwasa, S. Fujita, M. Shimokawabe and N. Takezawa, *Applied Catalysis A: General*, 1998, **170**, 269-275.
23. S. I. News, *Daily Breaking News on World Sugar and Ethanol Market Industry (18 August 2011)*, 2011.
24. B. Booundy, S. W. Diegel, L. Wright and S. C. Davis, *Biomass Energy Data Book: Edition 4*, U.S. Department of Energy, 4 edn., 2011.
25. L. R. Brown, in *Full planet, empty plates: The new geopolitics of food scarcity*, ed. E. P. Institute, W.W. Norton & Company, New York, 2012.
26. J. L. Sawin, D. Barnes, E. Martinot, A. McCrone, J. Roussell, R. Sims and V. S. O'Brien, *Renewables 2011 Global Status Report*, REN21 France, 2011.
27. J. R. Tavares, M. S. Sthel, L. S. Campos, M. V. Rocha, G. R. Lima, M. G. da Silva and H. Vargas, *Procedia Environmental Sciences*, 2011, **4**, 51-60.
28. T. C. C. d. Melo, G. B. Machado, C. R. P. Belchior, M. J. Colaço, J. E. M. Barros, E. J. de Oliveira and D. G. de Oliveira, *Fuel*, 2012, **97**, 796-804.
29. M. Al-Hasan, *Energy Conversion and Management*, 2003, **44**, 1547-1561.
30. H. Bayraktar, *Renewable Energy*, 2005, **30**, 1733-1747.
31. M. Koç, Y. Sekmen, T. Topgül and H. S. Yücesu, *Renewable Energy*, 2009, **34**, 2101-2106.
32. R. C. Costa and J. R. Sodré, *Fuel*, 2010, **89**, 287-293.
33. P. C. Vicentini and S. Kronberger, *Rating the performance of Brazilian flex fuel Vehicles*, SAE Technical Paper, 2005.
34. O. o. T. a. A. Quality, *Journal*, 2010, 1-3.
35. J. L. Sawin, *Worldwatch Institute*, 2008.
36. C. Jin, M. Yao, H. Liu, C.-f. F. Lee and J. Ji, *Renewable and Sustainable Energy Reviews*, 2011, **15**, 4080-4106.
37. A. Ranjan and V. Moholkar, 2009.
38. C. Weizmann, *Journal*, 1919.
39. O. Shapovalov and L. Ashkinazi, *Russian Journal of Applied Chemistry*, 2008, **81**, 2232-2236.
40. P. Patakova, D. Maxa, M. Rychtera, M. Linhova, P. Fribert, Z. Muzikova, J. Lipovsky, L. Paulova, M. Pospisil, G. Sebor and K. Melzoch, *Perspectives of Biobutanol Production and Use*, 2011.
41. S. Szwaja and J. D. Naber, *Fuel*, 2010, **89**, 1573-1582.
42. J. Niemistö, P. Saavalainen, R. Isomäki, T. Kolli, M. Huuhtanen and R. L. Keiski, *Journal*, 2013, 443-470.
43. K. R. Szulczyk, *International Journal of Energy and Environment*, 2010, **1**.

44. D. Ramey, in *Agricultural Biofuels: Technology, Sustainability and Profotability*, ButylFuel, LLC, Blacklick, Ohio, United States, pp. 137-146.

45. P. Aakko-Saksa, P. Koponen, J. Kihlman, M. Reinikainen, E. Skyttä, L. Rantanen-Kolehmainen and A. Engman, *Biogasoline options for conventional spark-ignition cars*, VTT Working Papers 187, 2011.

46. A. F. D. Center, *Journal*, 2014.

47. S. N. Naik, V. V. Goud, P. K. Rout and A. K. Dalai, *Renewable and Sustainable Energy Reviews*, 2010, **14**, 578-597.

48. D. Ramey and S. T. Yang, *Production of Butyric Acid and Butanol from Biomass Final Report*, U.S. Department of Energy Morgantown, WV, 2004.

49. D. T. Jones and D. R. Woods, *Microbiological Reviews*, 1986, **50**, 484-524.

50. I. Ceres, *Journal*, 2015, **2015**.

51. S. Kim and B. E. Dale, *Biomass and Bioenergy*, 2004, **26**, 361-375.

52. B. Hahn-Hägerdal, M. Galbe, M. F. Gorwa-Grauslund, G. Lidén and G. Zacchi, *Trends in Biotechnology*, 2006, **24**, 549-556.

53. P. Noomtim and B. Cheirsilp, *Energy Procedia*, 2011, **9**, 140-146.

54. H. Shukor, N. K. N. Al-Shorgani, P. Abdeshahian, A. A. Hamid, N. Anuar, N. A. Rahman and M. S. Kalil, *Bioresource Technology*, 2014, **170**, 565-573.

55. L. G. A. Ong, S. Abd-Aziz, S. Noraini, M. I. A. Karim and M. A. Hassan, *Applied Biochemistry and Biotechnology - Part A Enzyme Engineering and Biotechnology*, 2004, **118**, 73-79.

56. D. Mohapatra, S. Mishra and N. Sutar, *Journal of Scientific & Industrial Research*, 2010, **69**, 323-329.

57. J. Y. Tock, C. L. Lai, K. T. Lee, K. T. Tan and S. Bhatia, *Renewable and Sustainable Energy Reviews*, 2010, **14**, 798-805.

58. H. I. Velásquez-Arredondo, A. A. Ruiz-Colorado and S. De Oliveira junior, *Energy*, 2010, **35**, 3081-3087.

59. R. Sims, M. Taylor, J. Saddler and W. Mabee, *International Energy Agency*, 2008, 16-20.

60. S. Lee, J. G. Speight and S. K. Loyalka, *Handbook of alternative fuel technologies*, crc Press, 2014.

61. C. N. Hamelinck, G. Van Hooijdonk and A. P. Faaij, *Biomass and bioenergy*, 2005, **28**, 384-410.

62. A. DEMİRBAŞ, *Energy sources*, 2005, **27**, 327-337.

63. M. Von Sivers and G. Zacchi, *Bioresource Technology*, 1996, **56**, 131-140.

64. L. R. Lynd, R. T. Elamder and C. E. Wyman, *Applied Biochemistry and Biotechnology*, 1996, **57**, 741-761.

65. D. S. D. G. (DSD), *Journal*, 2005.

66. R. Wooley, M. Ruth, J. Sheehan, K. Ibsen, H. Majdeski and A. Galvez, *Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis current and futuristic scenarios*, DTIC Document, 1999.

67. J. Pickett, D. Anderson, D. Bowles, T. Bridgwater, P. Jarvis, N. Mortimer, M. Poliakoff and J. Woods, *The Royal Society, London, UK*, 2008.

68. T. Ezeji, N. Qureshi and H. Blaschek, *Applied microbiology and biotechnology*, 2004, **63**, 653-658.

69. A. Van Der Westhuizen, D. T. Jones and D. R. Woods, *Applied and environmental microbiology*, 1982, **44**, 1277-1281.

70. M. Kumar and K. Gayen, *Applied Energy*, 2011, **88**, 1999-2012.

71. N. Qureshi and H. Blaschek, *Journal of Industrial Microbiology and Biotechnology*, 2001, **27**, 292-297.

72. H. Liu, G. Wang and J. Zhang, *Journal*, 2013, 175-198.

73. T. Ezeji and H. P. Blaschek, *Bioresource Technology*, 2008, **99**, 5232-5242.

74. N. Qureshi, B. C. Saha, B. Dien, R. E. Hector and M. A. Cotta, *Biomass and Bioenergy*, 2010, **34**, 559-565.
75. N. Qureshi, B. C. Saha, R. E. Hector, S. R. Hughes and M. A. Cotta, *Biomass and Bioenergy*, 2008, **32**, 168-175.
76. N. Qureshi, B. C. Saha and M. A. Cotta, *Biomass and bioenergy*, 2008, **32**, 176-183.
77. N. Qureshi, T. C. Ezeji, J. Ebener, B. S. Dien, M. A. Cotta and H. P. Blaschek, *Bioresource Technology*, 2008, **99**, 5915-5922.
78. N. Qureshi, B. C. Saha, R. E. Hector, B. Dien, S. Hughes, S. Liu, L. Iten, M. J. Bowman, G. Sarath and M. A. Cotta, *Biomass and Bioenergy*, 2010, **34**, 566-571.
79. S. Liew, A. Arbakariya, M. Rosfarizan and A. Raha, *Malays J Microbiol*, 2006, **2**, 42-50.
80. T. Ezeji, N. Qureshi and H. P. Blaschek, *Process Biochemistry*, 2007, **42**, 34-39.
81. N. Qureshi and I. S. Maddox, *Journal of Fermentation and Bioengineering*, 1995, **80**, 185-189.
82. W.-C. Huang, D. E. Ramey and S.-T. Yang, *Applied biochemistry and biotechnology*, 2004, **115**, 887-898.
83. J. Dernotte, C. Mounaim-Rousselle, F. Halter and P. Seers, *Oil & Gas Science and Technology – Revue de l'Institut Français du Pétrole*, 2009, **65**, 345-351.
84. B. Yuksel, PhD thesis, Ataturk University, 1984.
85. D. American Petroleum Institute. Marketing and D. American Petroleum Institute. Refining, *Alcohols and Ethers: A Technical Assessment of Their Application as Fuels and Fuel Components*, American Petroleum Institute, 1988.
86. K. Owen and T. Coley, *Journal*, 1995.
87. Y. Yacoub, R. Bata and M. Gautam, *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 1998, **212**, 363-379.
88. M. Gautam, D. W. Martin and D. Carder, *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 2000, **214**, 165-182.
89. U. Larsen, T. Johansen and J. Schramm, *Ethanol as a Future Fuel for Road Transportation: Main report*, DTU Mekanik, 2009.
90. F. Chiba, H. Ichinose, K. Morita, M. Yoshioka, Y. Noguchi and T. Tsukagoshi, *High Concentration Ethanol Effect on SI Engine Emission*, SAE Technical Paper, 2010.
91. J. B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, United States, 1988.
92. B. M. Masum, H. H. Masjuki, M. A. Kalam, S. M. Palash, M. A. Wakil and S. Imtenan, *Energy Conversion and Management*, 2014, **88**, 382-390.
93. W.-D. Hsieh, R.-H. Chen, T.-L. Wu and T.-H. Lin, *Atmospheric Environment*, 2002, **36**, 403-410.
94. B. M. Masum, M. A. Kalam, H. H. Masjuki, S. M. A. Rahman and E. E. Daggig, *RSC Advances*, 2014, **4**, 51220-51227.
95. G. Najafi, B. Ghobadian, T. Tavakoli, D. R. Buttsworth, T. F. Yusaf and M. Faizollahnejad, *Applied Energy*, 2009, **86**, 630-639.
96. C.-W. Wu, R.-H. Chen, J.-Y. Pu and T.-H. Lin, *Atmospheric Environment*, 2004, **38**, 7093-7100.
97. B. M. Masum, H. H. Masjuki, M. A. Kalam, S. M. Palash and M. Habibullah, *Journal of Cleaner Production*, 2015, **86**, 230-237.
98. S. Saridemir, *Energy Education Science and Technology Part A: Energy Science and Research* 2012, **30**, 727-736.
99. J. Campos-Fernandez, J. M. Arnal, J. Gomez, N. Lacalle and M. P. Dorado, *Fuel*, 2013, **107**, 866-872.
100. F. Yüksel and B. Yüksel, *Renewable Energy*, 2004, **29**, 1181-1191.
101. R. Bata, A. Elrod and T. Lewandowskia, *SAE Technical Paper 890434*, 1989, DOI: 10.4271/890434.
102. Y. Xialong, Y. Jing and L. Tieping, *International Conference on Energy and Environment Technology*, 2009, 402-405.
103. M. Al-Hasan and M. Al-Momany, *Transport*, 2008, **23**, 306-310.
104. O. Can, I. Celikten and N. Usta, *Journal of Engineering Sciences*, 2005, **11**, 219-224.

105. J. Kumar, D. Trivedi, P. Mahar and R. Butola, *Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, 2013, **7**, 71-78.
106. M. B. Celik, *Applied Thermal Engineering*, 2008, **28**, 396-404.
107. J. Kumar, A. N. A.;, V. Verma and S. Kumar, *American Journal of Engineering Research*, 2013.
108. B. M. Masum, M. A. Kalam, H. H. Masjuki, S. M. Palash and I. M. R. Fattah, *RSC Advances*, 2014, **4**, 27898-27904.
109. A. Dhaundiyal, *International Journal of Applied Science and Engineering Research*, 2014, **3**, 129-152.
110. Y. Varol, C. Oner, H. F. Oztop and S. Altun, *Energy Sources, Part A*, 2014, **36**, 938-948.
111. S. Pukalskas, Z. Bogdanovicius, E. Sendzikiene, V. Makareviciene and P. Janulis, *Transport*, 2009, **24**, 301-307.
112. S. B. Shayan, S. Seyedpour, F. Ommi, S. Moosavy and M. Alizadeh, *International Journal of Automotive Engineering*, 2011, **1**.
113. M. K. Balki, C. Sayin and M. Canakci, *Fuel*, 2014, **115**, 901-906.
114. F. T. Ansari and A. P. Verma, *International Journal of Engineering*, 2012, **1**.
115. A. F. Khieralla, A. B. A. Ibrahim, L. A. Keir, S. M. Lino and V. N. Joeshp, unpublished work.
116. I. M. Rizwanul Fattah, H. H. Masjuki, M. A. Kalam, M. Mofijur and M. J. Abedin, *Energy Conversion and Management*, 2014, **79**, 265-272.
117. T. Topgül, H. S. Yücesu, C. Çinar and A. Koca, *Renewable Energy*, 2006, **31**, 2534-2542.
118. S. Saridemir and T. Ergin, *Energy Education Science and Technology Part A: Energy Science and Research*, 2012, **29**, 1343-1354.
119. A. Elfasakhany, *International Journal of Automotive Engineering*, 2014, **4**, 609-620.
120. S. B. Singh, A. Dhar and A. K. Agarwal, *Renewable Energy*, 2015, **76**, 706-716.
121. D. Turner, H. Xu, R. F. Cracknell, V. Natarajan and X. Chen, *Fuel*, 2011, **90**, 1999-2006.
122. B. Deng, J. Yang, D. Zhang, R. Feng, J. Fu, J. Liu, K. Li and X. Liu, *Applied Energy*, 2013, **108**, 248-260.
123. L. Siwale, L. Kristóf, A. Bereczky, M. Mbarawa and A. Kolesnikov, *Fuel Processing Technology*, 2014, **118**, 318-326.
124. B. Deng, J. Fu, D. Zhang, J. Yang, R. Feng, J. Liu, K. Li and X. Liu, *Energy*, 2013, **60**, 230-241.
125. F. Caiazzo, A. Ashok, I. A. Waitz, S. H. L. Yim and S. R. H. Barrett, *Atmospheric Environment*, 2013, **79**, 198-208.
126. R. Pease, *Journal*, 2012.
127. C. Soruşbay, *Journal*, n.d., 1-14.
128. A. Pikunas, S. Pukalskas and J. Grabys, *Journal of KONES Internal Combustion Engine*, 2003, **10**, 3-4.
129. H. S. Farkade and A. P. Panthre, *International Journal of Emerging Technology and Advanced Engineering*, 2012, **2**, 205-215.
130. C. A. Srinivasan and C. Saravanan, 2010.
131. E. Singh, M. K. Shukla, S. Pathak, V. Sood and N. Singh, *International Journal of Engineering Research & Technology (IJERT)*, 2014, **3**, 993-999.
132. C. D. Cooper and F. C. Alley, Air pollution control a design approach, http://catalog.hathitrust.org/api/volumes/oclc/30488899.html).
133. F. Normann, K. Andersson, B. Leckner and F. Johnsson, *Progress in Energy and Combustion Science*, 2009, **35**, 385-397.
134. A. Ozsezen, A. Turkcan, C. Sayin and M. Canakci, *Energy Exploration and Exploitation*, 2011, **29**, 525-541.
135. M. Canakci, A. N. Ozsezen, E. Alptekin and M. Eyidogan, *Renewable Energy*, 2013, **52**, 111-117.
136. A. N. Ozsezen and M. Canakci, *Energy*, 2011, **36**, 2747-2752.
137. W. Y. Lin, Y. Y. Chang and Y. R. Hsieh, *Journal of the Air & Waste Management Association (1995)*, 2010, **60**, 142-148.

138. E. Zervas, X. Montagne and J. Lahaye, *Environmental science & technology*, 2003, **37**, 3232-3238.
139. S. Liu, E. R. Cuty Clemente, T. Hu and Y. Wei, *Applied Thermal Engineering*, 2007, **27**, 1904-1910.
140. I. Gravalos, D. Moshou, T. Gialamas, P. Xyradakis, D. Kateris and Z. Tsiropoulos, *Renewable Energy*, 2013, **50**, 27-32.
141. I. Schifter, L. Diaz and E. Lopez-Salinas, *Journal of the Air & Waste Management Association (1995)*, 2005, **55**, 1289-1297.
142. E. Zervas and M. Tazerout, *Atmospheric Environment*, 2000, **34**, 3921-3929.
143. E. W. Kaiser, W. O. Siegl, Y. I. Henig, R. W. Anderson and F. H. Trinker, *Environmental science & technology*, 1991, **25**, 2005-2012.
144. G. A. Lavoie and P. N. Blumberg, *Combustion Science and Technology*, 1980, **21**, 225-258.
145. P. A. Lakshminarayanan and Y. V. Aghav, in *Modelling Diesel Combustion*, ed. F. F. Ling, Springer, 2010, ch. 11, pp. 147-166.
146. R. Blint and J. Bechtel, *Hydrocarbon combustion near a cooled wall*, SAE Technical Paper, 1982.
147. W. Daniel, 1957.
148. G. Lavoie, J. LoRusso and A. Adamczyk, in *Combustion Modeling in Reciprocating Engines*, Plenum Press, 1980, p. 409.
149. J. LoRusso, E. Kaiser and G. Lavoie, 1981.
150. F. Alasfour, *Energy Sources*, 1999, **21**, 379-394.
151. W. Daniel, *Engine variable effects on exhaust hydrocarbon composition (a single-cylinder engine study with propane as the fuel)*, SAE Technical Paper, 1967.
152. J. Wentworth, *Piston and ring variables affect exhaust hydrocarbon emissions*, SAE Technical Paper, 1968.
153. W. W. Pulkrabek, *Engineering fundamentals of the internal combustion engine*, Prentice Hall Upper Saddle River, NJ, 1997.
154. E. Kaiser, J. LoRusso, G. Lavoie and A. Adamczyk, *Combustion Science and Technology*, 1982, **28**, 69-73.
155. E. Kaiser, A. Adamczyk and G. Lavoie, 1981.
156. G. Carrier, F. Fendell and P. Feldman, 1981.
157. H. S. Yücesu, T. Topgül, C. Çinar and M. Okur, *Applied Thermal Engineering*, 2006, **26**, 2272-2278.
158. C. Sayin, *Fuel*, 2010, **89**, 3410-3415.
159. A. Yasar, *Metalurgija*, 2010, **49**, 335-338.
160. A. B. Taylor, D. P. Moran, A. J. Bell, N. G. Hodgson, I. S. Myburgh and J. J. Botha, *Gasoline/alcohol blends: exhaust emissions, performance and burn-rate in a multi-valve production engine*, SAE Technical Paper, 1996.
161. M. A. Ceviz and F. Yüksel, *Applied Thermal Engineering*, 2005, **25**, 917-925.
162. M. Thompson, *Journal*, 2005.
163. B. Wigg, R. Coverdill, C.-F. Lee and D. Kyritsis, *Emissions characteristics of neat butanol fuel using a port fuel-injected, spark-ignition engine*, SAE Technical Paper, 2011.
164. H. Bayindir, H. Yücesu and H. Aydin, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2010, **33**, 49-56.
165. N. Mittal, R. L. Athony, R. Bansal and C. Ramesh Kumar, *Alexandria Engineering Journal*, 2013, **52**, 285-293.
166. R. Feng, J. Fu, J. Yang, Y. Wang, Y. Li, B. Deng, J. Liu and D. Zhang, *Renewable Energy*, 2015, **81**, 113-122.
167. B.-Q. He, W. Jian-Xin, J.-M. Hao, X.-G. Yan and J.-H. Xiao, *Atmospheric Environment*, 2003, **37**, 949-957.

168. R. W. Rice, A. K. Sanyal, A. C. Elrod and R. M. Bata, *Journal of Engineering for Gas Turbines and Power*, 1991, **113**, 377-381.
169. X. Gu, Z. Huang, J. Cai, J. Gong, X. Wu and C.-f. Lee, *Fuel*, 2012, **93**, 611-617.
170. R. Feng, J. Yang, D. Zhang, B. Deng, J. Fu, J. Liu and X. Liu, *Energy Conversion and Management*, 2013, **74**, 192-200.
171. M. Pechout, M. Mazac and M. Vojtisek-Lom, *Effect of higher content n-butanol blends on combustion, exhaust emissions and catalyst performance of an unmodified SI vehicle engine*, SAE Technical Paper, 2012.
172. P. Zarante, M. J. Da Silva, O. S. Valente and J. R. Sodré, *vol*, 2011, **9**, 35-39.
173. R. Magnusson, C. Nilsson and B. Andersson, *Environmental science & technology*, 2002, **36**, 1656-1664.
174. H.-R. Chao, T.-C. Lin, M.-R. Chao, F.-H. Chang, C.-I. Huang and C.-B. Chen, *Journal of Hazardous Materials*, 2000, **73**, 39-54.
175. G. Rideout, M. Kirshenblatt and C. Prakash, *Emissions from methanol, ethanol, and diesel powered urban transit buses*, SAE Technical Paper, 1994.
176. T. Wallner and R. Frazee, *Study of regulated and non-regulated emissions from combustion of gasoline, alcohol fuels and their blends in a DI-SI engine*, SAE Technical Paper, 2010.
177. T. Wallner, N. Shidore and A. Ickes, 2010.
178. I. Coordinating Research Council, *Intermediate-level ethanol blends engine durability study*, 2012.
179. F. Tester, *Journal*, 2009.
180. D. Hilbert, *Contract*, 2011, **303**, 275-3000.
181. H. Jessen, *Journal*, 2013.
182. N. Marek and J. Evanoff, 2001.
183. A. C. Hansen, Q. Zhang and P. W. L. Lyne, *Bioresource Technology*, 2005, **96**, 277-285.
184. S. Jaroonjitsathian, N. Akarapanjavit, S. S. Sa-norh and S. Chanchaona, *Investigation of 2-Wheeler Performance, Emissions, Driveability and Durability: Effect of Ethanol-Blended Gasoline*, SAE Technical Paper, 2007.
185. T. Cousseau, J. Sebastian and A. Sinatora, Lyon, France, 2015.
186. C. Wyman, *Handbook on bioethanol: production and utilization*, CRC press, 1996.
187. Z. Stephian and S. Oleksiak, *Journal*, 2014.
188. C. Argakiotis, R. Mishra, C. Stubbs and W. Weston, *Renewable Energy and Power Quality Journal*, 2014.
189. M. Boons, R. Van den Bulk and T. King, *The impact of E85 use on lubricant performance*, Report 0148-7191, SAE Technical Paper, 2008.
190. R. E. Cantley, *Asle Transactions*, 1977, **20**, 244-248.
191. E. Tomanik, *Some tribological issues on flex-fuel engines*, MAHLE Metal Leve SA, Sao Paulo, Brazil, 2012.
192. H. L. Costa and H. Spikes, *Tribology Transactions*, 2015, **58**, 158-168.

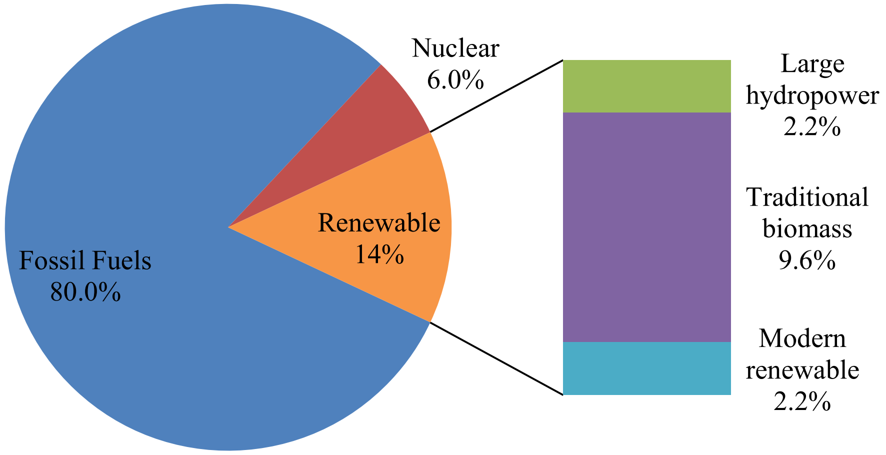


Fig. 1 Fuels contribution to total world energy consumption [3].

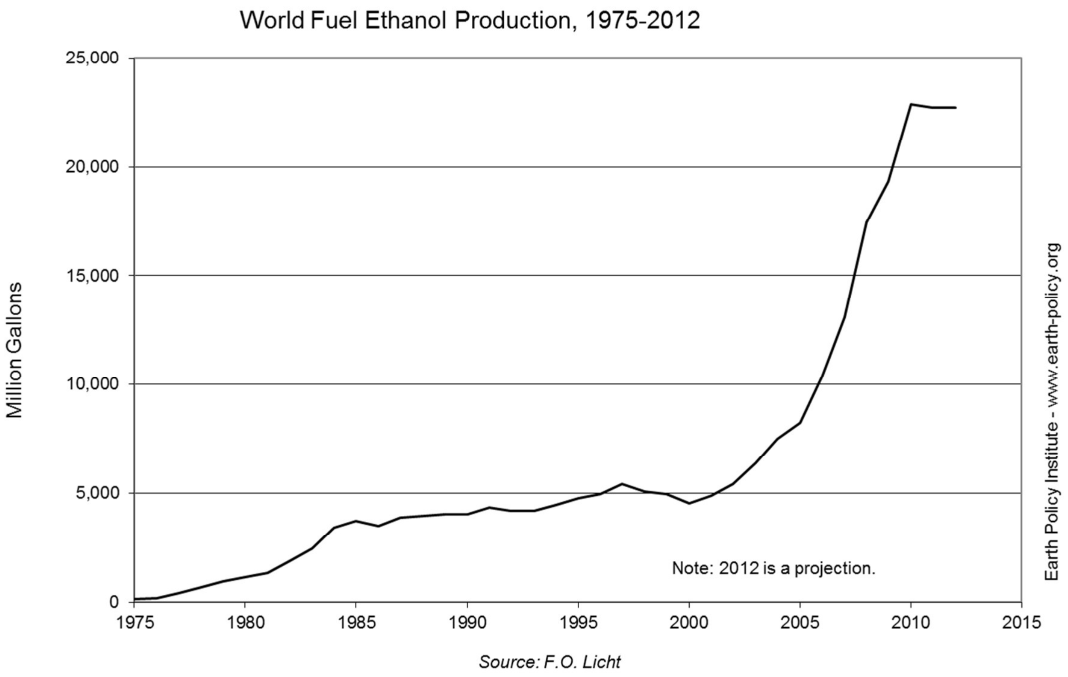


Fig. 2 Graph of world fuel ethanol production, 1975-2012 [25].

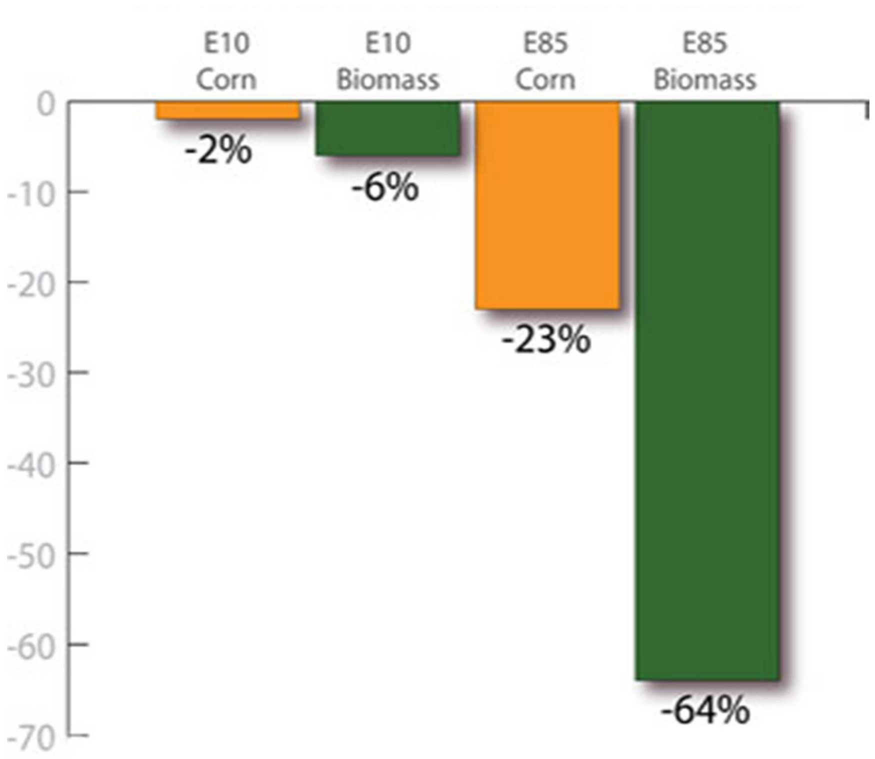


Fig. 3 Reduction of Greenhouse Gas (GHG) emissions from cellulosic bioethanol and corns-derived bioethanol blends [50].

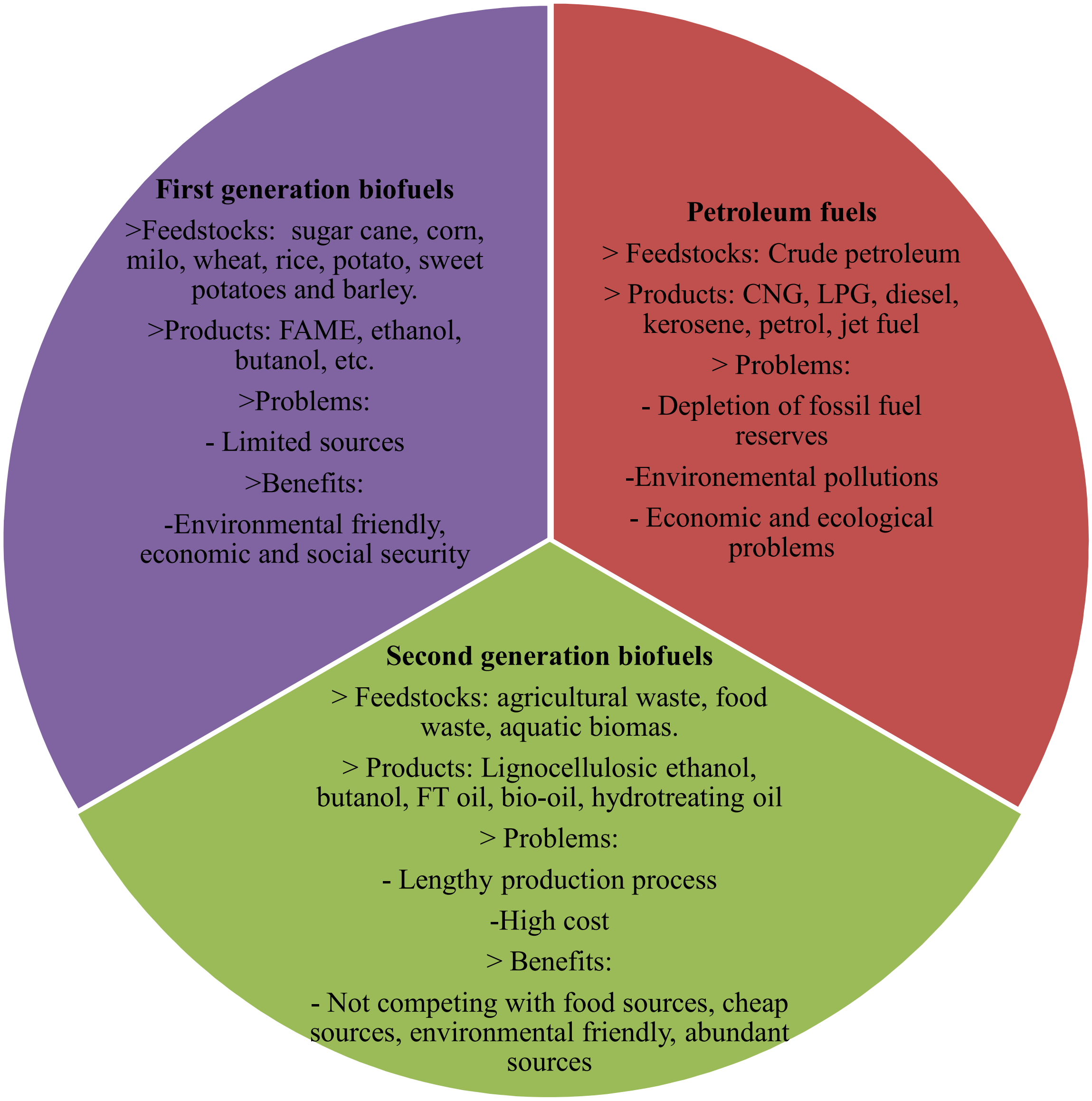


Fig. 4 Comparison of the petroleum refinery products, first and second generation of the biofuels production [47].

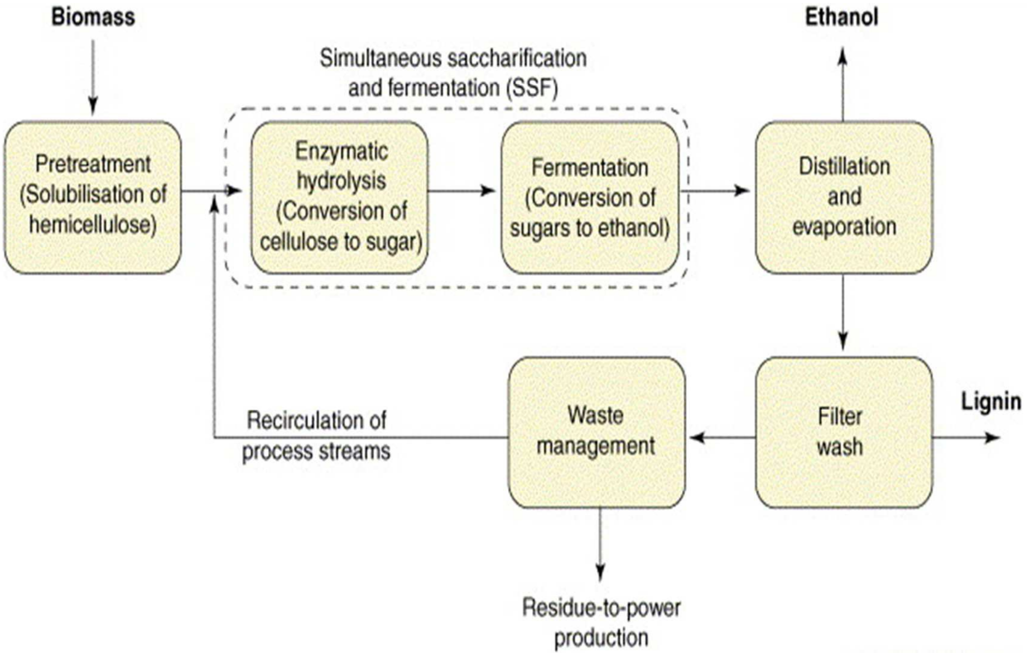


Fig. 5 Production process for bioethanol from lignocellulosic biomass [51].

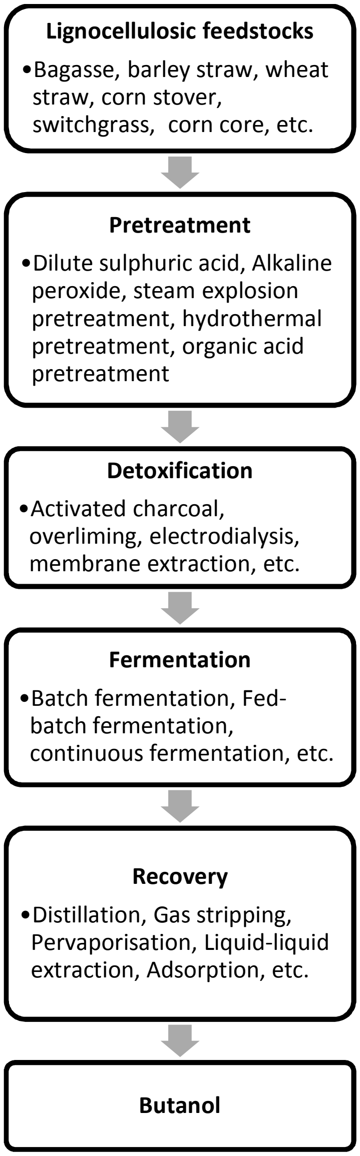
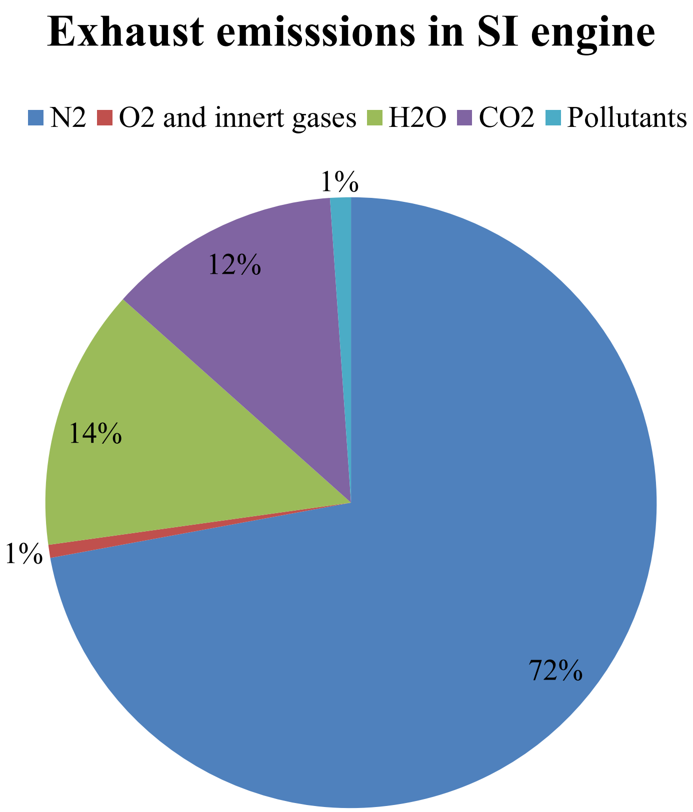


Fig. 6 Production process for biobutanol from lignocellulosic feedstocks [72, 73].



| SI engines | |
|---|---|
| **Pollutants** | (%) |
| PM | 0.0008 |
| NOx | 0.13 |
| HC | 0.09 |
| CO | 0.90 |

Fig. 7 The pie chart of exhaust emissions in SI engine [127].

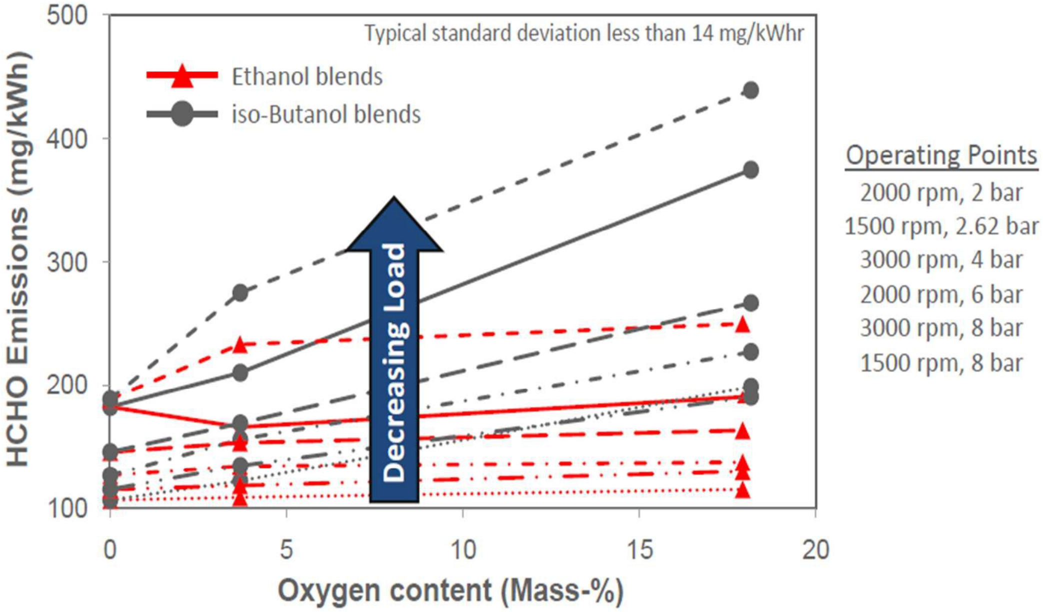


Fig. 8 Graph of formaldehyde emissions for isobutanol and ethanol fuel blends [177].

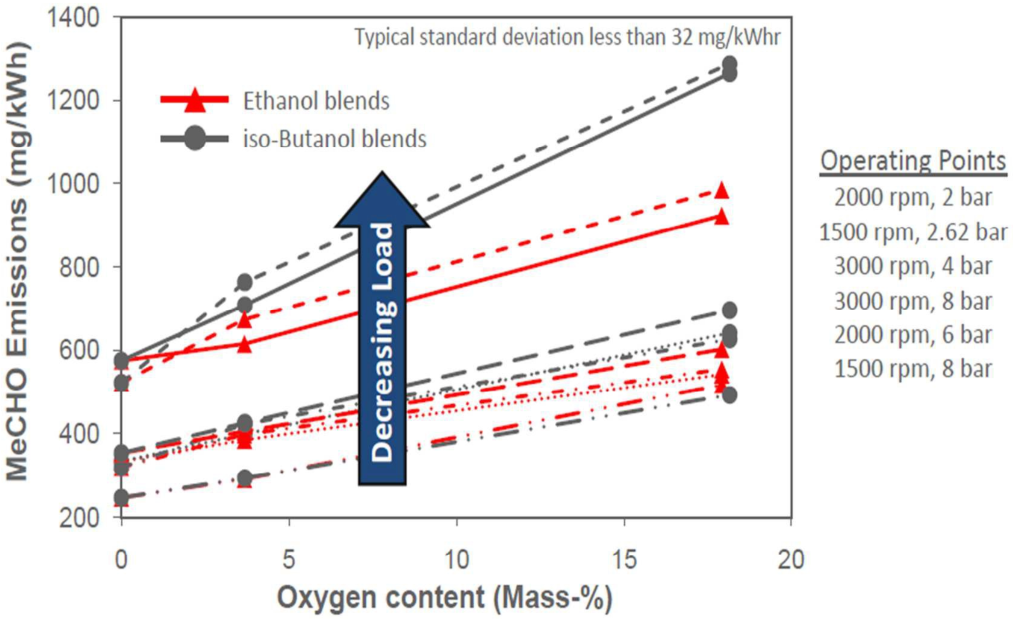


Fig. 9 Graph of acetaldehyde emissions for isobutanol and ethanol fuel blends [177].

(a) E0 piston

(b) E15 piston

Fig. 10 Piston carbon deposit comparison for cylinder 2 [180].

Fig. 11 Connecting rod carbon deposit comparison for cylinder 2, E0 connecting rod on Left, E15 connecting rod on Right [180].

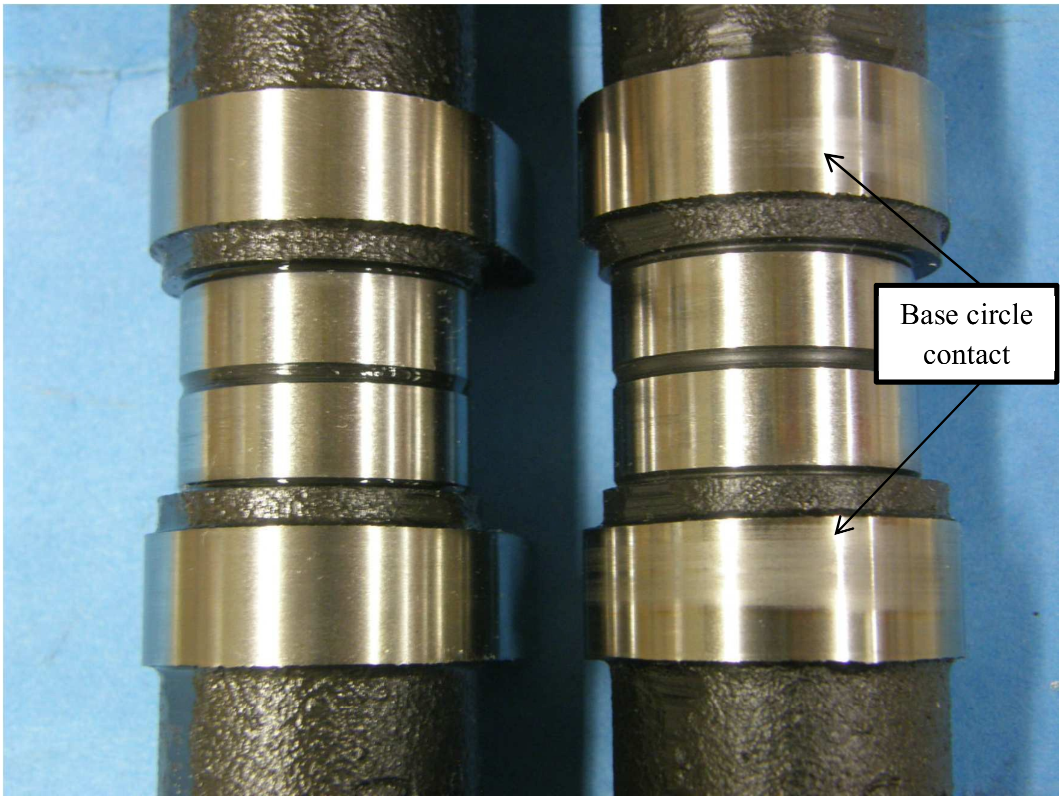


Fig. 12 Exhaust cam lobes base circle details for cylinder 3, E0 cam lobe on Left, E15 cam lobe on Right [180].

Table 1 Bioethanol-gasoline fuel blends used in different countries [8, 35].

| **Country** | **Bioethanol-gasoline fuel blend** |
|---|---|
| Angola | E10 |
| Argentina | E5 |
| Australia | E4: The blends are used in South wales<br>E5: The blends are used in Queensland |
| Brazil | E25-E75: Higher blends are used for flex fuel vehicles<br>E100 |
| Canada | E5: The blends are used in National; British Columbia, Alberta & Ontario provinces<br>E7.5: The blends are used in Saskatchewan province<br>E8.5: The blends are used in Manitoba province |
| Colombia | E8 |
| Costa Rica | E7 |
| Ethiopia | E5 |
| Guatemala | E5 |
| India | E5 |
| Indonesia | E3 |
| Jamaica | E10 |
| Malawi | E10 |
| Malaysia | Not available |
| Mozambique | E10: The blends are used in 2012-2012<br>E15: The blends are expected to be used in year 2016-2020<br>E20: The blends are expected to be used in year 2021 onwards |
| Paraguay | E24 |
| Peru | E7.8 |
| Philippines | E10 |
| South Africa | E10 |
| South Korea | Not available |
| Sudan | E5 |
| Thailand | E5 |
| Turkey | E2 |
| United States | E10 (gasohol): The blends used in Missouri, Montana, Florida, Hawaii, New Mexico, Oregon states<br>E70-E85: Blends varies with states |
| Uruguay | E5: The blends are expected to be used in 2015 |
| Vietnam | E5 |
| Zambia | E10 |

**E2: 2 vol% ethanol-98 vol% gasoline; E3: 3 vol% ethanol-97 vol% gasoline; E4: 4 vol% ethanol-96 vol% gasoline; E5: 5 vol% ethanol-95 vol% gasoline; E7: 7 vol% ethanol-93 vol% gasoline; E7.5: 7.5 vol% ethanol-92.5 vol% gasoline; E7.8: 7.8 vol% ethanol-92.2 vol% gasoline; E8: 8 vol% ethanol-92 vol% gasoline; E8.5: 8.5 vol% ethanol-91.5 vol% gasoline; E10: 10 vol% ethanol-90 vol% gasoline; E15: 15 vol% ethanol-85 vol% gasoline; E20: 20 vol% ethanol-80 vol% gasoline; E25: 25 vol% ethanol-75 vol% gasoline; E75: 75 vol% ethanol-25 vol% gasoline; E85: 85 vol% ethanol-15 vol% gasoline; E100: 100 vol% ethanol or pure ethanol**

Table 2 Molecular structure and main application of butanol isomers [36, 40, 41]

| Butanol isomers | Molecular structure | Main applications |
|---|---|---|
| 1-butanol (n-butanol) | $CH_3$-$CH_2$-$CH_2$-$CH_2OH$ | Solvents – for paints, resins, dyes, etc.<br>Plasticizers – improve plastic process<br>Chemical intermediate – for butyl esters or butyl ethers etc.<br>Cosmetics – eye makeup, lipsticks<br>Gasoline additive |
| Sec-butanol (2-butanol) | $CH_3CH(OH)CH_2CH_3$ | Solvents<br>Chemical intermediate – for butanone, etc.<br>Industrial cleaners – paint removers<br>Perfumes or in artifial flavors |
| tert-butanol | $(CH_3)_3COH$ | Solvent<br>Denaturant for ethanol<br>Industrial cleaners – paint removers<br>Gasoline additives – for octane booster and oxygenate<br>Chemical intermediate – for MTBE, ETBE, TBHP, etc. |
| Isobutanol | $CH_3(CH_2)_3OH$ | Solvent and additive – for paint<br>Gasoline additive<br>Industrial cleaners – paint removers<br>Ink ingredient |

Table 3 Biomass feedstocks and their potential ethanol yield [46, 47].

| **Feedstocks** | **Potential ethanol yield, (litre/dry tones of feedstock)** |
|---|---|
| Corn grain | 470 |
| Corn stover | 428 |
| Rice straw | 416 |
| Cotton gin trash | 215 |
| Forest thinnings | 309 |
| Hardwood sawdust | 382 |
| Baggase | 437 |
| Mixed paper | 440 |
| Switchgrass* | 366 |

*** Switchgrass Alamo Whole Plant**

**Source: U.S. Department of Energy Biomass Program, Theoretical Ethanol Yield Calculator and Biomass Feedstock Composition and Property Database**

Table 4 Bioethanol routes from different raw material of feedstocks [14].

| Raw materials | Process |
|---|---|
| Wood | Acid hydrolysis and fermentation |
| Wood | Enzymatic hydrolysis and fermentation |
| Straw | Acid hydrolysis and fermentation |
| Straw | Enzymatic hydrolysis and fermentation |
| Wheat | Malting and fermentation |
| Sugar cane | Fermentation |
| Sugar beet | Fermentation |
| Corn grain | Fermentation |
| Corn stalk | Acid hydrolysis and fermentation |
| Sweet sorgum | Fermentation |

Table 5 Estimation costs of the bioethanol production from different feedstocks (exclusive of taxes) [14, 67].

| | **Year 2006** | **Long term about 2030** |
|---|---|---|
| Price of oil, US$/ barrel | 50-80 | |
| Corresponding pre-tax price of petroleum products, US cents/L | 35-60[a] | |
| Corresponding price of petroleum products with taxes included, | 150-200 in EU[b] | |
| US cents/L (retail price) | About 80 in USA | |
| Bioethanol from sugar cane | 25-50 | 25-35 |
| Bioethanol from corn | 60-80 | 35-55 |
| Bioethanol from beet | 60-80 | 40-60 |
| Bioethanol from wheat | 70-95 | 45-65 |
| Bioethanol from lignocellulose | 80-110 | 25-65 |

**[a] Note range differs from row 1, for several factors such as refinery costs.**

**[b] Excluding a few outliers above and below the range.**

Table 6 Comparison of biomass feedstocks and their potential biobutanol yield/ productivity via different fermentation process [40, 70].

| **Feedstocks or substrates** | **Fermentation process** | **Strain used** | **Yield (g/g)/ productivity (g/ L.h)** | **Maximum titer of ABE (g/L)** | **Ref** |
|---|---|---|---|---|---|
| Barley straw | Batch fermentation | C. beijerinkii P260 | 0.43/ 0.39 | 26.64 | 73 |
| Wheat straw | Batch fermentation | C. beijerinkii P260 | 0.41/ 0.31 | 21.42 | 74 |
|  | Fed-batch fermentation | C. beijerinkii P260 | -/ 0.36 | 16.59 | 75 |
| Corn fibers | Batch fermentation | C. beijerinkii BA101 | 0.36-0.39/ 0.10 | 9.3 | 76 |
| Corn stover & switchgrass (1:1) | Batch fermentation | C. beijerinkii P260 | 0.43/ 0.21 | 21.06 | 77 |
| Switchgrass | Batch fermentation | C. beijerinkii P260 | 0.37/ 0.09 | 14.61 | 77 |
| Sago starch | Free cell continuous fermentation | C. saccharobutylicum DSM13864 | 0.29/ 0.85 | 9.1 | 78 |
| Degermed corn | Free cell continuous fermentation | C. beijerinkii BA101 | -/ 0.29-0.30 | 14.28 | 79 |
| Whey permeate | Immobilized cells continues fermentation | C. acetobutylicum P262 | 3.5-3.6/ 0.36-1.10 | 8.6 | 80 |
| Corn | Immobilized cells continues fermentation | C. acetobutylicum ATCC 55025 | 0.42/ 4.6 | 12.50 (butanol) | 81 |
| Sugar beet juice |  | C. beijerinkii CCM 6182 | 0.37/ 0.40 | - | 39 |

Table 7 Physicochemical properties of gasoline, bioethanol and biobutanol.

| **Property** | **Gasoline** | **Bioethanol** | **Biobutanol** | **Ref** |
|---|---|---|---|---|
| Chemical Formula | ~$C_8H_{15.6}$ | $C_2H_5OH$ | $C_4H_9OH$ | 83 |
| Molecular weight | 100-105 | 46.07 | 74.12 | 84, 85 |
| Oxygen content (wt.%) | 0 | 34.73 | 21.59 | 40, 43 |
| Reid vapor pressure, RVP (kPa) | 45-90 | 17 | 2.3 | 40 |
| Research octane number, RON | 95 | 106-130 | 94 | 40, 86 |
| Motor octane number, MON | 85 | 89-103 | 80 | 40 |
| Molar mass (kg/kmol) | 111.21 | 46.07 | 74.12 | 87, 88 |
| Specific gravity at 20$^{o}$C | 0.7392 | 0.7894 | 0.8097 | 87, 88 |
| Boiling point ($^{o}$C) | 30-215 | 78.3 | 117.7 | 40 |
| Flash point ($^{o}$C) | -43 | 8 | 35 | 87 |
| Auto ignition temperature ($^{o}$C) | 257 | 423 | 365 | 87 |
| Stoichiometric air-fuel ratio | 14.8 | 9 | 11.1 | 40 |
| Adiabatic flame temperature ($^{o}$C) | 1970 | 1923 | 1960 | 87 |
| Density (Kg/m$^3$) | 720-750 | 794 | 809 | 40 |
| Low heating value, LHV (MJ/kg) | 44.4 | 28.9 | 33.1 | 40 |
| Heat of vaporization, HoV (MJ/kg) | 0.32 | 0.92 | 0.71 | 40 |
| Kinematic viscosity at 20$^{o}$C (mm$^2$/s) | 0.4-0.8 | 1.5 | 3.6 | 40 |

Table 8 Effects of ethanol and butanol addition into gasoline blends on T, BP, BSFC, BTE and EGT.

| **Engine** | **Tested blend fuel** | **Operating condition** | **T** | **BP** | **BSFC** | **BTE** | **EGT** | **[Ref]** |
|---|---|---|---|---|---|---|---|---|
| Hydra, 1C, CR: 5:1-13:1, d= 80.26 mm, s= 88.9 mm | E0, E50, E85 | Varying speed (1500-5000 rpm); CR: 10:1 and 11:1<br>100% WOT throttle | E% ↑, T ↑. | E%, BP ↑. | E% ↑, BSFC ↑ | - | - | 31 |
| New Sentra GA16DE, 1600 cc, d= 76.0 mm, s=88.0 mm, CR=9.5 | E0, E5, E10, E20, E30 | Varying speed (1000-4000 rpm)<br>Varying throttle(0-100%) | E%, T ↑ | - | Unchanged due to fuel injection strategy | - | - | 93 |
| GA6D, 4C, 1594 cc, CR=10:1, MPI | DAE10, DAE20, DAE30, DAE50, Gasoline | Varying speed (1000-4000 rpm)<br>Throttle fixed at 50% | DAE% ↑, T ↑ | DAE% ↑, BP ↑ | DAE% ↑, BSFC ↑. | DAE% ↑, BTE ↑ | - | 94 |
| 8V-4C inline SOHC,CR= 9.7, d=71 mm, s= 83.6 mm, 1323 cc | E5, E10, E15, E20 (potato waste bioethanol) | Varying speed (1000-5000 rpm) | E%, T ↑ | E%, BP ↑ | E% ↑, BSFC ↑ | E% ↑, BTE ↑ | - | 95 |
| New Sentra GA16DE, 4C, 8V- DOHC, 1600 cc, d=76 mm, s= 88 mm, CR: 9.5 | E0, E5, E10, E20, E30 | Varying speed (3000, 4000 rpm)<br>Vaying throttle (0-100%)<br>WOT | E% ↑, T ↑. | - | - | - | - | 96 |
| Proton Campro, 4C, MPEI, 1596 cc, d=78 mm, s=84 mm, CR=10:1 | Alcohol blends (MaxR, MaxH , MaxD, E15), Gasoline | Varying speed (1000 - 6000 rpm) | T of alcohol blends > gasoline | - | BSFC of alcohol blends > gasoline | BTE of alcohol blends > gasoline | EGT of alcohol blends < gasoline | 97 |

| Engine | Tested blend fuel | Operating condition | T | BP | BSFC | BTE | EGT | [Ref] |
|---|---|---|---|---|---|---|---|---|
| Proton Campro, 4C, 1596 cc, d=78 mm, s=84 mm, CR=10:1 | Alcohol blends (MaxR, MaxH, MaxD, E15)<br>Gasoline | Varying speed (1000 -6000 rpm)<br>100% load condition | T of alcohol blends > gasoline | - | BSFC of alcohol blends > gasoline | - | - | 92 |
| Gunt CT 100.20, 1C, AC, 4S, CR: 7:1, 400 cc, d=87.3 mm, s= 66.7mm | E0, E10, E20, E30, E40 | Speed at 2500 and 3250 rpm<br>Full throttle 100%<br>Engine oil Temp $90^{o}$C | E% ↑, T ↑. | E%, BP ↑. | E% ↑, BSFC ↑ | - | E% ↑, EGT ↓ | 98 |
| Opel record L, WC, 4C, 1668cc, d=74mm, s = 85 mm, CR=8:1 | E60, UG | Varying engine speed (idle to max speed)<br>Varying throttle 25% -100% | E% ↑, T ↓. | E% ↑, BP ↓. | - | - | - | 100 |
| 1S, Fuel injection, d=56mm, s=49.5mm, CR=9.2 | Bu30, Gasoline | Cooling water temp. $80^{o}$C,<br>Oil temperature > $70^{o}$C<br>Varying speed 3000-8500rpm | $T_{Bu30}$ is comparable to $T_{gasoline}$. | $BP_{Bu30}$ is comparable to $BP_{gasoline}$. | Bu% ↑, BSFC ↑. | - | - | 102 |
| 4C, 1596 cc, d=78 mm, s=84 mm, CR=10:1, MPEFI | M20, E20, P20, Bu20 | Varying speed (1000-6000 rpm)<br>At 100% load condition | T of alcohol blends > gasoline | - | BSFC of alcohol blends > gasoline | BTE of alcohol blends > gasoline | EGT of alcohol blends < gasoline | 108 |
| SI engine, WC, CR= 8, 256.56 cc, d= 70 mm, s= 66.7mm | E0, E10- E35<br>Bu0-Bu35 | Varying engine speed 1000-1500 rpm | - | - | E%↑,BSFC ↑ | E% ↑, BTE ↓<br>Bu% ↑, BTE ↓ | - | 109 |

| Engine | Tested blend fuel | Operating condition | T | BP | BSFC | BTE | EGT | [Ref] |
|---|---|---|---|---|---|---|---|---|
| Lombardini LM 250, 4S, 1C, 250cc, CR= 6-10, AC & WC | E0, E25, E50, E75, E100 | CR= 6/1, speed 2000rpm<br>Full throttle | - | E% 50↑, BP ↑.<br>>E50, BP ↓. | E% ↑, BSFC ↑. | - | - | 106 |
| 4S, 4C,WC, Eddy current dynamometer, CR=9.2:1, d=68.5mm, s= 72mm, | E0, E5, E10, E15, E20 | Varying speed (2100-5000rpm) | - | - | E%↑, BSFC ↑ | - | - | 105 |
| Toyota-Tercel-3A, 4S, 4C, 1452cc, CR=9:1, | E0, E2.5-E25 | Varying speed (1000-4000 rpm) | E% ↑ max 20%, T ↑. | Unchanged | E% ↑ max 20%,BSFC↓. | E% max 20%, BTE ↑. | - | 29 |
| Ford, 4C, 4S, EFI, d= 89mm, s= 95mm, CR= 11.1 | M10, E10, Bu10, Gasoline | Varying speed (1000-4000rpm)<br>Adjust throttle position to maintain the same break T. | - | - | BSFC of alcohol blends > gasoline | BTE of alcohol blends < gasoline | EGT of alcohol blends > gasoline | 110 |
| Otto engine, 1392cc, CR= 9.5, d=73.5mm, s= 82mm | Bu0, Bu30, Bu50, | Varying speed (2500-4000rpm) | - | - | Bu% ↑, BSFC ↑. | - | - | 111 |
| Honda D16Z6 engine, 4C, 16 valves, 1600cc, CR=9.6 | Bu0, Bu20, Bu40, Bu60, Bu80 | Speed at 2000rpm,<br>BMEP of 262kPa,<br>IMEP of 3.2 bars. | - | - | Bu% ↑, BSFC ↑. | - | - | 83 |
| LPGE (DATSU LT 200), 1C, 4S, AC, CR= 8.5 | M100, E100, Gasoline | Varying speed<br>Full throttle | T of alcohol blends > gasoline | - | BSFC of alcohol blends > gasoline | BTE of alcohol blends > gasoline | - | 113 |

| Engine | Tested blend fuel | Operating condition | T | BP | BSFC | BTE | EGT | [Ref] |
|---|---|---|---|---|---|---|---|---|
| Waukesha, 1C, d= 8.26cm, s= 11.43cm, 612cc, | Gasoline, M, E, Bu, Pe and Pr blends | Speed 1000 rpm<br>Wide open throttle | - | - | BSFC of all blends > gasoline , except E2.5 | No. carbon of alcohol ↑, BTE ↓ | - | 87 |
| 1C, 4S, enfield, AC, WC, d= 70mm, s= 60mm, CR= 10 | E0, E20, E40, E60, E80, E100 | Varying engine load (0, 440, 880, 1320, 1760, 2200 W)<br>Constant speed 2800rpm. | - | - | E% ↑, BSFC ↑. | BTE alcohol blends > gasoline | E% ↑, EGT ↓. | 114 |
| Honda EMS3000 gasoline generator, 1C, 4S, AC, 272cc, d= 76mm, s= 95mm | E0, E10, E15, E20, E25 | Varying loads ( 0-100%) | E% ↑, T ↓. | E% ↑, BP ↓. | E% ↑, BSFC ↓. | E% ↑, BTE ↓. | - | 115 |
| Hydra, 1C, CR: 5:1-13:1, d= 80.26 mm, s= 88.9 mm | E0, E10, E20, E40, E60 | Varying CR 8:1, 9:1, 10:1<br>Constant speed 2000 rpm<br>Full throttle | E% ↑, T ↑. | - | E% ↑, BSFC ↑ | - | E% ↑, EGT ↓. | 117 |
| 1C, 4S, AC, d= 65.1mm, s= 44.4mm, CR= 7, 600cc | E0, E3, E7, E10 | Varying speed (2600-3500rpm)<br>Full throttle | E% ↑, T ↑. | - | BSFC of blends > gasoline | - | E% ↑, EGT ↓. | 119 |
| Zen/Maruti Suzuki, 3C, 4S, WC, MPFI, 993cc, d= 72mm, s= 61mm, CR= 8.8 | Bu0, Bu5, Bu10, Bu20, Bu 50, Bu75 | Varying speed (1500-4500 rpm)<br>Varying torque (0-66Nm) | - | - | Bu% ↑, BSFC ↑. | Bu% ↑, BTE ↓. | Bu% ↑, EGT ↓. | 120 |

**MPI/ MPFI= Multiport fuel injection, DI= Direct injection, MPEI= Multipoint electronic injection, MFIE= Multiport fuel injection engine, EFI= Electronic fuel injection, C= cylinder, S= stroke, d= bore, CR= compression ratio, WC= water cooled, AC= air cooled, ↓= decrease, ↑= increase, E= Ethanol, M=Methanol, Bu= Butanol, Pr= Propanol, Pe= Pentanol, DAE= Denatured anhydrous ethanol, MaxH= Maximum heating value optimum blend, MaxR= Maximum research octane number optimum blend, MaxD= Maximum petroleum displacement optimum blend**

Table 9 Effect of ethanol and butanol addition into gasoline blends on in cylinder pressure ICP and HRR.

| Engine | Tested blend fuel | Operating condition | ICP | HRR | [Ref] |
|---|---|---|---|---|---|
| 1.4L, Fiat FFV engine | E0, E30, E50, E80, E100 | Varying speed (1500-4500 rpm)<br>Varying torque (60 , 105 Nm) | E% ↑, ICP ↑. | E% ↑, HRR ↑. | 28 |
| LPGE (DATSU LT 200), 1C, 4S, AC, CR= 8.5 | M100, E100, Gasoline | Varying speed<br>Full throttle | ICP of alcohol blends higher than gasoline | HRR of alcohol blends higher than gasoline | 113 |
| 1C, 4S SI engine, d= 56 mm, s= 49.5, 121.9 cc, CR: 9.2 | Bu35, Gasoline | Full load<br>Varying speed (3000-8500 rpm) | Bu35 gives higher ICP than gasoline | - | 122 |
| Suzuki RS-416 1.6L, model T10M16A, d= 78 mm, s= 83 mm, CR= 11.1, 4C, 4V, MPI | Gasoline, M20, M70, M53Bu17 | Lamda 1.1<br>Constant speed 2500 rpm<br>Load 2.4-7.8 bars | Alcohols give higher ICP than gasoline | Alcohols give higher HRR | 123 |
| Proton Campro, 4C, 1596 cc, d=78 mm, s=84 mm, CR=10:1 | Alcohol blends (MaxR, MaxH, MaxD, E15)<br>Gasoline | Varying speed (1000 -6000 rpm)<br>100% load condition | ICP of alcohol blends higher than gasoline | HRR of alcohol blends higher than gasoline | 92 |
| 4V, 1C, d= 90 mm, s= 88.9mm, CR= 11.5:1, DI | E0, E10, E20, E30, E50, E85, E100 | Constant speed 1500 rpm<br>Constant load 3.4 bar IMEP | Ethanol have higher ICP than gasoline | E% ↑, HRR ↑. | 121 |
| 4S, 1C, AC, 121.9 cc, d= 56 mm, s= 49.5 mm, CR= 9.2 | Bu30, Bu35, Bu0 | Full load<br>Varying speed (3000 to 8500 rpm) | Bu% ↑, ICP ↑. | Bu% ↑, HRR ↑. | 124 |

**MPI/ MPFI= Multiport fuel injection, DI= Direct injection, FFV= Flex fuel vehicle, C= cylinder, S= stroke, d= bore, CR= compression ratio, WC= water cooled, AC= air cooled, ↓= decrease, ↑= increase, E= Ethanol, M=Methanol, Bu= Butanol, MaxH= Maximum heating value optimum blend, MaxR= Maximum research octane number optimum blend, MaxD= Maximum petroleum displacement optimum blend**

Table 10 Effect of ethanol and butanol addition into gasoline blends on exhaust emissions of $CO_2$, $NO_x$, HC, CO.

| Engine | Tested blend fuel | Operating condition | $CO_2$ | $NO_x$ | HC | CO | [Ref] |
|---|---|---|---|---|---|---|---|
| 4E-FE DOHC 16V engine, 1332 cc, CR = 9.8, MPI fuel system | E0, E10 | Full load<br>Varying speed (1500-6500 rpm) | E10 > E0 ($CO_2$ ↑ by 5-10%) | - | E10 < E0 up to 5800 rpm | E10 < E0 (CO ↓ by 10-30%) | 128 |
| Opel record L, WC, 4C, 1668cc, d=74mm, s = 85 mm, CR=8:1 | E60, E0 | Varying engine speed (idle to max speed)<br>Varying throttle 25% -100% | E% ↑, $CO_2$ (↑ 20%). | - | E% ↑, HC (↓ 80%). | E% ↑, CO (↓ 50%). | 100 |
| Greaves MK-25, 1C, CR = 2.5 to 8, d= 70mm, s= 66.7mm, AC, WC | M5, M10, M15, E7, E14, E19, Bu12, Bu23, Bu35, gasoline | Constant speed 3000 rpm<br>Load from 0 to full load | M%, E%, Bu% ↑, $CO_2$ ↑. | - | M%, E%, Bu% ↑, HC ↓. | M%, E%, Bu% ↑, CO ↓. | 129 |
| Make Maruti Wagon- R MPFI, 4C, 4S, s= 61mm, d= 72mm, 1100cc, CR= 9.4 | E5, E10, E15, E20 | Varying speed (2100-5000 rpm)<br>Varying load (no load and with load 5kg) | E% ↑, $CO_2$ ↓. | - | E% ↑, HC ↑. | - | 107 |
| 3C, 4S, d= 86.5mm, s= 72mm, 796cc, CR= 8.7, WC | E60+2.0, E50+1.0 isoheptanol additives | Varying speed (2000-2800 rpm) | E% ↑, $CO_2$ ↓. | E% ↑, NOx ↓ | E% ↑, HC ↓ | E% ↑, CO ↓. | 130 |
| Birla Ecogen Genset, 4S, AC, 1C, d= 73mm, s= 61mm, 256cc, CR= 5.1 | E10, Bu10, gasoline | At constant speed 3000rpm | $CO_2$ from Bu10 < gasoline and E10 | NO from E10 > gasoline and Bu10 | HC from E10 < Bu10 < gasoline | CO from E10 < Bu10 < gasoline | 131 |

| Engine | Tested blend fuel | Operating condition | $CO_2$ | $NO_x$ | HC | CO | [Ref] |
|---|---|---|---|---|---|---|---|
| Proton Campro, 4C, MPEI, 1596 cc, d=78 mm, s=84 mm, CR=10:1 | Alcohol blends, MaxR, MaxH, MaxD,E15, Gasoline | Varying speed (1000 - 6000 rpm) | - | NOx of E15 > optimized blends > gasoline | HC of alcohol blends < gasoline | CO of alcohol blends < gasoline | 97 |
| Chasis dynamometer 1.4i SI engine Honda Civic, 4S, WC, MPI, 1398cc, CR= 10.4, d= 75mm, s= 79mm | E5, E10, M5, M10 | Drive at speed 4 manually with gear ratio 1:1<br>4 diff wheel power 5-20kW<br>At 2 different speeds of 80 km/h and 100 km/h | M%, E% ↑, $CO_2$ ↓ at 80km/h except M10 at 100km/h | M%, E% ↑, NOx ↓ at 80km/h except M10 at 100km/h | M%, E% ↑, HC ↓ at 80 km/h and 100km/h | M%, E% ↑, CO ↓ at 80 km/h. | 135 |
| Honda GX 160, 1C SI engine, 4S, AC, d= 68mm, s= 45mm, CR= 8.5, 163cc | E0, E3, E6, E9 | Constant speed of 3600rpm<br>Varying power 865, 1730 and 2595W | - | E% ↑, NOx ↓. | E% ↑, HC ↓. | E% ↑, CO ↓. | 137 |
| 1C, 4S SI engine, Jaguar guided DI, d= 90mm, s=88.9mm, 565.6cc, CR=11.5 | E0, E10, E20, E30, E50, E85, E100 | Oil temp 85±3 °C<br>Water temp 93±3 °C<br>Constant speed 1500 rpm<br>Constant load 3.4bar IMEP | - | For 1 injection; E% ↑, NOx ↓.<br>For split injection; E100, NOx ↑. | E% ↑, HC ↓. | For 1 injection; E% ↑, CO ↓.<br>For split injection; E85 and E100, CO ↑. | 121 |
| 3 different groups;<br>GT-1; 1989-1990 MY<br>GT-2;12 1993-1998 MY<br>GT-3; 14 1999-2002 MY<br>Chasis dynamometer; Horiba ECDM-48 electric dynamometer | Gasoline blends; L-MTBE, H-MTBE, E, H-AROM, H-OLEF, L-SULF, M-SULF, H-SULF, METRO, Rest Country | Fuels were tested randomly for each vehicle except for sulphur content which tested from low to high sulphur. | - | Small increase of NOx from oxygenated compounds L-MTBE and E. | - | E% ↑, CO ↓ (3-6%) compared to MTBE. | 141 |

| Engine | Tested blend fuel | Operating condition | $CO_2$ | $NO_x$ | HC | CO | [Ref] |
|---|---|---|---|---|---|---|---|
| 1C, 4S SI engine, WC, 763cc, d= 90mm, s= 120mm | For experiment;<br>E1.5 to E12.<br>For numerical;<br>blends up to E21 | Constant speed at 1500rpm<br>Varying CR= 7.75 and 8.25<br>At full throttle condition | - | E% ↑, NO ↑. | - | E% ↑, CO ↓. | 30 |
| Waukesha, 1C, d= 8.26cm, s= 11.43cm, 611.7cc, | Gasoline, M, E, Bu, Pe and Pr blends | Speed 1000 rpm<br>Wide open throttle | $CO_2$ of alcohol and gasoline are almost identical. | NOx of alcohol > gasoline (12-16%) | HC of alcohol < gasoline | CO of alcohol and gasoline are almost identical. | 88 |
| Hydra, 1C, CR: 5:1-13:1, d= 80.26 mm, s= 88.9 mm | E0, E50, E85 | Varying speed (1500-5000 rpm); CR: 10:1 and 11:1<br>100% WOT throttle | - | E% ↑, $NO_x$ ↓. | E% ↑, HC ↓. | E% ↑, CO ↓. | 31 |
| Hydra, 1C, CR: 5:1-13:1, d= 80.26 mm, s= 88.9 mm | E0, E10, E20, E40, E60 | Varying speed (2000, 3000, 5000 rpm)<br>At full throttle WOT<br>Varying 6 CR (8:1 - 13:1) | - | - | E% ↑, HC ↓. | E% ↑, CO ↓. | 157 |
| Hydra, 1C, CR: 5:1-13:1, d= 80.26 mm, s= 88.9 mm | E0, E10, E20, E40, E60 | Varying CR; 8:1, 9:1, 10:1<br>Constant speed 2000 rpm<br>At full throttle | - | - | E% ↑, HC ↓. | E% ↑, CO ↓. | 117 |
| Lombardini 1C SI engine, CR= 8.6, 349 cc, AC, d= 82mm, s= 66mm, 4S | M5, M15, M25, M35, M50, Bu5, Bu15, Bu25, Bu35, Bu50, gasoline | Constant speed 3000rpm<br>Varying load 800, 1600 and 2400W | M% ↑ up to 25%, $CO_2$ ↑.<br>$CO_2$ of Bu% blend almost same to gasoline | M% ↑, $NO_x$ ↓.<br>NOx of Bu% blend almost same to gasoline | M% ↑and Bu% ↑, HC ↓. | M% ↑and Bu% ↑, CO ↓. | 159 |

| Engine | Tested blend fuel | Operating condition | $CO_2$ | $NO_x$ | HC | CO | [Ref] |
|---|---|---|---|---|---|---|---|
| FIAT 4C, 4S, d= 86.4mm, s= 67.4mm, CR= 9.2, 1581cc, WC | E0, E5, E10, E15, E20 | Oil temp 50$^{o}$C + 5<br>Constant speed 2000rpm | E% ↑ up to 10%, $CO_2$ ↑. | - | E% ↑ up to 10%, HC ↓. | E% ↑ up to 10%, CO ↓. | 161 |
| Briggs and Stratton 1C 4S SI engine, d= 79.24mm, s= 61.27mm, 305cc, CR= 8.1 | Gasoline, Bu10, Bu15 | Constant engine speed<br>Varying loads<br>Coated and uncoated engine head. | - | NO ↑ for all Bu% in coated engine compared to uncoated head | Bu% ↑, HC ↓ for both coated and base engine. | CO ↓ for all Bu% in coated engine compared with uncoated head. | 165 |
| 1C, 4S SI motorcycle engine, CR= 9.2 | Gasoline, Bu30. Bu35 | Varying speed 3000 to 8500 rpm, full load,<br>Max break torque | Bu% ↑, $CO_2$ ↑. | Bu% ↑, $NO_x$ ↑. | Bu% ↑, HC ↓. | Bu% ↑, CO ↓. | 166 |
| SI engine, EFI, d= 90.82mm, s= 76.95mm, CR= 8.2 mm, | E0, E10, E30 | Close-loop control at part engine loads; Open loop control at full engine load | - | E% ↑, $NO_x$ ↓. | E% ↑, HC ↓. | E% ↑, CO ↓. | 167 |
| HH368Q SI engine, 3C, CR= 9.4, PFI, d= 68.5mm, s= 72mm, 796cc | Bu0, Bu10, Bu30, Bu40, Bu100 | Varying loads<br>Constant speed 3000rpm<br>Fixed stoichiometric AFR | | Bu% ↑, $NO_x$ ↑ | Bu% ↑, HC ↓ except Bu100 > gasoline | Bu% ↑, CO ↓ except Bu100 > gasoline | 169 |
| 1C, SI motorcycle engine, AC, d= 56.5mm, s= 49.5mm, 124.1cc, CR= 9.2 | Gasoline, Bu35 | Full load 3500- 9000rpm<br>Partial load 6500- 8500rpm | Bu% ↑, $CO_2$ ↑. | E% ↑, NOx ↑. | E% ↑, HC ↓. | E% ↑, CO ↓. | 170 |

**MPI/MPFI= Multiport fuel injection, DI= Direct injection, MPEI= Multipoint electronic injection, EFI= Electronic fuel injection, PFI= Port fuel injection, C= cylinder, S= stroke, d= bore, CR= compression ratio, WC= water cooled, AC= air cooled, ↓= decrease, ↑= increase, E= Ethanol, M=Methanol, Bu= Butanol, Pr= Propanol, Pe= Pentanol, MaxH= Maximum heating value optimum blend, MaxR= Maximum research octane number optimum blend, MaxD= Maximum petroleum displacement optimum blend**