Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 15 (4): 619-625, 2015
ISSN 1812-5654

ansinet
Asian Network for Scientific Information

REVIEW ARTICLE OPEN ACCESS

DOI: 10.3923/jas.2015.619.625

Role of Oxygenated Additives for Diesel Fuel Blend "A Short Review"

Muhammad Saad Khan, Iqbal Ahmed, Ibrahim Bin Abdul Mutalib and Azmi Bostum
Department of Chemical Engineering, Faculty of Engineering, University Technology PETRONAS, Tronoh, Malaysia

ARTICLE INFO
Article History:
Received: February 25, 2014
Accepted: January 10, 2015

Corresponding Author:
Iqbal Ahmed,
Department of Chemical Engineering,
Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, Tronoh, 31750,
Perak, Malaysia

ABSTRACT
Diesel is a main source of fuel among petroleum product but ecological degradation and exhaustion of petroleum reserves are matters of great concern around the world. Finding a suitable fuel alternative to diesel is an urgent need. Comprehensive studies were carried out as an alternative fuel. In this perspective, alternative oxygenated-diesel fuel blends are currently receiving renewed interest. For this context, the use of Oxygenated Bio-Fuels (OBF) like ethanol, methanol, Dimethyl Ether (DME) and bio-diesel in combination with diesel is an effective measure to substitute renewable fuels and reduce Particulate Matter (PM) from in-use diesel compression-ignition engines. Additionally the study is specific to diesel fuel blends; like ethanol-diesel, bio diesel-diesel, gaseous fuel-diesel and oxygenated fuel-diesel blend and their feasibilities as an alternative for diesel fuel.

Key words: Bio-diesel, blend fuel, DME, ethanol, exhaust emission, gaseous fuel, oxygenative fuel

INTRODUCTION

The diesel technology plays a vital role in importance of world economy because of its distinctive combination of energy productivity, power, reliability and durability. More than 90% of commercial trucks are powered by diesel engines, as are two-thirds of all farm and construction equipment and 100% of all freight locomotives, river barges and other marine work vessels. Diesel engines also power electric generators used for distributed generation or as emergency back-up power such as those used by hospitals. The categories of diesel engines are as varied as their application, from small, high-speed indirect-injection engines to low-speed direct-injection alongside with cylinders varying 1 m (3 ft) in diameter. Their success originates by their economy, efficiency and reliability (Han *et al*., 2011).

In the year of 1859, crude oil had discovered in Pennsylvania, USA. The first product refined from crude was lamp oil (kerosene). Because only a fraction of the crude made good lamp oil, refiners had to work out what to do with the rest of the barrel. Rudolf diesel, recognizing that the liquid petroleum by-products might be better engine fuels than coal dust, began to experiment with one of them. This fuel change, coupled with some mechanical design changes, resulted in a successful prototype engine in 1895. Today, both the engine and the fuel still bear his name (Bacha *et al*., 2007).

Right after the discovery of Rudolf diesel engine numerous grades are existing according to their uses for diesel compression ignition engines (like cars, truck, railroads and marine engines) and light heating oil for commercial and industrial uses. The advancement in the internal combustion engine began for the late eighteenth century. Gentle but steady progress had made over the next hundred years. By 1892, Rudolf diesel had received a patent for a compression ignition reciprocating engine. However, his original design which used coal dust as the fuel, did not work (Diesel, 1895; Machacon *et al*., 2001).

The term "Diesel fuel" is generic; it refers to any fuel for a compression ignition engine (Bacha *et al*., 2007). The first commercial diesel engines were very large and operated at low speeds. They had used to power ships, trains and industrial plants. By the 1930s, diesel engines were also powering trucks and buses. An effort in the late 30's to extend the engine's use to passenger cars had interrupted by World War II. After the war, diesel passenger cars became very popular in Europe but they have not enjoyed comparable success in the United States yet (Bacha *et al*., 2007).

Generally, diesel fuel is the refinery product accomplished from crude oil distillation process after the kerosene oil. Diesel fuel is a type of distillate fuel which distillate between the temperature ranges of 180-380°C (356-716°F). Usually, petroleum-derived diesel fuel is composed of nearly 75% saturated hydrocarbons (mainly paraffin's including n-, iso- and cyclo-paraffins), besides 25% aromatic hydrocarbons (including naphthalene and alkyl benzenes). The average molecular formula of common diesel is $C_{12}H_{23}$, ranging almost from $C_{10}H_{20}$ to $C_{15}H_{28}$ (John, 2009).

High worldwide demand for diesel fuel and other distillate fuel oils, especially in Europe, China, India and the United States and a tight global refining capacity available to meet demand during the period of high economic growth from 2002 to mid-2008. Due to high demand of distillate fuel oils particularly diesel fuel, decreasing of crude oil reserves and their accelerating prices have placed progressively more sensitive loads on the trade balances of non-oil producing countries; in the meantime, they have come to characterize as a potential threat to the survival of the developing and industrialized countries. Besides that, the clean diesel is one of many technologies-including the use of biodiesel, ethanol and hybrid-electric power-that have potential for reducing energy consumption and GHG emissions. The following are some basic facts about diesel power and its relevance to these issues as policymakers consider options for addressing these national challenges.

Consequently, substantial attention had given on the development of alternative fuel sources now in various countries all around the world. Particular focus emphasized on the bio-fuels which possess the added advantage of being renewable fuels that can replanted through the growth of plants or production of livestock hence showing an *adhoc* advantage in reducing the emitted carbon dioxide. There is a commitment made by the United States government to upsurge bio-energy three fold, in ten years' time which has added huge motivation to the search for viable bio-fuels (Rakopoulos *et al*., 2008a). Regarding the environmental aspect, composed, sustainable and efficient end use technologies remains identified as key opportunities for achievement of the Kyoto targets of greenhouse gas emissions reduction. European Union decides for the transport sector energy savings of 5-10% in the medium term and an aggregate of 25% in the long term (by the year 2020) have targeted, with an expected censored of carbon dioxide emissions by 8% by the year 2010. The European Union has issued a directive order on the use of bio-fuels, accounting for at least 2% of the fuel market for gasoline and diesel fuel sold as transport fuels by the end of year 2005, while growing in stages to a minimum of 5.75% by the end of 2010 (Hansen *et al*., 2005; Rakopoulos *et al*., 2007; Rakopoulos *et al*., 2008b).

CALL FOR THE ADDITIONAL FUEL BLENDS

Concerns above the availability, price and carbon and other emissions from petroleum-based fuels having issues which encourage the researches of alternative fuels for transportation vehicles (Shirk *et al*., 2008; Murugesan *et al*., 2009). Numerous types of fuels have investigated in recent years for improving the quality and performance of diesel fuel. For the reduction of discharged pollutants, researchers have focused their concentration on the area of fuel-associated techniques; for example, the use of alternative fuels often in fumigated form, or gaseous fuels of renewable nature that have pleasant impact on environment (Chen *et al*., 2011; Ting and Reader, 2005; Morsy, 2007; Rakopoulos *et al*., 2008a; Wall, 2008). Additionally oxygenated fuels that shown the ability to reduce particulate emissions (Ashok and Saravanan, 2007; Esarte *et al*., 2010; Hansen *et al*., 2005; Lin and Wang, 2004a, b; Rakopoulos *et al*., 2008b; Ren *et al*., 2008; Sathiyagnanam *et al*., 2010; Shi *et al*., 2005).

Moreover, for the advantages of decreasing petroleum dependence and rising renewable fuels use; E-diesel conveys the additional benefits of dropping diesel Particulate Matter (PM) emissions and CO emissions from engines. Numerous researchers have reported 20-40% PM reductions along with 20-30% reduction in CO attained due to the insertion of ethanol in diesel fuel. The effect of E-diesel on NOx emissions have been generally found insignificant (Ribeiro *et al*., 2007).

BLEND OF ETHANOL-DIESEL FUEL

Ethanol fuel has considered as a prime renewable energy; it can be prepared from entire kinds of raw materials such as sugar cane, cassava, sorghum, molasses, barley, sugar beets, corn and waste biomass materials, etc. Through, using of already improved and established technologies make the ethanol frequent choice. As a outcome, the ethanol has been widely used as fuel, primarily in Brazil, or by means of gasoline additive for improving of octane and to enhance the combustion in USA and Canada (Hansen *et al*., 2005; Xing-Cai *et al*., 2004).

Despite the fact that, the ethanol quite readily blends with gasoline to form steady solutions at any blend ratio. Nonetheless, blends of ethanol and diesel fuel (E-diesel) have less steady. Anhydrous ethanol effortlessly blends with diesel fuel to form stable solutions having up to a tens of percent ethanol at warm ambient temperatures (Gerdes and Suppes, 2001; Shi *et al*., 2005). Conversely, at temperatures beneath to 10°C, the blend start splits into dual phases for ethanol contents of 20% or higher (Gerdes and Suppes, 2001). There are alternative additive-based methodologies for preserving the stable blends at a low temperature. First, adding of emulsifiers (surfactants) that produce stable emulsions or micro-emulsions. Other technique has accumulation of co-solvents that could produce stable solutions. Past work especially in the 1980s, focused on emulsifiers and it revealed that E-diesel emulsions have technically virtuous enough fuels for recurrent diesel engines. Then again, the comparatively higher price of ethanol production at that time put E-diesel blend at an economic drawback (Bayraktar, 2008).

In recent years, with the development of technology, a number of researches have investigated the ethanol-diesel blend fuel used in CI engines (Lofvenberg, 2002; Corkwell and Jackson, 2002). Similarly, Ashok and Saravanan (2007) perform experimental study on a 4-cylinder light duty high speed DI diesel engine fueled with various proportions of CN improver volume in ethanol-diesel blend fuels. First of all, a dosage and cetane number improver were selected, 2% (by volume) of dosage was added to 15% ethanol-diesel blend fuel (15% ethanol, 2% dosage for all, 83% diesel fuel and the volume of CN improver was ignored) and the CN improver in blends were 0, 0.2 and 0.4%, respectively. Without any modification on the diesel engine parameters, the Brake Specific Fuel Consumption (BSFC), exhaust emissions including Bosch smoke number, CO, NOx and HC and in-cylinder pressure date were measured at different engine operating conditions when diesel engine fueled with ethanol-diesel blend fuels and compared to the baseline diesel fuel.

Bio-ethanol has a higher octane number, broader flammability limits, higher flame speeds and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time and leaner burn engine which lead to theoretical efficiency advantages over gasoline in an internal combustion engine. Their major problem is associated with their highly increased viscosity, 10-20 times greater than that of normal diesel fuel. Thus, although short-term tests using neat vegetable oils showed promising results, problems appeared after the engine had operated for longer periods. These included injector coking with trumpet formation, more carbon deposits and piston oil ring sticking, as well as thickening and gelling of the engine lubricating oil. To solve the problems associated with the very high viscosity of neat vegetable oils, the following usual methods have adopted, blending in small blend ratios with normal diesel fuel, micro-emulsification with methanol or ethanol, cracking and their conversion into bio-diesel fuels. The latter have manufactured from their corresponding vegetable oils, in batch or continuous systems, mainly through the transesterification process, where one ester has converted into polyesters.

E-diesel operations also rises concerns related to possible contrary impacts on engine and vehicle performance. E-diesel has inferior volumetric heat content (MJ L^{-1}), so some engine power loss would practice. Other concerns associated to engine efficiency loss or overall performance due to the minor cetane number of E-diesel unless a cetane improver is included in the additive package. Enlarged fuel pump wear has an additional concern due to the decreased lubricity of ethanol (Corkwell and Jackson, 2002; Hansen *et al*., 2005).

Torres-Jimenez *et al.* (2011) concluded that the tested ethanol-diesel fuel blends present similar properties values compared to those of pure diesel fuel, because all properties tested, excepting flash point, were within the diesel fuel standard limits. Density and viscosity decreases by ethanol addition, thus indicating retarded injection timing and not problems related to atomization, respectively. Due to the high ethanol volatility, some problems may occur during storage and it can also influence significantly injection timing, ignition and combustion characteristics (Torres-Jimenez *et al*., 2011).

Owing to the hygroscopic nature of ethanol, water content increased by ethanol addition, so special attention must be paid to avoid the absorption of water from the ambient humidity, if not, it can deteriorate ever more blend stability and causes corrosion and aqueous microorganisms growth. Based on this field trial, up to 15% (v/v) ethanol/85% (v/v) diesel fuel blends can be recommended as fuel for diesel engines once flash point and blend stability are improved by the use of additives and provided that engine performance adequately (Gerdes and Suppes, 2001; Kim and Choi, 2008; Torres-Jimenez *et al*., 2011).

BLEND OF DME-DIESEL FUEL

DME possess the decent thermochemical characteristics and it can be manufactured at a low cost due to recently developed technologies, it has been considered as a promising alternative fuel for compression-ignition engines (Ying *et al*., 2008). DME has a high cetane number (N55) which suggests that DME is appropriate for auto-ignition. The chemical structure of DME, CH_3-O-CH_3, indicates that DME contains 35 by wt.% oxygen and has no carbon-carbon bonds; this nature of DME pointedly decreases precursors for smoke formation since combustion. Many investigators (Fleisch *et al*., 1995; Kapus and Ofner, 1995) and various other researchers have demonstrated and concluded as:

- DME can achieve ultra-low emissions
- Its energy efficiency is equal to or better than conventional diesel engines
- Its exhaust gas reactivity is very low
- Its engine combustion noise can be similar to that of gasoline engines and lower than that of diesel engine if appropriate injection characteristics have employed
- It can also make from various resources, such as coal, natural gas etc

Ying *et al.* (2008) found that the insertion of DME into diesel fuel vigorously changes the physicochemical properties of fuels. With an increase of DME mass fraction, density, kinematic viscosity, low calorific value and aromatic fractions of the blends decrease. Simultaneously, cetane number, C/H ratio and oxygen content of the blends are enhanced which has some effects on the ignition and combustion of the blends with 10, 15 and 20% DME by mass. The vapor pressure of DME/diesel blends is lower than that of pure DME and it decreases with an increase of diesel in blend fuel which is beneficial to the elimination of vapor lock in the fuel supply system at engines.

- The addition of DME could lead to the decreased spray penetration but increased spray angle

- The energy consumption could reduce a little by adding a low fraction DME into diesel due to DME's ability of oxygen supply by itself and its better atomization. However, when DME mass fraction increases to the some certain, the energy consumption also increases due to an extension of fuel supply duration and late combustion phase
- The higher the DME content, the smaller the amount of heat release during the premixed combustion stage
- The impacts of DME content on emissions vary with engine operating conditions. At high load conditions, smoke emissions reduce about 58-68% for blend fuel engine in comparison to that for diesel engine. At low loads, smoke emissions for blend fuel engine are almost comparable to that for diesel engine. With the addition of DME, NOx emissions decrease a little, while CO emissions and unburned HC emissions increase at most operating conditions. If the fuel supply advance angle is retarded appropriately, the power output would be improved somewhat and NOx emission could be reduced further

BLEND OF GASEOUS-DIESEL FUEL

The gaseous fuels are receiving additional encouraging retort from researchers and consumer paralleled to earlier time, because of recent developments. Gas undoubtedly founded as the fossil fuel of slightest environmental influence. After burnt, it creates nearly insignificant amount of SOx and comparatively lower NOx which having the main components of acid rain. Similarly, it gives considerably a smaller amount CO_2, a fundamental reason for the greenhouse effect, than most oil products and coal (Papagiannakis *et al*., 2010; Sahoo *et al*., 2009; Shirk *et al*., 2008).

Gaseous fuels have higher octane numbers, accordingly, appropriate for engines with moderately high compression ratio. Gaseous fuels also having potential to remain suitable for advanced compression engines; because it has already known that it struggle against knock, moreover than conventional liquid fuels, along with producing fewer polluting exhaust gases. By applying appropriate conditions, their mixing and combustion properties satisfied for lean combustion. Consequently, they having more economically and of environmentally beneficial to use gaseous fuel in diesel engines that use the ‘dual-fuel’ concept (Sahoo *et al*., 2009; Shirk *et al*., 2008).

Because of lesser running expenses and the usage of alternate fuel sources with dual-fuel engines have paying attention frequent investigators to practice this engine in diverse areas of concentration (Sahoo *et al*., 2009). The preliminary experimentations on dual-fuel method had performed by Cave-Browne-Cave (1929). Besides that Helmore and Stokes (1930), induced burning hydrogen as an alternate fuel in diesel engines. After hydrogen burn completely, there had adecline of liquid fuel load occurred and saving of 20% diesel fuel attained (Sahoo *et al*., 2009).

Gaseous fuels have well thought-out as good quality alternative fuels for passenger cars, truck carriage and stationary engines that can deliver equally good environmental outcome and energy security. In contrast, little of the engine operating and design parameters namely, speed, load, compression ratio, pilot fuel mass, pilot fuel injection timing, inlet diverse condition, composition of gaseous fuel contestants may vary; the performance of the dual-fuel gaseous engines have widely affected. Numerous researchers to examine the effect of the above-mentioned parameters on the exhaust emission, performance and ignition characteristics of dual-fuel engines have carried out various studies. These investigations from the researchers have conducted in different test engines with a variety of gaseous primary fuels and pilot fuels (Sahoo *et al*., 2009; Selim, 2004).

DIESEL-HYDROGEN GAS FUEL

The unique combustion properties of hydrogen and higher calorific value of 141 MJ kg^{-1} make it an ideal choice for its use in compression ignition engines. Hydrogen-fuelled engines with almost near-zero emissions and higher efficiencies exceeding today’s Port-Fuel-Injected (PFI) engines having a probable near-term choice and a bridge to hydrogen fuel-cell vehicles, where fuel cell go through development to make it economically feasible (Bose and Maji, 2009; Shirk *et al*., 2008; Stanislaus *et al*., 2010). The previous researcher’s efforts to discover the performance and emission characteristics of hydrogen on both engines, spark plug ignition and compression ignition engine operated in dual fuel mode with hydrogen as an alternative fuel (Bose and Maji, 2009).

Szwaja *et al*. (2009) investigated hydrogen diesel blend in their research the hydrogen gas has premixed with the entering air and induct throughout intake valve opening by the indigenously developed electro-mechanical device of solenoid actuation. The performance and emission characteristics with hydrogen-diesel blends and neat diesel fuel have compared (Bose and Maji, 2009).

BLEND OF BIODIESEL-DIESEL FUEL

High petroleum prices and the undesirable environmental impact of using fossil fuels, as well as the need to encourage rural development, are the primary reasons for the increased attention in bio-fuels. While in the 1970s, one-half of the petroleum consumed was used to produce transportation fuels, it is expected that more than two-thirds of the petroleum produced will be employed by 2030 for this purpose. Biomass has the perspective to alleviate the use of petroleum, since it is the only renewable alternative source for carbon-based fuels and chemicals (Basha *et al*., 2009).

Bio-oil has been employed as a fuel to produce electricity in tailored gas turbines and diesel engines (Lu *et al*., 2008). These oils have not succeeded significantly; however, they can be used in their present form as transportation fuels. There is an urgent need to develop new approaches to utilize these oils as sources of fuel additives or extenders that maintain fuel characteristics. The high acidity, low thermal stability, less calorific value, high viscosity and poor lubrication are some of the properties limiting their direct use as transportation fuel (Alptekin and Canakci, 2008; Basha *et al*., 2009; Guarieiro *et al*., 2009; Moser, 2009; Sayin and Gumus, 2011; Singh and Singh, 2010).

Fully refining bio-oil to obtain transportation fuels and chemicals is a long-term goal of many researchers. However, successful deployment of bio-oil refineries will depend on several new separation and reaction technologies which may take time to move from the laboratory to the industrial scale. In this context, creating blends of bio-oil with other transportation fuels could be a viable short-term alternative to utilize an important fraction of these oils (Singh and Singh, 2010).

Bio-diesels are methyl or ethyl esters of fatty acids with properties very comparable with those obtained for petroleum-derived diesel. Bio-diesel is frequently derived from the trans-esterification of vegetable oils or animal fats with alcohols using acidic or basic catalysts (Basha *et al*., 2009; Kannan *et al*., 2011). These fuels are completely miscible with petroleum derived fuels and have been proposed as an alternative to increase the lubricity of petroleum distilled fractions (Moser, 2009). Commercial bio diesels have generally produced from soybean, canola, rapeseed, sunflower and palm oil. Although these fuels are better solvents than petroleum derived diesel, they tend to have lower oxidation stability and comparatively poor cold flow properties (Alptekin and Canakci, 2008; Singh and Singh, 2010). The formation of crystals at relatively low down temperatures is one of the major hurdles for the use of bio-diesel in cold weathers. The increase in the content of methyl and ethyl esters of saturated fatty acids in the range C_{16}-C_{18} deteriorates since the cold flow properties of bio-diesel. Conversely, oil rich in unsaturated fatty acids has better cold flow properties but exhibits lower oxidation stability. The oxidation stability of bio-diesels can be improved by the addition of phenolic compounds which are known to be excellent antioxidants. Reviews on the fuel properties of biodiesels can be found elsewhere (Balat and Balat, 2008; Singh and Singh, 2010).

Biodiesel, produced from renewable and often domestic sources, represents a more sustainable source of energy and will therefore play an increasingly significant role in providing the energy requirements for transportation. Therefore, more and more researches are focused on the biodiesel engine performances and its emissions in the past 10 years. Although there have always been inconsistent trends for biodiesel engine performances and its emissions due to the different tested engines, the different operating conditions or driving cycles, the different used biodiesel or reference diesel, the different measurement techniques or instruments etc.

Xue *et al*. (2011) eternally reviewed the biodiesel production and their impact on engine performance and has come up with following conclusion "Overall, biodiesel, especially for the blends with a small portion of biodiesel, is technically feasible as an alternative fuel in CI engines with no or minor modifications to engine. For environmental and economic reasons, their popularity may soon grow. However, more researches and development in biodiesel resources and engine design are needed" (Xue *et al*., 2011).

- The further improvement in production of biodiesel should be performed in the future to promote biodiesel properties and quality. The further development in additives which improve consumption of biodiesel should be needed to favour power recovery, economy and emissions especially for NOx emissions
- It should be done to readjust or redesign engine or/and its control systems for biodiesel, especially for optimizing ignition and injection and EGR control to achieve a more efficient combustion and thus meet the needs of biodiesel engine
- The further studies on biodiesel engine endurance tests should be executed to make clear the reason and mechanism of wears, because the studies on these aspects are fewer so far due to the time-consuming tests
- The further studies on the low temperature performance of biodiesel engine should be fulfilled because biodiesel presents higher viscosity than diesel which could affect the emissions due to the different size of droplets and the different primary zone equivalence ratio for biodiesel and diesel without any change in fuel nozzle
- The further studies on non-regulated emissions of biodiesel should be carried out to obtain conclusive trend, especially for the carbonyl compounds emissions

CONCLUSION

The following conclusions have attained through short review of diesel blends.

- Diesel fuel having wider applications, besides that the main problem related to diesel fuel is the harmful exhaust emission
- Ethanol-diesel blend achieved the significant attention from the researcher but it having a minor energy contents and less stability of the blend are the critical issues
- Gaseous diesel fuel is also precise applicable blend fuel but engine modification requirement are the key problems needs to be settled
- Biodiesel is an alternative prosper blend, it having a higher cetane number and energy content, although higher viscosity of biodiesel and increased amount of NOx emission requires further research on the biodiesel fuels

ACKNOWLEDGMENTS

The authors would like to express their sincere gratitude to University Technology PETRONAS (UTP) for provided the laboratory facilities and financial support during the research.

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