International Conference on Renewable Energies and Power Quality (ICREPQ'14)
Cordoba (Spain), 8th to 10th April, 2014
Renewable Energy and Power Quality Journal (RE&PQJ)
ISSN 2172-038 X, No.12, April 2014

Alcohol-diesel fuel blends and their effect in performance and exhaust emissions

M.I. Gregorio Arenas[1], M.D. Redel-Macías[2], A. Ortega[1], F.R. Lara[3], M.P. Dorado[1]

[1]Dep. PhysicalChemistry and Applied Thermodynamics, Ed Leonardo da Vinci, Campus de Rabanales, Campus de Excelencia Internacional ceiA3, 14071 Cordoba, Spain.
Phone number: 0034 957 218332, M.I. Gregorio Arenas email: i42grarm@uco.es,
A. Ortega email; aortega@ujaen.es, M.P. Dorado email: pilar.dorado@uco.es

[2]Dep. Rural Engineering, Ed Leonardo da Vinci, Campus de Rabanales, 14071 Cordoba, Spain.
Phone number: 0034 957 212222, M.D. Redel-Macías email: mdredel@uco.es

[3]Dep. of Electrical Engineering, Ed Leonardo da Vinci, Campus de Rabanales, Campus de Excelencia Internacional ceiA3, 14071 Cordoba, Spain.
Phone number: 0034 957 218356, F.R. Raya email: el1laraf@uco.es

Abstract. The growing demand of fossil fuel and the rising of its price strengthen the incessant search for energy alternatives. The use of alcohol-diesel fuel blends in diesel engines has recently received interest as an alternative fuel for use in spark ignition (SI) engine. However, little research concerning diesel fuel has been found. Moreover, alcohols can improve the combustion phase due to an increase of the oxygen content and reduce exhaust emissions as soot and particulate matter, besides knock. The most used alcohols in blends with diesel fuel are methanol and ethanol, butanol added recently. In contrast, there are very few studies about propanol and pentanol blended with diesel fuel, although engine results are remarkable. Some of them could be even produced via biorefinery, thus being better to the environment than the petroleum-based fuels. Nevertheless, the main challenge is to overcome disadvantages of alcohols including low lubricity, difficulty of vaporization and high auto-ignition temperature and definitely, their well-know immiscible problem with diesel fuel being required co-solvents or emulsifiers. Besides, these additives are used to enhance the properties of the fuel, like the increase of the cetane number or the production of a stable blend.

Keywords

Blended fuels; ethanol; methanol; propanol; butanol; pentanol

1. Introduction

In the last years many research have been developed to find an alternative to the derived fossil fuel. This is due to petroleum-based fuels are obtained from limited reserves, the price of crude oil keep rising and its demand is increasing every year [1]. No less important are the environmental reasons. The engine exhaust emissions, like carbon monoxide (CO), particulate matter (PM) or nitrogen oxides (NO_x), have impact on air quality, human health and climate [2]. The European Union limited the maximum levels of emissions from vehicles since 1992 with the norm EURO I. Nowadays the EURO V and then the EURO VI are more stringent.

The use of blends of alcohol-diesel blends is very common to reduce greenhouse gas emissions and improving some properties of the fuels. Alcohols due to their oxygen content have a complete burning power enhancing the combustion efficiency [3] and reducing the soot formation, particulate matter and knock [4-6]. Lower alcohol (methanol and ethanol) are the most often used. Their production could be cheaper and better to the environment than the petroleum fuels and biodiesel production [1, 7]. However the use of alcohols has several disadvantages. The main drawback is the solubility with diesel fuel that caused a phase separation. This instability and the possible techniques to prevent it have been thoroughly studied [4, 8]. It depends on both the composition of the diesel fuel and alcohol, and the temperature. For example, ethanol (low alcohol) blends with diesel fuel below 10ºC shows two phases [9]. Furthermore, both the percentage of alcohol in the blend and water content of the alcohol have also influence on it. For these reasons, some additives are used to enhance the solubility when mixed into diesel fuel. On the other hand, adding alcohol into diesel fuel, the properties of the blends changes mainly due to its lower cetane number, viscosity and lubricity, as well as its lower heating value and ignitability [3, 4, 6]. Moreover, these properties are dependent on both the chain length and the absence of branches in the alcohol [3].

2. Alcohols

A. Methanol

Methanol is a simple compound formed by a carbon atom attached to three hydrogen atoms and a hydroxyl group (-OH). Its chemical formula is CH_3OH and it is colorless, light, polar, water miscible and flammable at room

temperature. Furthermore, methanol has a high toxicity in humans. The raw material from which methanol is obtained could be renewable resources such as wood, agricultural biomass materials, waste biomass and municipal wastes. However, non-renewable natural gas is the most used for its production [10-12].
Although at present methanol is used as either blend of conventional fuels in the existing engines, there are more studies about methanol-gasoline blends than methanol-diesel blends [13]. This could be due to the miscibility problem between methanol and diesel fuel. One possible solution is using additives that are capable of increasing the solubility [11, 12, 14].
Methanol quality as fuel is related to its high specific heat and significant oxygen content. The viscosity of the methanol is lower than the viscosity of diesel fuel so it can be easily injected, atomized and mixed with the air introduced into the cylinder of the engine [12, 13, 15]. However, the low cetane number of methanol makes autoignition difficult as well as the high latent heat of vaporization and high ignition temperature. Moreover it has more corrosiveness, lower density and energy content than diesel fuel and, it has a poor behaviour on cold start and high aldehyde emissions at cold start, warming up and low load operations [12, 13, 16, 17].
It should be noted that both methanol and ethanol (which is explained below) are in the transesterification process for obtaining biodiesel and for mixing with this biodiesel to overcome its problems of higher viscosity [18].

B. Ethanol

Ethanol, along with methanol, belongs to the known lower alcohols. It has the same chemical formula than di-methyl-ether (C_2H_6O) but its thermodynamic behaviour is different [1, 19]. The use of ethanol in engines has been widely studied. One of the main reasons is its potential as alternative of derivate petroleum fuels. It is a renewable resource and it can be obtained by alcoholic fermentation of vegetable materials such as corn, barley, molasses, sugar cane, sugar beets, sorghum [18, 20-23]. On the other hand, agricultural or municipal residues like straw and waste from woods, food and paper processing are used to obtain ethanol by highly efficient, low cost and demonstrated processes [24-27].
Some advantages of ethanol are its high oxygen concentration and low sulphur content. In spite of that, the use of ethanol directly in engines is unfeasible due to limitations in technology, however ethanol-diesel fuel blends are being investigated [28].
In this sense, several ethanol blending ration have been studied, being the most important disadvantages their low solubility. It is caused by their difference in chemical structure and their dependence on the temperature, water content and the percentage of ethanol into the blend [29]. Therefore different techniques have been applied to solve it for example: mixing ethanol and diesel fuel in a fuel tank just before to injection, using an emulsifier or co-solvent, fumigating the ethanol to the intake air charge or using a dual injection with a separate injection system for each fuel[8, 26, 30-32]. The two last options require more proportions of ethanol and it need technical modifications in the engine. The others demand a low percentage of ethanol however it need stabilizer additives and cetane improver to achieve good engine performances [24, 33].
The addition of ethanol in diesel fuel generates some physic-chemical modifications. The fuel viscosity and lubricity decrease with ethanol addition so the lubrication of the fuel injection system can be significantly affected [30]. The break specific fuel consumption increased dues to the low heat value of ethanol, around 2/3 of diesel fuel [34]. Also, its low cetane number along with its high heat of vaporization causes self-ignition resistance in diesel engine [35].
On the other hand, in terms of emissions ethanol has recognized advantages. Its high oxygen content produces more complete combustion so it reduces some emission, in particular carbon monoxide and particulate matter, and increases carbon dioxide emission[15, 23]. Finally, some investigation reported an increment of carbonyl compound emissions with the use of ethanol blends [36].

C. Propanol

Within known as higher alcohols, propanol is the one with less number of carbons and lower chain length. In particular, it has three carbon atoms and a hydroxyl group (-OH). The position of this hydroxyl group defines the types of isomer and its properties. It can be obtained by non fossil fuels like others alcohols and it is called biopropanol. Its production is based in a fermentation process of sugar present in biomass.
The properties of propanol as a fuel are similar than the others alcohols. The viscosity, heating value and flash point of propanol is lower than diesel fuel and it provides oxygen atoms that reduce exhaust emissions[7].
The used or addition of propanol in engine has not been reported by any authors. Lapuerta et al. [4] studied the stability and others properties of diesel fuel mix with some alcohols, including propanol. The authors found that propanol, along with butanol and pentanol has better solubility than ethanol and methanol into diesel fuel blends. It is due to its lower polarity. Besides, they showed that the instability appears with a gel phase.

D. Butanol

Other alcohol that is being studied as biofuel or additive is butanol. Up to now it has not been studied as much as ethanol or methanol due to its use as a chemical compound in food industry, its production from non-petroleum is undeveloped and it had higher cost, but now the interest in butanol has grown considerably [37]. Also, the structure of butanol is more complex than the previous alcohols showed. It has four carbon atoms, which can form either a straight-chain or branched structure, and the hydroxyl group (-OH) whose location defines an isomer of n-butanol. Furthermore, each butanol isomer has different physical properties nonetheless their applications are very similar, for example they are used as solvents, industrial cleaners or gasoline additives [38].
The straight-chain molecule structure of butanol can be produce through petrochemical ways and from biomass. It has other uses beyond cosmetics and plasticizers production. The addition of butanol as co-solvent is very

common and also every year there are more investigation about the use of butanol-diesel blends in an engine[22, 39]. The properties of higher alcohols, like butanol and pentanol, are closer to diesel fuel than lower alcohols [40]. Compared with the most used alcohols to blend into diesel fuel, i.e. ethanol and methanol, butanol has higher heating value so it contains more energy and reduces the fuel consumption. It possesses higher cetane number, lower vapor pressure and fewer tendencies to cavitation problem. Also, its autoignition temperature is lower which improves ignition problems at cold start and, on account of it is less hydrophilic, it is less corrosive and less likely to separate in diesel blends if the fuel is contaminated with water [19, 38, 40, 41]. In spite of these properties similar to diesel fuel, the use of butanol alone is not compatible with some component of diesel engine and its heating value is still lower than conventional diesel fuel [38].

In this sense, researches about butanol as an alternative fuel are increasing. In general, the addition of butanol in diesel fuel rises slightly the brake specific fuel consumption and the brake termal efficiency. The exhaust gas temperature, nitrogen oxides and carbon monoxide are reduced with the butanol blending ratio while the amount of unburned hydrocarbons and nitric oxide could grow. In the exhaust emission, the most prominent is the reduction of the smoke opacity [40, 42-45].

E. Pentanol

Other emerging alcohol for use in engine is pentanol ($C_5H_{12}O_2$). It has five-carbon structure so it belongs to higher alcohols. Its molecular formula is the same for different isomers which change on the position of the hydroxyl group (-OH) and carbon chain structure. Pentanol isomers are used in products such as paint and coatings, as solvent for chemical reaction or as additive for lubrication oil, among others. Regarding their use as fuel, it has been investigated with other applications of pentanol isomers [46], for example in the esterification reaction to produce biodiesel, instead of methanol. Even though, 1-pentanol (CH_3-$(CH_2)_3$-CH_2OH) is the isomer of pentanol more studied with diesel fuel. It may be produced in a biorefinery through the integration of ethanol formation via fermentation or methanol formation via biomass gasification with conversion of these alcohol intermediates into pentanol [3, 4].

In relation to the properties of 1-pentanol, these are similar to the properties of diesel fuel so its consideration as an alternative fuel and its study is required. Despite that, to use alone 1-pentanol in a diesel engine are needed some modifications [3]. If it is mixed with diesel fuel there are no problems of miscibility and stability at temperatures above 0°C, but below this temperature could appear a gel phase in the blend [4].

According to some investigations, more carbon atoms reduce the value of vaporization latent heat and the percentage of oxygen content. In addition, viscosity of 1-pentanol is lower than diesel fuel and it could produce better fuel atomization but it worsens the lubrication of fuel injection systems. Some investigation showed no lubricity problems until 25% of pentanol in the blend [3], but other ones limit the concentrations of 1-pentanol below 10% due to other alcohols which have lower chain length compensate the lower lubricity by their volatility [4]. Finally, the handling and storage of 1-pentanol blends are considered safe because of its flash point is above 37.8ºC and it is not consider flammable [3].

3. Additives

The additives are used in fuels to improve some properties and, consequently, to optimize the engine operation or to reduce toxic pollutant emissions to the atmosphere. According to Ribeiro et al [6], additives used in commercial diesel oil can be classified as additives to reduce pernicious emissions and the engine's wear and to improve fluid stability, viscosity index and the ignition.

Focusing on alcohol and diesel fuel blends, it only need to add something to the mixture to be used in an engine without any modification. The most outstanding additives are needed to increase the cetane number, reduce exhaust emissions and obtain a stable blend. The properties and characteristics of the blend could change depending on the molecular structure of the alcohol (lower or higher alcohol) [3], so the type and percentage of the necessary additive might be different.

Mixing diesel fuel with ethanol or methanol, two phases would appear in some minutes. Three of the most influential parameters on the instability of the alcohol-diesel fuel blends are humidity, temperature and the percentage of alcohol added [4]. Other authors found that aromatic hydrocarbons and paraffin content of diesel affect to the blend stability[47].

On the other hand, alcohols with more number of carbons and, therefore, with bigger molecules have less solubility problems. By Lapuerta et al[4], pentanol, butanol and propanol showed similar stability results taking into account the temperature and the percentage of alcohol added into the blends. With the use of higher alcohol at temperature above 0ºC there is a stable blend, with the exception of 60-94% of pentanol in the blend. Below 0ºC it showed instability with gel formation. However, with ethanol and methanol two liquid phases appeared even at higher temperatures. These two phases were due to the different polarities of the components of the mixture. The hydrocarbons which are present in diesel fuel are nonpolar and, for example, ethanol is a polar substance so they do not have affinity [48]. They would need a similar molecular structure or to add a stability additives to achieve a stable mixture and therefore a more beneficial fuel for use in an engine.

The stability additives can be classified as surfactants (emulsifiers) and co-solvents. Surfactants are chemical species with a polar-nonpolar nature which influence through surface tension. By adding a surfactant into an ethanol-diesel blend lots of droplets or micelles of ethanol are produced in the diesel fuel phase. This is called emulsion or microemulsion and it usually requires a heating and stirring step. Some examples of surfactants could be an emulsifying agent by 'Betz GE' [26, 27, 49], multifunctional organic additives[33] or biodiesel [28, 50].

As regards co-solvents, they generate a homogeneous blend because they act as a bridging agent through molecular compatibility and bonding. The use of co-solvents is simpler because it can be prepared by splash

blending [6, 9]. In previous works, it has been employed co-solvents like Tetrahydrofuran (C_4H_8O) [35], dodecanol ($C_{12}H_{26}O$) [14, 15, 51] and butanol [22].

4. Conclusion

Many research and different studies guarantee an alternative to de fossil fuel with alcohols in diesel engines. At the beginning, blends of an alcohol with diesel fuel have been investigated due to the use of alcohols directly in the diesel engine has some limitations.

These blends have many advantages as the increase of oxygen content and a lower viscosity. However its lubricity is worse than diesel fuel, the low cetane number delays the self-ignition and there is an increase in break specific fuel consumption.

The solubility of lower alcohols and the gel formation at low temperatures with high alcohols are the worst disadvantages. For this reason many additives has been investigated. But it is necessary a detailed study about the behavior of these mixtures with additives at different temperatures and proportions. Furthermore, it should be observed their influence on engine performance and emissions.

As regard engine emissions with alcohol-diesel fuel blends has been demonstrated that the application of alcohol blends reduce the CO, PM and NO_x emissions.

Acknowledgement

Authors gratefully acknowledge to the Spanish Ministry of Education and Scienceand the Andalusian Economy, Innovation and Science Council, Spain for the financial support (ENE2010-15159 and TEP-4994, respectively).

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