Fuel 236 (2019) 65–74

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Effects of C3–C5 alcohols on solubility of alcohols/diesel blends

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ARTICLE INFO

Keywords:
Solubility
Alcohols/diesel blends
Three to five carbon numbers alcohols
Water
Phase separation

ABSTRACT

Alcohols with three to five carbon numbers are renewable fuels for blending with diesel fuel, but the separation and purification of the alcohols from solution by fermentation is of great economic significance. If it is possible for alcohol and diesel blending system to contain part of water, the energy can be saved during the alcohol production process. Moreover, alcohols are more hygroscopic than diesel fuel, the blends of alcohols and diesel fuel will absorb water from ambient humidity if the tank is not adequately sealed during the storage and carriage and the excessive water concentration in the blends will cause phase separation. To avoid phase separation, it is important to test the blends of alcohols and diesel for their capacity to hold water. However, little study has been undertaken to systematically investigate the maximum allowable water concentration of alcohols and diesel blends. Therefore, in the current study, different three to five carbon numbers alcohols (*n*-propanol, *iso*-propanol, *n*-butanol, *iso*-butanol, *sec*-butanol, *tert*-butanol, *n*-pentanol, *iso*-pentanol, *tert*-pentanol) were prepared to blend with diesel to investigate the ability to hold water in the system at different ambient temperatures. The alcohol concentration of the blend varied from 10% to 90% in 10% increments in volume. Then water was gradually titrated into the blends by a high-precision pipette until it was no more a homogeneous liquid and the free water occurred, meaning t the start of phase separation. Results showed that all tested alcohols in this study could blend with diesel at any ratio without water addition. When ambient temperature was 0 and 30 °C, the allowable water concentration for butanol is the maximum in the system which is the first time to find out four carbon alcohols is the inflection point to be amphiphile in ternary fuel system. Among butanol isomers, *tert*-butanol could hold more water resulting of its special spherical structure compared to other isomers. Furthermore, to evaluate the influence of temperature on phase solubility, four different temperatures (0, 30, 50, 70 °C) were chosen. For alcohols (*n*-propanol, *iso*-propanol and *tert*-butanol) which were miscible with water, the allowable water concentration was gradually increased as increasing temperature. But for the other alcohols tested in this study, the water concentration admitted in the system gradually decreased with temperature increased.

1. Introduction

Accompanied by a decline in world petroleum reserves, the increase in prices of the conventional petroleum fuels and restrictions on exhaust emissions from internal combustion (IC) engines triggered by environmental concerns, there is an urgent need for suitable alternative fuels for use in diesel engines [1–7]. Diesel engines are indispensable equipment in transport, agriculture and power generation sectors for their higher fuel conversion efficiency, higher power output and higher torque capability compared to gasoline engines [8,9]. However, the main problem associated with diesel engines is that they are the major sources of NOx and smoke. The combustion of petroleum fuels significantly increases the CO_2 in the atmosphere. The utilization of fuels derived from renewable sources is one of the ways to reduce the emissions of Nox, smoke, and CO_2 [10].

Alcohols, biomass based fuels, either single or blended with conventional petroleum based fuels are the most important alternative fuels for internal combustion engines [3,11]. Alcohol fuels such as methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), butanol (C_4H_9OH) and pentanol ($C_5H_{11}OH$) could be used with fossil-based fuels in various percentages for diesel engines as a clean alternative fuel source [12,13]. Among of them, low carbon alcohols like methanol and ethanol were extensively researched in spark-ignition engines due to their better anti-knock characteristics and low CO and UHC emissions

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https://doi.org/10.1016/j.fuel.2018.08.129
Received 9 April 2018; Received in revised form 1 August 2018; Accepted 29 August 2018
0016-2361/

[14]. Methanol can be produced from coal or petrol based fuels with low cost production, but it has a restrictive solubility with diesel fuel. Ethanol is a biomass-based renewable fuel, which can be produced by alcoholic fermentation of sugar from vegetable materials, such as corn, sugar cane, sugar beets, barley, sweet sorghum, cassava, molasses, etc. Meantime, ethanol can also be obtained by agricultural residues, such as straw, feedstock and waste woods by using already improved and demonstrated technologies [15]. While ethanol was successfully blend with gasoline in spark-ignition engines [16,17], and had the advantage over methanol of higher miscibility with the diesel fuel, but there were still some drawbacks of using ethanol in compression-ignition engines [17–21], as shown in the follows.

1. Ethanol has limited solubility in diesel fuel. Phase separation and water tolerance in ethanol–diesel blend fuel are crucial problem, especially at lower temperatures.
2. Ethanol fuel has an extremely low cetane number, whereas the diesel engine is preferred to high cetane number fuels which makes auto-ignition easily and gives small ignition delay.
3. The dynamic viscosity of ethanol is much lower than that of diesel fuel, so that the lubricity is a potential concern of ethanol–diesel blend fuel.
4. Ethanol has much lower flash point than diesel fuel and higher vapor formation potential in confined spaces, thus requiring extra precautions to ensure safe handling and use of these blends.

Recently, higher carbon alcohols such as propanol, butanol and pentanol are gathering attention because of their advantages over the low carbon alcohols, and therefore, having more potential in being the next generation biofuel [13,22,23]. Generally, propanol, butanol and pentanol have higher cetane numbers, calorific values, viscosities, flame speeds while having lower latent heat of evaporations, ignition temperatures and corrosion risks when compared to low carbon alcohols. Moreover, these higher alcohols can easily be blended with diesel without any phase separation which is contributed to their high carbon content, low polarity, and less hygroscopic nature [13]. In addition, flash points of higher alcohols are quite high which makes them safer to store, handle and deliver in the existing distribution infrastructure. Though longer chain alcohols have less oxygen content, they can still enhance the premixed combustion phase with their relatively longer ignition delay allowing sufficient mixing of air/fuel and also improve the diffusion combustion phase. Furthermore, alcohols with longer carbon chains consume lesser energy during its production when compared to other lower carbon alcohols since the biological process of breaking down macromolecules can stop earlier and save more energy [24,25].

Propanol, a three carbon alcohol, has less affinity for water in comparison to methanol and ethanol. It has two isomers, namely *n*-propanol and *iso*-propanol, respectively. Propanol can be produced from feedstocks such as biomass or municipal solid waste. These feedstocks are gasified into syngas (CO, H_2 and CO_2) and then converted into biofuels using microbial catalysts such as *Clostridium ljungdahlii* and *Clostridium ragsdalei*. However, microbial production of propanol from *Clostridium* species via, threonine catabolism or from yeast in beer fermentation yielded only very small quantities of less than 70 mg/L. There is also no existing micro-organism that can naturally produce propanol from glucose in substantial quantities. Therefore, researchers have turned to bio-synthetic pathways to produce industry-relevant quantities of propanol from *Escherichia coli*, a microorganism that can be easily manipulated than the traditional complex *Clostridium* species. Recently several biochemical, genetic, and metabolic engineering strategies are being devised to enhance the coproduction of *n*-propanol and ethanol from a novel engineered *Escherichia coli* [24]. Propanol is used as a solvent to bind lower alcohols with diesel and also as a blending component with diesel fuel in diesel engine. There are relatively few researches about using propanol for blending with diesel fuel. The current limited study works found that the blends of propanol and diesel showed longer ignition delay, higher rates of heat release and pressure rise. The thermal efficiency of the engine decreased marginally with the use of fuel blends. The blends of propanol and diesel decreased the CO, Nox and smoke emissions of the engine considerably [26,27].

Butanol is also a biomass based renewable fuel that can be produced by fermentation of biomass, such as algae, corn, and other plant materials containing cellulose that can not be used for food and otherwise go to waste. There exists four isomers based on the location of the hydroxyl group (–OH) and carbon chain structure, namely *n*-butanol, *sec*-butanol, *iso*-butanol and *tert*-butanol. Four isomers have the same formula and heating value but have different molecular structures that affect the physicochemical properties of isomers such as solubility. In addition, their production methods are different, butanol production from biomass tends to yield mainly straight chain molecules [12]. Among of those four isomers, *n*-butanol seems to be a very strong alcohol competitor using in diesel engines, because it does not suffer from the same drawbacks as ethanol. Butanol is of particular interest as a renewable bio-fuel as it is less hydrophilic and it possesses higher heating value, higher cetane number, lower vapor pressure, and higher miscibility than ethanol. Thus, the problems associated with ethanol as a diesel fuel, mentioned previously, are solved to a considerable extent as using *n*-butanol, which makes fuel properties much closer to diesel fuel than ethanol [28–31]. A lot of study works had been conducted on engines fueling the blends of butanol/diesel and these results presented that lower Nox and soot emissions and higher thermal efficiency with the addition of butanol [28–31].

Pentanol, a long-chain alcohol contains five-carbon structure, which has eight isomers. Pentanol being an alcohol with longer carbon chains also consumed lesser energy during its production when compared to other lower alcohols [32]. In last decade, many research groups and bio-technology companies pay more attention to increase the yield of higher alcohols like butanol and pentanol from cellulose by modern fermentation processes using new strains of *Clostridium* species and by biosynthesis from glucose using genetically engineered micro-organisms like *Escherichia coli*, *Cyanobacteria* and *Saccharomyces cerevisiae*. There is also an alternative route in which biomass can be gasified or steam-reformed or partially oxidized to produce synthesis-gas (CO, H_2 and CO_2) which can be catalytically converted into higher alcohols by a process called higher-alcohol synthesis (HAS) [24]. Compared to other short-chain alcohols, pentanol has higher energy density, larger cetane number, better blend stability and less hygroscopic nature. These advantages make pentanol very competitive as an alternative fuel in diesel engines [31,33–35]. It was found that the blends of *n*-pentanol and diesel had an obvious advantage over neat diesel fuel in reducing the Nox emissions, particulate mass and number concentration, and increasing the brake thermal efficiency [36,37].

Even if alcohol is a renewable fuel for blending with diesel fuel, the separation and purification of the alcohols from solution by fermentation is of great economic significance. For example, butanol is a long chain carbon saturated alcohol with higher boiling point, lower saturated vapor pressure, and its volatility is much lower compared to water under the same conditions. Therefore, it is difficult to use the traditional distillation method to separate butanol from water. If alcohol and diesel blending system can contain part of water, a lot of energy will be saved during the alcohol production process. Moreover, alcohols are more hygroscopic than diesel fuel, it may occur during the storage and carriage if the tank is not adequately sealed, the blends of alcohols and diesel fuel would absorb water from ambient humidity [38]. It has been demonstrated that excessive water concentration in the blends will cause phase separation [39]. So it is important to test the blends of alcohols and diesel for their capacity to hold water without phase separation. However, little study has been undertaken to systematically investigate the maximum allowable water concentration of alcohols (propanol, butanol, pentanol) and diesel blends. On the other hand, the