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Effects of different alcohols additives on solubility of hydrous ethanol/diesel fuel blends

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HIGHLIGHTS

- Systematized solubility of higher alcohols in 90%ethanol/diesel blends was achieved.
- Low temperature and high water-containing break phase stable of ethanol/diesel.
- Alcohols with higher carbon numbers provide a better inter-soluble capacity.
- Straight chain structure shows better hydrotropy than cyclic and branched alcohols.
- Hydroxy group shows a better hydrotropy than ketone group.

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ABSTRACT

The purpose of this study was to evaluate effects of different alcohols on the solubility of the blends between diesel and hydrous ethanol (with 10 vol.% water) at various temperatures of 5, 15, and 30 °C. Among these alcohols, *n*-butanol, *n*-hexanol, *n*-octanol and *n*-dodecanol were selected for investigating the influence of alcohol chain length on solubility, while the effect of straight and branched chain on solubility was studied via comparing with four isomers of butanol (*n*-butanol, 2-butanol, iso-butanol and *tert*-butanol). Additionally, effects of various functional groups including both hydroxy and ketone group were studied by using cyclohexanol and cyclohexanone. The blend on hydrous ethanol (10 vol.% water) and diesel fuel was acted as an analyte with different diesel blending ratios varied from 0 to 100 vol.% in 10 vol.% increments. Then the given alcohol (titrant) was gradually added into the centrifuge tube by a high-precision pipette until phase boundaries of ternary system appeared. Results show that alcohols with higher carbon numbers provide a better inter-soluble capacity, but a higher carbon-number alcohol such as *n*-dodecanol correlates with a lower pour point which leads to the gelling for the blends. Based on the performance of 6-carbon alcohols on phase stability, it is clearly that the straight chain structure and hydroxy group shows a better hydrotropy than cyclic structure and ketone group, respectively. For butanol isomers, straight chain butanols have better soluble capacity than that of branched structures. Taking these factors into account, *n*-hexanol and *n*-octanol can be recommended as a co-solvent additive for hydrous ethanol/diesel system due to the acceptable fuel properties and soluble performance.

1. Introduction

Diesel fuel has been extensively used for engineering machinery, automobiles, and shipping power equipment due to its high fuel efficiency and excellent drivability [1]. But, for the past several decades, the oil crisis is becoming increasingly serious and the combustion of fossil-based resources today occupies over two-thirds of the global dominating energy utilization [2], which also reflects our overwhelming reliance on fossil fuels as usual. In addition, the excessive consumption of mineral fuels leads to various types of air pollutants including oxides of nitrogen (NOx), particulate matter (PM), carbon monoxide (CO) and other harmful ingredients, and around 63% of greenhouse gas emissions such as carbon dioxide (CO_2) are derived from the direct combustion of fuels [3]. Thus, novel approaches for the production of green and sustainable renewable energy, particularly biofuels which only emit slight CO_2 gas in overall life-cycle [4,5], have become one of the top research items in engine development.

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Ethanol, which is yielded mainly from the sugary or starchy materials, e.g. corn, sugar cane, waste biomass materials, has an abundant feedstock base for its production in the global scope and becomes the most broadly used bio-fuels today [6–8]. Statistical data showed that, in USA, over 7.3 billion gasoline-equivalent gallons of ethanol were served as petrol additives in 2009 [6]. The International Energy Agency also indicated that the ethanol supply would climb from 1 million barrels of oil equivalent per day (mboe/d) in 2010 to 3.4 mboe/d in 2035 [9]. Moreover, considering the favorable physical and chemical properties such as the higher oxygen content or octane number, ethanol receives considerable attention and has been the most studied alcohol for blending with conventional mineral fuels [10–15]. In reality, ethanol has been extensively used in gasoline engines, but of its not yet implemented large scale commercial on diesel engines. Generally, there are several serious obstacles for using ethanol/diesel blend:

(1) Defects exist in the first generation biofuels, and major issue is that the current ethanol manufacture is restricted by its potential intimidation to food security and the “blend-wall” problem [16–18]. Therefore, the further application in diesel engines is restricted to some extent.
(2) Ethanol has very finite miscibility in diesel fuel [19–22]. Thus, the ethanol/diesel mixtures present the phase separation.

Ever since the development of high efficient, low cost pathways for producing bio-ethanol from cellulose biomass (second generation) and algal biomass (third generation) [23,24], the primary drawback has been transformed into the second issue. The ethanol/diesel blends can assume phase separation over a wide range of temperatures and water contents due to their difference in chemical structures and characteristics [25,27]. Fernando and Hanna [26] surveyed that most ethanol/diesel mixtures separated promptly into two distinct phases at room temperature. Therefore, in order to guarantee the phase stabilities of whole mixture systems and the blending fuel properties, some additives are required to be added [8,13,14,20,22]. Biodiesel is frequently used to act as a co-solvent or an emulsifying agent. Chotwichien et al. [28] researched that utilization of palm oil methyl, ethyl, and butyl esters as co-solvents in pure ethanol/diesel blend, and eventually, the addition of different palm oils improved the solubility and compensated the loss of density, viscosity, cetane number, etc. of ternary mixtures. Makareviciene et al. [19] and Kwanchareon et al. [29] observed the consistent result as Chotwichien et al. but also indicated the water tolerance of diesel-biodiesel-ethanol fuel blends were clearly not ideal. Kwanchareon et al. [29] explained that presence of just bits of water (5% water in volume) enhanced the polarity of the hydroxyl group of ethanol molecule and as a result, non-polar diesel could not be compatible with aqueous ethanol in any proportion at room temperature. De Caro et al. [21] further discovered that pure ethanol was greatly soluble in diesel at contents of about 0–30% and 70–100%, while most zones of miscibility turned cloudiness when the water content of ethanol surpassed 1%. In other words, the water resistance of three-component systems ultimately could embody the soluble ability of co-solvents just like phase separation temperature. In fact, the ambient water should be inhaled inevitably during the storage and transportation process, which readily destructs the stabilization of ethanol/diesel blend.

But actually, when the blends ensure complete solubility, the appropriate amount of water in fuel is beneficial to the engine combustion and emissions [30–32]. Chang et al. [31] studied a diesel engine generator running on blends of 20 vol.% ABE (acetone-butanol-ethanol) and only 0.5 vol.% water with diesel fuel (ABE20W0.5 for short). They concluded that ABE20W0.5 enhanced the BTE (brake thermal efficiencies) by 1.92–2.49%, which corresponded with a decreased BSFC (brake specific fuel consumption) of 1.94–2.63%, and significantly reduced NOx and PM emission factors by 23.5–27.0% and 17.8–33.1%, respectively, when compared with the results of ABE20W0 at various engine loads. Martinez-Frias et al. [32] investigated that a homogeneous charge compression ignition (HCCI) engine with high-efficiency heat recovery could work on a 35% ethanol-in-water blend while attaining a high BTE (38.7%) and a very less NOx emissions (1.6 ppm). Similar results have also been obtained by Olberding et al. [33], which they used hydrous ethanol with 30% water in gasoline engine and demonstrated that hydrous ethanol addition showed higher thermal efficiency and lower NOx and CO emissions than pure gasoline fuel. Besides, Martinez-Frias et al. [32] and Shapouri et al. [34,35] highlighted the view that aqueous ethanol should pay more attention, since large amounts of extra money and up to 37% of the total output energy (ethanol and co-products) in ethanol production were spent in water removal. In total extra 37% output energy for water removal, the distillation covered 23% and the dehydration covered 14%. Meanwhile, Ladisch and Dyck [36] and Munsin et al. [37] also presented that the major energy depletion for the distillation of ethanol started sharply increasing once ethanol concentrations exceeded 90 vol.%. This means that the application of hydrous ethanol should be larger than 10 vol.% water content based on the economic manner.

Generally, in order to address the contradiction between the higher water content and phase separation in ethanol/diesel fuel blend, the best option for generating a homogenous mixture is to add a co-solvent with excellent soluble capacity [25]. Higher alcohols (C_4 and larger) own hydrogen donor groups (—OH) in association with molecular functional groups that accept hydrogen, which interact more strongly with the polar materials. Besides, through van der Walls forces, the non-polarity or low polarity carbon chains of higher alcohols possess good affinity with the hydrocarbons of diesel. For this reason, alcohol additives present a much better soluble performance in theory. And in reality, higher carbon-number alcohols, especially *n*-butanol as a relatively short straight-chain alcohol, have been applied as a co-solvent additive in ethanol/diesel and methanol/diesel blends [38,39], but the systematized researches on their ability to promote stability of hydrous ethanol have not yet been completely established. In addition, other higher carbon-number straight-chain alcohols and some different molecular structures such as branched, cyclic alcohols have also not been compared.

Hence, in this research, different higher carbon-number alcohols have been mixed with 90% ethanol/diesel blends. Among these alcohols, *n*-butanol (4-carbon), *n*-hexanol (6-carbon), *n*-octanol (8-carbon) and *n*-dodecanol (12-carbon) were selected for investigating the influence of alcohol chain length, while the effect of straight and branched chain about solubility was studied via comparing with the result differences of four isomers of butanol (*n*-butanol, 2-butanol, iso-butanol and *tert*-butanol). Additionally, the influence of hydroxyl and ketone group was focused by using cyclohexanol and cyclohexanone as co-solvents. The critical tasks were to ascertain the phase behaviors of hydrous ethanol/diesel systems with various co-solvents and component concentrations, and the dependence upon ambient temperatures. And finally, through combined with physicochemical properties and soluble capacity of alcohol additives, a premium and stable alcohol co-solvent fuel should be obtained.

2. Materials and methods

Conventional diesel fuel was supplied by Sinopec Co., Ltd., Beijing Yanshan Branch in this study. The water content of premium