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Castor oil enhanced effect on fuel ethanol-diesel fuel blend properties

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HIGHLIGHTS

- Castor oil improves stability and solubility of ethanol/diesel fuel blends.
- Ternary mixture components show antagonistic effects concerning main fuel properties.
- Models to predict main fuel properties based on mixture composition are provided.
- A compromise between mixture fuel properties is found using Derringer optimization.
- A ternary mixture providing optimum main fuel properties has been found.

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ABSTRACT

Ethanol is a low chain alcohol that could partially substitute diesel fuel to operate compression ignition engines. Its renewable origin and oxygenated structure make ethanol a candidate fuel for internal combustion engines. Main drawbacks of ethanol as a fuel are its low heating value, viscosity, lubricity, cetane number and limited miscibility if mixed with diesel fuel. Additives may enhance its solubility, although with a cost increase. In the present study, castor oil is proposed as an additional component to be added to ethanol-diesel fuel blends. Castor oil and its seeds are not suitable as food neither for humans nor for animals, thus avoiding the possible conflict about the use of land for food or energy, as arises from the use of edible oil/seeds. The presence of a hydroxyl group in the ricinoleic acid increases the polarity of this oil, enhancing ethanol-diesel fuel miscibility. As a result, ternary blends of ethanol, ultra-low sulphur diesel fuel and castor oil have been analyzed considering blend solubility, heating value, kinematic viscosity and cold flow properties, among most critical properties of diesel fuels. Ternary-component mixture prediction models of relevant fuel properties, i.e. kinematic viscosity, cold filter plugging point and high calorific value have been developed. Blend composition that simultaneously optimizes the three fuel properties has been proposed using the desirability function of Derringer. Results from simulation have been experimentally validated, providing a fuel blend composed by diesel fuel, ethanol and castor oil that shows satisfactory values of some of the most significant physical and chemical fuel properties. The presence of a hydroxyl group in the ricinoleic acid provides superior ignitability, lubricant and solubility characteristics with respect to other additives/components, making it a potential suitable candidate as a blend component to enhance ethanol/diesel fuel blends.

1. Introduction

In 2012, the EU transport sector demanded up to 70% of total diesel fuel consumed in the whole European Union (2.5 Mt) [1]. Diesel fuel combustion has been reported as the major contributor of atmospheric levels of particulate matter and nitric oxides emissions, being hazardous to both environment and human beings [2]. In addition, as it is stated by the Paris agreement about climate change, reducing the use of non-renewable fuels is urgent to keep the world temperature rise below 2 °C above pre-industrial levels. Therefore, a solution to energy, mobility

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and transport needs could be provided by fossil-fuel replacement with renewable and advanced fuels. It has been reported that optimized use of advanced biofuel in combination with other engine technologies, i.e. EGR could produce favorable particle-NO_x trade-off [3,4], mainly when oxygenate fuels are employed [5]. In this context, it is important to notice that alcohols include oxygen in the fuel molecule and could be blended with fossil-based fuel to operate both spark and compression ignition engines [6,7]. Alcohols, both short chain (namely methanol [8], ethanol [9,10] and butanol [11]) and longer chain alcohols [12], i.e. 1-hexanol [13], cyclohexanol [14] and *n*-octanol [15] have been used in compression ignition engines, promoting a better combustion and lower gaseous and particle emissions. For instance, Ajav and others [16] tested, in a single-cylinder engine at constant speed (1500 rpm) and four levels of load (25, 50, 75 and 100%), mixtures of ethanol/diesel fuel (5, 10, 15 and 20% ethanol in the blends). These oxygenated mixtures led to a reduction of carbon monoxide and nitrogen oxide emissions. However, most studies proposing the use of ethanol blended with diesel fuel recommend low percentages of alcohol due to several detrimental properties of alcohol fuels when used in compression ignition engines, i.e. low solubility, ignitability, heating value and lubricity [17].

One of the major shortcomings derived from the use of methanol or ethanol mixed with diesel fuel is their reduced solubility, forcing to lower the presence of alcohol to percentages below 20%. Although solubility of ethanol in ultra-low sulphur diesel fuel (ULSD) is higher than that of methanol blends (methanol presents higher polarity due to a shorter hydrocarbon chain, which means it is almost not soluble in diesel fuel), its solubility depends on the number of hydrocarbons present in diesel fuel, wax content, temperature and moisture content of the blend [18]. For this reason, additives in percentages below 10% are often used to improve solubility of blends [10,19]; although, the cost of these additives is a major limitation. Torres-Jiménez and others [20] studied the physicochemical properties of ethanol/ULSD blends, with percentages of ethanol from 5 to 15% v/v. They concluded that the presence of ethanol did not influence fuel properties, excepting flash point and blend stability. Authors found that 15% v/v ethanol could be used directly and without additives in blends with diesel fuel, but the use of an additive is needed to improve stability and flash point of the blend. Moreover, they found that to keep a single phase, blend temperature should be above 30 °C; however, for temperatures below 30 °C, two phases were formed in less than a month. Similarly, Huang and others [21] studied solubility and behavior of ethanol (from 10 to 30% v/v)/diesel fuel mixtures using n-butanol as additive. Stability and solubility tests showed that no mixture was stable after three days. Lapuerta et al. [17] measured stability of ethanol-diesel fuel blends using optical equipment, specifically designed for the characterization of liquid emulsions, suspensions and solutions. Authors found out that at 25 °C, blends with more than 20%v/v ethanol were not miscible. Li and others [22] used a stabilizing additive (1.5%) in blends of diesel fuel with ethanol (5–20% in volume) and achieved a significant reduction of smoke and NO_x emissions.

Vegetable oils and biodiesel have also been researched as a fuel component to alcohol-diesel fuel blends, forming a so-called ternary fuel blend. The high lubricity of biodiesel and vegetable oil as well as their potential to enhance both ethanol/diesel fuel and butanol/diesel fuel blend stability has been demonstrated in several works [11,23,24]. Castor oil (CO) has been traditionally used in cosmetics and even in the biodiesel industry, among others [25]. Provided that castor oil/seeds cannot be used for feeding purposes, alternative industrial uses, i.e. promoting business opportunities for marginal rural areas, become an attractive idea [26]. According to this, the effectivity of CO used as lubricating oil for engines has been demonstrated [27]. According to FAO database (FAOSTAT), four countries (India, China, Mozambique and Brazil) produce 96% of the world's supply of castor oil (1,700,000 t of seeds, in 2016). Total castor production may vary yearly due to changes in rainfall and the size of cultivated areas. In a recent study [28], it was concluded that diversification of cultivation areas and the use of irrigation are needed for an extensive use of CO.

CO presents low solubility with diesel fuel, but acceptable in case of alcohol. Other authors have used different strategies to enable the use of higher percentages of alcohols in compression ignition engines. Wei et al. [8] proposed the strategy of a high premixed ratio to directly inject into the chamber 70% methanol blended with diesel fuel, finding out a high decrease of soot and NO_x. Ethanol-diesel blends also feature an increase in auto-ignition delay times [29] due to decrease in cetane number, which could be around 35 for 25% ethanol and 25 for 45% ethanol. Increase in auto-ignition delay times can be overcome if pressure and temperature levels at the injection timing, inside the combustion chamber, are increased, for example by varying the compression ratio [30]. Cross effects of compression ratio and low cetane numbers have already been highlighted for ethanol-diesel fuel blends, biodiesel fuels and naphta-like fuels [31]. Variable compression ratio could be able to overcome variation in cetane number by adapting compression ratio for different amounts of ethanol up to 45%, while for higher ethanol content, the required compression ratio would be very high for diesel fuel. Surface ignition [32] could also be employed to overcome the low cetane number of alcohol fuels.

In the present study, the potential of CO as solubility, lubricity and energy density enhancer to improve ethanol/ULSD blends has been studied. CO composition comprises one hydroxyl group in the fatty acid and one apolar group in other long-chain fatty acids, making castor oil a surfactant material. The hydroxyl group also has superior ignitability and lubricant properties as well as higher flash point compared to other fatty acids, making it a potential suitable candidate as a blend component to enhance ethanol/diesel fuel blends. In this sense, for the first time, a comprehensive study to select optimal ethanol, CO and diesel fuel blend has been performed. Solubility and viscosity of several ternary blends comprising ethanol, ULSD and CO are analyzed to preselect ternary fuel blends. Besides, mixture optimization based on fuel properties (Derringer method) has been carried out, and property prediction models have been designed. To validate the model, relevant chemical and physical properties of the predicted optimum mixture have been experimentally measured.

2. Materials and methods

2.1. Fuels

Ethanol 99.8% v/v was provided by SCHARLAB (Barcelona, Spain). Castor oil (*Ricinus communis*) was purchased from GUINAMA (Valencia, Spain). Fuel ternary blends include ethanol, castor oil and ULSD fuel (meeting EN 590 standard). Straight ULSD (with no biodiesel addition) was provided by CEPSA oil refinery (Huelva, Spain).

Table 1 shows some of the most representative fuel properties of ternary blend components. For solubility reasons, the mixing order must be met in the following way: firstly, oil and ethanol were mixed together; later, ULSD was added. To produce a homogeneous blend, it was vigorously shaken for one minute. Blends were kept in a glass container to check solubility and physical stability with time.

2.2. Experimental design

In a starting screening experimental study, a McLean-Anderson design was followed. For each corner of the triangle, the minimum value was 10% vol., while the maximum was 80% vol. of each component in the fuel blends (Fig. 1). During the initial screening experimental study, 36 runs were performed. Blends were visually examined every hour, during one day time, to remove blends that were both stratified in two layers during the settling time and depicted viscosity values beyond that of ULSD fuel.

Based on results achieved from the screening experimental study, blend values were selected to build the mixture design of experiments