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Modified diesel prepared by stabilization of water as nanodroplets in diesel/colza oil blend: Study of phase behavior and affecting parameters

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A B S T R A C T

In recent decades, using of vegetable oils has gained major attention as an alternative and renewable fuel source. But, the high viscosity of vegetable oils makes them to be problematic for the fuel engines in long-term use. Blending of vegetable oils with diesel as modified diesel fuel has been considered as the most common method for reducing the negative effects of vegetable oils, such as high viscosity. The main purpose of this research is to study the phase behavior of new w/o microemulsion systems with focus on formulating an optimized fuel system. The effects of several parameters such as surfactant, co-surfactant, blends of several surfactants (HLB), temperature, stirring speed and stirring time on the physical properties of the studied systems, such as viscosity, water droplet sizes were examined. The optimum system formulated here was composed of diesel/colza oil blend (80:20 wt%) 44 wt%, Span 80 as surfactant 4 wt%, 1-butanol as co-surfactant 47 wt% and 5 wt% water. The size of water droplets in the formulated optimum system has been about 4.6 nm and the system showed no phase separation for up to 9 months on the shelf.

1. Introduction

With the rapid industrial development, the necessity and need for new energy resources along with the rapid extraction and reduction of natural reservoirs and limited refining capacity of fossil fuel, many countries have started to intensive investment in research on renewable energy technologies. Nowadays, in the most of developed countries, biofuel is used as a new and renewable natural resource of the fuels. Considering this issue, vegetable oils [1], such as cotton oil [2] now has turned to be one of the options that have indicated a good efficiency like diesel fuel and it is believed that it can be used as an alternative fuel [3]. Utilizing of the vegetable oils as biofuel in the diesel engines has several remarkable features, including reduction of emission of non-burned hydrocarbons, carbon monoxide, suspended solid particles in the air, decreasing the emission of greenhouse gas and other harmful emissive compounds compared to the normal fossil fuels [4]. Biodiesel has been introduced as new alternative fuel, advantageous regarding environmental and sustainability issues [5] with various trends of application [6]. This fuel was produced from different vegetables such as canola oil [7]. Colza oil as member of the vegetable oils family has a particular importance, as it can be processed to be used as biodiesel [6], or also blended with diesel oil [8]. This oil can be injected directly into the engine as plant oil [9,10]. At the time, when engine starting to operate, the viscosity of diesel fuel is very important and plays a great role. In general, the biofuel has a higher viscosity than diesel, hence, it reveals a poor performance than diesel [11]. In fact, this high viscosity of vegetable oil imparts a big restriction on their direct use in engine [12,13]. Therefore, attempts have been made to overcome these restrictions [14]. As an almost simple and the best approach to overcome the viscosity problem of the vegetable oils is to mix them with diesel fuel [15]. Meanwhile, there are different techniques to solve the high viscosity problem of vegetable oils which are including: dilution, biodiesel and microemulsion techniques. The microemulsification allows to use a blend of vegetable oil with diesel and introduce water into the fuel with or without using additives such as methanol, ethanol, or 1-butanol [12,13,16]. The microemulsion technique as a significant approach is introduced to decrease the problems encountered in the use of neat diesels [14]. The microemulsions are prepared simply by mixing proper amounts of oil, water, surfactant and co-surfactant. Depending on the relative ratios of oily and water phase, three kinds of microemulsions, i.e., oil-in-water (o/w), bicontinuous and water-in-oil microemulsions (w/o) can be formed. The solubilizing of water in oil in a w/o microemulsion displays different properties in the system. These imparted properties enables the reversed microemulsions to be applied in many fields of research and applications, such as fuels [17,18]. Reversed micelle microemulsion is a suitable technique for the production of modified diesel with proper viscosity using of vegetable oil and diesel in the presence of water [19]. One of the important benefits of using

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water in microemulsion systems is the enhancement of fuel octane number [20], and also increase of diesel fuel combustion productivity and hence, a significant reduction in the emissions of nitrogen oxides (NOx) and particulate matters (PM) from the exhaust gas output [21,22]. The investigations was revealed that the water in fuel droplets formed in the water in fuel (oil) emulsions enhances the fuel properties in many aspects, by the micro-explosion effect [23], improving the environmental and energy related issues of the fuel. Various types of water containing-fuel emulsions were investigated showing different effects on the engine performance of the neat fuel [23,24]. However, the most important advantage of the micro-emulsified fuels is to reduce their environmental effects and also to allow the use of some potential biofuels such as vegetable oils without any need for further processing steps. In a water in oil (w/o) microemulsion small droplets of water is formed which were surrounded with oil and stabilized by surfactant and/or co-surfactant molecules [25]. In any microemulsion system, surfactant play an important role and in general, non-ionic surfactants are more beneficial than ionic ones, as the addition of salt is not needed for formulating reversed phase micelles [15]. For preparation of fuel microemulsions the use of anionic, cationic, nonionic surfactants or their mixtures were reported in some literature [26]. The blending of several surfactants was confirmed to have a significant impact on the properties of microemulsion systems [27]. In general, the hydrophilic–lipophilic balance (HLB) concept was used to reach to an optimal surfactant performance by blending of several surfactants. HLB concept provides an appropriate method for the classification of surfactants and their mixtures. The surfactant systems with low HLB values were displayed to lipophilic surfactants, whereas high values to hydrophilic surfactants [28]. In w/o microemulsions systems, surfactants with HLB values of 3–8 were needed, while the o/w microemulsions can be prepared using surfactant systems with HLB values of 9–12. In this research, several nonionic surfactants, including hydrophilic and lipophilic surfactants, were adopted in these experiments and they were blended to form binary mixed surfactant systems which were used to stabilize water-in-biofuel microemulsions [29].

The main objective of this work is to formulate w/o microemulsion systems which can be used as an alternative diesel fuel. The specific goals are as following:

1. Determination of the phase behavior of the systems containing different surfactants or their blends in reverse w/o microemulsions with water, diesel/vegetable oil blends and co-surfactant.
2. Studying the effects of type of co-surfactant on the phase behavior.
3. Designing systems with dynamic viscosity values comparable to neat diesel fuel.
4. Investigation of the effect of temperature, stirring speed and stirring time on the water droplet size in the microemulsions.

2. Experimental

2.1. Materials

Polyethylene glycol sorbitanmonooleate (Tween 80), sorbitanmonooleate (Span 80), polyethylene glycol hexadecyl ether (Brij 30) and polyoxyethyleneoctyl phenyl ether (Triton X-100) were purchased from Aldrich. Ethanol (96%, Kimia Alcohol Zanjan Company, Zanjan, Iran), 1-propanol, 1-butanol, 1-hexanol, 1-octanol and isoamyl alcohol (3-Methyl-1-butanol) (99%) as co-surfactants were of technical grade and used after distillation. Diesel fuel was purchased from a local gas station. The composition of the used colza oil was measured by Gas Chromatography–Mass Spectrometry system (GC–MS, model TRACE-ISQ), utilizing an Agilent column model DB-35 MS (30 m × 0.25 mm × 0.25 μm). Composition of the colza oil was identified as given in Table 1. Distilled water was used in all experiments.

Table 1
Composition of colza oil, determined by GC–MS.

No	Compound name	Relative ratio (%)
1	N-Hexadecanoic acid	7.4
2	10-Octadecanoic acid	2.3
3	Oleic acid	87.3
4	Z,E-2-methyl–3,13-octadecanol	1.2
5	Oleyl alcohol	1.0
6	1-Hexyl-1-nitrocyclohexane	0.8

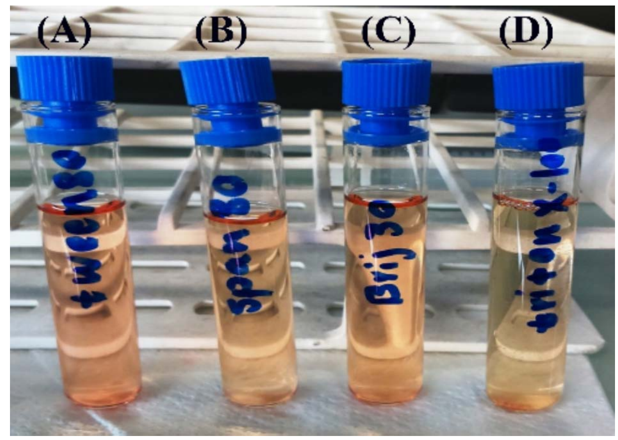

Fig. 1. The visual appearance of diesel/colza oil/water 5 wt% and 1-butanol systems with different surfactants: A) Tween 80, B) Span 80, C) Brij 30 and D) Triton x-100.

2.2. Methods

2.2.1. Microemulsion preparation

As a general procedure, the w/o microemulsions were obtained by mixing of four components, comprising of: aqueous phase (water), oil phase (80:20 wt% blend of diesel and colza oil), a surfactant (Tween 80, Span 80, Brij 30 or Triton X-100) and a co-surfactants (ethyl, propyl, butyl, hexyl, octyl and isoamyl alcohol) with defined ratios that are shown on ternary phase diagrams. Indeed, the microemulsions were prepared on the weight basis of the components. In a 15 ml glass vial a fixed amount of surfactant and diesel/colza oil blend mixture in the presence of various percentages of water was titrated by a co-surfactant to see the phase change boundaries. Typically, different amounts (4–20 wt%) of water with 3 ml of diesel/colza oil blend was added into the proper amount of surfactant and titrated with co-surfactant to formulate one phase reversed microemulsions. The surfactant, co-surfactant, water, diesel/colza oil mixtures were kept under constant stirring (500, 1000 or 1500 rpm) to allow the systems to reach equilibrium at the desired temperature in the range of 20 or 40 °C. The effect of varying temperature, stirring speed and stirring time on the microemulsion stability and water droplet size were studied. The formation of the microemulsion phase was realized by the appearance of a clear, transparent and homogeneous solution [30].

2.2.2. Ternary phase diagrams

Ternary phase diagrams were used to investigate the phase behavior and miscibility of the microemulsion systems in a constant temperature. Ternary phase diagram is an equilateral triangle, consisting three vertices for three components present in the microemulsion system. Normally, the two vertices laying at the bottom of triangle were used to represent the amount of diesel/colza oil/surfactant mixture (A) and water (B), respectively at the left and right sides of triangle. The third vertex laying at the top of triangle shows the co-surfactant (C) content of the system. The composition of the system at each point in ternary phase diagrams demonstrated by weight fraction. The weight fractions have been used here in this work [31].