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Emulsified fuels based on fatty acid distillates and rapeseed oil: A physicochemical characterization

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ABSTRACT

The emulsification of water in vegetable oils is one of the most promising techniques reported in order to reach an engine-friendly fuel with proper physicochemical properties, allowing improvements in the atomization process and exhaust emissions. For this reason, the scope of this investigation is to formulate and characterize emulsified fuels using different continuous phases, as well as to analyze the influence of the increase of the surfactant concentration on the system stability. The emulsified systems were formulated using ultrasonic equipment and consisted of continuous phase rapeseed oil and fatty acid distillates mixed with diesel fuel. Additional components such as deionized water, ethanol and octanol, as well as sorbitan monooleate and polyoxyethylene sorbitan monooleate as surfactant, were used. The formulated dispersed systems were covered under different experimental factors and summarized in ternary diagrams. Several stable dispersed systems were achieved (emulsions and microemulsions); but only with the introduction of diesel fuel to the formulations, proper viscosity values were achieved. An increase of the viscosity with increasing the amount of water was noted. The water droplets sizes of emulsified rapeseed oil were smaller than in the emulsified fatty acid distillates. Finally, an increase of surfactant percentage in the emulsification process improved the dispersed systems' stability and their optical appearance, whereas also slight differences in density, viscosity and surface tension values were noted.

1. Introduction

The limited fossil fuel's reserves, greenhouse gas emissions, global warming, recent changes in fossil fuel's prices and their influence on the energy scenario are currently worldwide problems. This situation has motivated governments, automotive industries, energy-producing industries and the scientific community around the world to search for suitable alternatives. As a result of these efforts several initiatives such as the carbon credit, subsidies to improve energy efficiency, reduce energy consumption, and promoting the use of renewable energy sources, have been launched.

In this context, engine/vehicle manufacturers are taking into account the recently promulgated tightened emissions standards. The development of new technologies incorporating improvements in vibration, noise control and fuel economy has been accompanied with special attention on reducing emissions. However, most of the engines and their systems continue to be developed for non-renewable fuels.

In concordance with Tan et al. [1] and Senthil Kumar et al. [2], renewable liquid fuels such as vegetable oils and animal fats represent promising alternatives for compression ignition engines because of their properties close to diesel fuel. Vegetable oils can be obtained from different alternative sources around the world (e.g., waste and non-edible feedstocks). However, their low volatility, cetane number and heating value, as well as high viscosity are not in accordance to the ASTM diesel fuel and biodiesel standards (see reported values by Esteban et al. [3]).

The direct use of vegetable oils on diesel engines causes several problems such as lower combustion efficiency due to the poor atomization process and changes in the ignition delay. For this reason and seeking for a more engine-friendly fuel, it is necessary to change the feedstock properties applying different methods such as: preheating, blending with diesel fuel, transesterification,

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cracking/pyrolysis or emulsification. The advantages and drawbacks of each method have been pointed out elsewhere [4,5].

Among these methods, emulsification has an additional attraction future linked with its capacity of decreasing diesel engine exhaust emissions such as nitrogen oxides (NOx). Also, it is not a sophisticated method because modifications of the original engine design and special equipments are not necessary. The formulation of an emulsion involves no complex chemical reactions [6]. It also produces no by-products unlike transesterification [6]. In addition, due to the micro-explosion phenomenon as a consequence of the dispersed water into the emulsified fuel, it is also possible to improve the atomization process and recover in part the combustion efficiency when it is used as diesel engine fuel.

The physicochemical properties of an emulsified fuel play a decisive role in the behavior of the engine performance and exhaust emissions. The formulation and characterization of emulsified fuels using vegetable oils have been reported [7–15]. An important number of these investigations reached emulsified systems with viscosity values non-comparable to the ASTM diesel fuel or biodiesel standards, greatly limiting their potential use. For this reason, this investigation addresses the formulation and characterization of emulsified fuels from vegetable oils (rapeseed oil and fatty acid distillates) seeking for viscosity levels according to the ASTM biodiesel standard.

2. Materials and methods

2.1. Emulsified fuels formulation

Emulsified systems were formulated using rapeseed oil (RO), fatty acid distillates (FAD) and their blends with diesel fuel as continuous phase. The FAD was collected from the Cuban soybean oil refining industry. Also, rapeseed oil and diesel fuel were provided from a Belgian supplier. The physicochemical properties of the neat fuels used for the emulsification process are shown in Table 1.

Additional components such as deionized water, ethanol and octanol as co-surfactants were used, besides sorbitan monooleate (Span 80) and polyoxyethylene sorbitan monooleate (Tween 80) as surfactants. The physicochemical properties of deionized water, surfactants and co-surfactants are shown in Tables 2 and 3, respectively. Span 80 and Tween 80 have been recommended for emulsification as a good stabilizer, both are miscible and their mixtures bring the possibility of obtaining surfactants with different hydrophilic-lipophilic balance (HLB) numbers (from 4.3 to 15) in concordance with each continuous phase (i.e. required HLB). According to Debnath et al. [18] the HLB number is a non-dimensional value, ranging from 0 to 20. Taking into account that hydrophilic molecules are those, which interact with or dissolve in, water and other polar substances; whereas a lipophilic molecule dissolves in fats, oils, lipids, and non-polar solvents [18], different researchers [14,19–21] emphasize that the surfactants used in order to formulate dispersed systems must be selected according to the HLB number. In addition, a mixture of hydrophilic and hydrophobic surfactants generally brings more stable emulsions [11,22,23].

Table 1
Physicochemical properties of neat fuels.

Properties	Rapeseed oil	FAD	Diesel fuel
Kinematic Viscosity @40 °C (mm^2/sec)	29.8	28.6	4
Density @40 °C (g/cm^3)	0.905	0.908	0.818
Surface tension @25 °C (mN/m)	33.4	27.9	27.5
Water content (%)	NS	0.387	<0.05
Lower heating value (MJ/kg)	37.6–39.7[a]	36.5	43

[a] Typical values reported [16,17], FAD: Fatty acid distillates.

Table 2
Physicochemical properties of deionized water.

Item	Value
pH	7
Conductivity (μS/cm)	1
Total hardness (ppm)	<1
Density @40 °C (g/cm^3)	0.998
Kinematic Viscosity @40 °C (mm^2/sec)	0.658

Table 3
Physicochemical properties of surfactants and co-surfactants.

Chemical name	Chemical formula	HLB	Kinematic Viscosity (mm^2/sec)	Density (g/cm^3)	Ref.
Sorbitan monooleate (*Span 80*)	$C_{24}H_{44}O_6$	4.3	300	0.99	[26,27]
Polyoxyethylene sorbitan monooleate (*Tween 80*)	$C_{64}H_{124}O_{26}$	15.0	165	1.06	[5,11,28]
Ethanol	C_2H_5OH	–	1.1	0.79	[25]
Octanol	$C_8H_{17}OH$	–	4.4	0.83	

HLB: Hydrophilic-lipophilic balance.

An equation (Eq. (1)) proposed by Mollet and Grubenmann [24] and Bhimani et al. [11] was used in order to obtain surfactants with different HLB number. Through this equation, the mass percentage (%) of the surfactants involved in the mixture was obtained.

$$\%\text{Surfactant A} = [100 \cdot (X - HLB_B)] \cdot (HLB_A - HLB_B)^{-1} \quad (1)$$

$$\%\text{Surfactant B} = 100 - \%\text{Surfactant A} \quad (2)$$

where

X: Required HLB.
HLB_A: Hydrophilic-lipophilic balance of the surfactant A.
HLB_B: Hydrophilic-lipophilic balance of the surfactant B.

The ethanol as co-surfactant was selected due to its miscibility in water, lower viscosity and good dilution into each continuous phase. Moreover, ethanol is a renewable fuel that can be obtained by fermentation of agricultural wastes [20], among others. On the other hand, octanol was selected as co-surfactant because it is a long chain alcohol which physicochemical properties (e.g., cetane number and heating value) close to diesel fuel, rapeseed oil and fatty acid distillates, in spite of its lower miscibility in water. Also, an additional attraction is the microbial production of octanol as a naturally excreted biofuel with diesel-like properties, as was published by Akhtar et al. [25].

Formulated dispersed systems were studied under different experimental conditions such as the amount of water, surfactant type (e.g., percentage and required HLB), co-surfactant and continuous phase. To obtain a required HLB, several dispersed systems with HLB values ranging from 4.3 to 15 were first prepared by blending the surfactants in different ratios, in accordance with Orafidiya and Oladimeji [29]. A second set of dispersed systems was later prepared using the percentage of surfactant which achieved the most stable emulsified system from the first series. Finally, the emulsified fuels formulated in each set were summarized in ternary diagrams.

The emulsification was conducted using a high-power ultrasonic lab device (Hielscher Ultrasonic UP200S) with a frequency of 24 kHz, impulsion of 70% and amplitude of 90%. The ultrasonic technique was selected because it is an effective choice to produce dispersed systems at high-intensity, in agreement with researchers such as Wilhelm et al. [30], Lin and Chen [31]. The volume