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Physicochemical and rheological characterization of diesel fuel nanoemulsions at different water and surfactant contents

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ABSTRACT

This work aiming to produce a diesel fuel nanoemulsions with high performance exploited a new preparation technique of low energy emulsification method namely batch addition. This technique helps in production of diesel fuel nanoemulsions has a small water droplet sizes, highly transparent appearance and performance from points of view of physicochemical and rheology behaviors over a period of time as 3 months. To achieve this aim, twenty nanoemulsions were prepared at conditions of water and surfactant contents ranging from [5 to 10] to [4 to 10] wt/wt, of total weight of nanoemulsion, respectively at ambient temperature. The prepared nanoemulsions were evaluated for the rheological behaviors at interval time as 0, 1, 2 and 3 months. The results indicated that the rheological properties of the prepared emulsions behave as non-Newtonian flow in the range of shear rate from 132 to 191 s^{-1} with a yield value (τ) ranged from 2.14 to 5.11 D/cm^2 at 6 wt% water content, 30 °C and 2 months time laps followed by Newtonian regime.

1. Introduction

Generally, emulsions possess a droplets size range from 10 to 100 μm. Because of the unfavorable contact between the water and the oil droplets in the emulsified system, emulsion is unstable thermodynamically system, therefore, the collapse of the emulsion system with time is toke place [1]. Nanoemulsions are a category of emulsions that have small droplets size dimensions of 50 to 200 nm [1]. Recently, nanoemulsions are utilized in several industrial sectors as agriculture, food, textiles and fuel emulsions [1,2]. In comparison with other emulsions types, nanoemulsion is kinetically stable for long time. It keeps the water droplet diameter predominantly smaller than others emulsions over time [3]. The stabilization of nanoemulsions is governed by two mechanisms namely; coalescence and Oswald ripening [4]. The most important theory that utilized to calculate the Oswald ripening is Lifshitz–Slyozov and Wagner theory [5,6]. The outcomes of the droplet emulsion stabilization depend mainly on the concentration of dispersed phase and surfactant, and the methods used in the emulsion formation. In several industries, nanoemulsions are formed using two emulsification methods namely: low- [7] and/or high-emulsification methods [8]. These methods create violent demolished forces that mechanically dismantle the oil into very teeny droplets [9]. Although high-energy emulsification methods allow a great control of the droplet size and a large choice of composition, low-energy emulsification methods are interesting because they take advantage of the energy stored in the system to promote the formation of small droplets [10]. High energy method as high pressure homogenization (HPH) and ultrasonication consume significant energy (ranging from10^8 to10^{10} W kg^{-1}) to perform tiny droplets. In contrast, for low energy method, the consuming energy utilized to form small droplets by the formation of internal chemical energy of the system is ($\approx 10^3$ W kg^{-1}) [10]. In the last two decades, direct emulsification systems (i.e. membranes and microfluidic devices) have been introduced for producing monodisperse emulsions at low energy consumption. Unlike in homogenization, in these systems droplets are made at their final size without further refinement. Microfluidic emulsification devices can be divided into two categories based on the droplet formation mechanism: shear-based and spontaneous or interfacial tension driven. In shear-based systems (e.g. T-, and Y-junctions) the flow of both phases influences the droplet size, while in spontaneous systems (e.g. microchannels and EDGE devices) only the dispersed phase does so [11]. Nanoemulsion fuel is a finely dispersed mixture of water in diesel fuel as continuous phase without visible separation. Some known advantages of nanoemulsion fuel are improved the combustion efficiency and reduced the polluted emissions that are released from the diesel engine as nitrous oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO) and carbon dioxide (CO_2) [12]. The most factors affecting the stability and engineering performance of nominations are its theological properties. It is known fact that the rheology of emulsion necessary for using it in some industrial applications as fuel processing [13]. However, the slightly change of the water droplet formulations and/or Ostwald repining process causes the rheological behavior of the nanoemulsion to be modified. The increase in water content in animation causes its behavior to be pseudo-plastic and to

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be time-dependent at higher shear rate [14]. As a fact, two factors have a great effect on the rheological properties of emulsions system as the viscosity of continuous phase and the interfacial rheology between the droplets [15]. Three different forces play a key note in the rheology of nanoemulsion described by [16,17]. These forces are 1) Brownian Diffusion, 2) hydrodynamic interaction and 3) surface forces (repulsive or attractive). This work aims to prepare highly kinetically stable water-in-diesel fuel nanoemulsions using a modified low energy emulsification technique, which used at previously described work [17]. The performance of the prepared nanoemulsions was evaluated from points of view of physicochemical and rheology characterizations over a long period of time as 90 days. To achieve this objective, twenty water-in-diesel fuel nanoemulsions were prepared and evaluated for the stability at optimum HLB during different period of time laps as 0, 15, 30, 60 and 90 days. The rheological characteristics of the formed nanoemulsions were studied as a function of water loading, surfactant concentration, temperature and storage time.

2. Material and methods

2.1. Diesel fuel

A local commercial sample of diesel fuel (**Grade 2**) was supplied by Misr petroleum company, Assiut, Egypt and has the physicochemical properties of the used diesel fuel as illustrated in Table 1. Before emulsion preparation, diesel fuel sample was filtrated several times to fulfillment its purity.

2.2. Surfactants

Two different analytical grades of non-ionic emulsifiers namely: polyoxyethylene 20 sorbitan trioleate (HLB = 11) and sorbitan monooleate (HLB = 4.3) donated as **T5** and **S8**, respectively as emulsion were purchased from Fluka Chemie GmbH, Germany. The water used in all experiments was bi-distils.

2.3. Formation of water-in-diesel fuel nanoemulsions

2.3.1. Nanoemulsions formation (batch addition)

Twenty samples of water-in-diesel fuel nanoemulsions were prepared by one-step low energy method namely batch addition method described by [17]. In this step, 5, 6, 7, 8, 9 and 10% (wt/wt) of bi-distilled water was added to a mixture of diesel fuel and blend emulsifiers of (**T5**) and (**S8**). The concentration of the blend emulsifiers (**MTS)** is 4, 6, 8 10% (wt/wt) from the total weight of emulsion. Water was dosed in constant rate (0.2 ml/2 min) and continuous stirring rotated at 1500 rpm (Scheme 1). The optimum HLB value of 10 ($\mathbf{HLB_{MTS}}$) is utilized for forming stable nanoemulsion [18]. The mixed $\mathbf{HLB_{MTS}}$ value was calculated as follows:

$$HLB_{MTS} = (HLB_{T5} \times (T5)\%) + (HLB_{S8} \times (S8)\%) \quad (1)$$

where; HLB_{T5}, HLB_{S5} and HLB_{MTS} are the HLB values of T5 (11.0), S8 (4.3) and the mixed surfactants (MTS), and T5% and S8% are the mass percentages of T5 and S8 in the mixed surfactants, respectively [18].

2.3.2. Water droplet size measurement

The water droplet radii ($\mathbf{Z_{avg}}$) of the prepared diesel fuel nanoemulsions were measured by dynamic light scattering (Malvern Zetasizer HT-ZS, Worcestershire, United Kingdom) at scattering angle 173° with an argon-laser (λ = 488 nm) and working temperature 25 °C. The mean hydrodynamic diameter (D_h) was calculated by the Stokes-Einstein Eq. (2) [19]:

$$D = \frac{kT}{3\pi\eta D_h} \quad (2)$$

where; $\boldsymbol{D}$ is the diffusion coefficient, $\boldsymbol{k}$ is the Boltzmann constant, $\boldsymbol{T}$ is the absolute temperature, and $\boldsymbol{\eta}$ is the viscosity of the medium. The particle size and size distribution were determined using Contin analysis mode. The refractive index ($\boldsymbol{r_d}$) for pure diesel fuel and water were determined by ABBE refractometers (DR-A1, ATAGO Co., LTD, Japan) and were found to be 1.46 and 1.33, respectively.

2.3.3. Calorific value, CA, (heat of combustion)

The calorific value of the pure diesel fuel and the prepared nanoemulsions was measured by Anton Parr 6200 isoperibol calorimeter, Parr instrument company, USA according to ASTM D4809. CA is determined using the following equation:

$$\text{Calorific value} = \text{gross heat of combustion (Hg)} \times 1.8 \quad (3)$$

where $\mathbf{H_g}$ is calculated as follows:

$$H_g = \frac{\text{Temperature rise} \times \text{energy equivelent of benzoic acid}}{\text{weight of the sample}}.$$

2.3.4. Rheological behavior of water-in-diesel fuel nanoemulsion

The rheological behavior (dynamic viscosity) of pure diesel fuel, water and the prepared diesel fuel nanoemulsions were measured using a Brookfield Rheometer type (Brookfield Engineering Laboratories, Inc., Middleboro, MA 02346–1031, USA). The cone spindle was of type LV(SC4-18), BOB/STATOR (PVS-B1-D-HC). The cup type was Hastelloy C. the dynamic viscosity was measured at temperature and shear rates ranging from 20 to 60 °C and 1–331 s^{-1}, respectively. The influence of time variation (aging time) as 0, 1, 2 and 3 months on the rheological behavior for all the prepared diesel fuel nanoemulsion were conducted at the same previously conditions of temperature and shear rates.

Table 1
Physical properties of pure diesel fuel.

Item	ASTM standard	Standard Limit value*	Results
Color at 40 °C	D1500–07	Minimum, 4	5
Flash point, °C	D93–11	Minimum, 55	59
Kinematic viscosity at 40 °C	D445–12		
Minimum		1.6	1.8
Maximum		7	
Specific gravity 60/60 °F	D792 – 13		
Minimum		0.820	0.830
Maximum		0.870	
Pour point at winter seasons, °C (maximum 3)	D97–11	>–3	–3
Calorific value, MJ/kg	D4868–11	Minimum, 44.3	44.6
Ash content, mass %	D482–11	Maximum, 0.01	0.01
Sulfur content, mass %	D2622–11	Maximum, 1	1
Water content , %	D4006–11	Nil	Nil

3. Results and discussion

3.1. Determination of the optimum hydrophilic-lipophilic balance value (HLB)

One of the most factors affect the preparation of highly stable nanoemulsion is HLB value of the used emulsifiers [18]. For measuring the optimum HLB_{MTS}, different HLB_{MTS} values of the blend emulsifiers (MTS) as 9.6, 9.8, 10, 10.2 and 10.4 wt/wt, water content (ϕ) of 5 wt/wt% and MTS concentration of 10 wt/wt% was utilized. 14 days is the minimum time required and recommended for diesel fuel nanoemulsion stability to be satisfied. The smallest water droplet radii ($\mathbf{Z_{avg}}$) of 26.23 ± 1.1without phase separation was exhibited by HLB_{MTS}