Fuel 221 (2018) 165–170

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Emulsification characteristics of nano-emulsions of solketal in diesel prepared using microwave irradiation

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ARTICLE INFO

Keywords:
Glycerol acetonide
Nano-emulsion
Microwave irradiation
Emulsification stability
Dispersed phase

ABSTRACT

Glycerol acetonide, also termed solketal, which is chemically derived from bio-glycerol, was used as a combustion improver in the dispersed emulsion phase in this study. Nano-emulsions of ultra-low sulfur diesel (ULSD) containing nano-sized droplets of solketal were produced using microwave irradiation and compared with those produced by mechanical homogenizing. A non-ionic surfactant mixture of Tween 80 and Span 80, with a combined hydrophile-lipophile balance (HLB) adjusted to 10 by the weight proportion of the two surfactants was added to assist the emulsion formation. The characteristics of the emulsions produced using the two methods were analyzed and compared. The experimental results show that nano-emulsions can only form when up to 15 wt% of surfactant and no more than 5 wt% of solketal are added. The nano-emulsions from microwave irradiation had a larger mean droplet size, more concentrated one-peak distribution of droplet size, and lower kinematic viscosity and emulsification stability (ES) than those from the mechanical homogenizer. Higher solketal content in the emulsion increased the mean droplet size and kinematic viscosity of the nano-emulsions prepared using either method, and decreased the emulsification stability. The nano-emulsions with 3 wt% solketal in the dispersed phase also had superior characteristics including the lowest mean droplet size and highest ES. This is thus suggested to be the optimum composition.

1. Introduction

Biodiesel is one of the most frequently used biofuels in the world. It is produced through transesterification, in which vegetable oils, animal fats or algal lipids exchange esters with short-chain alcohol. About 10 wt% crude glycerol, blended with various impurities such as catalysts, methanol, unreacted triglycerides and alcohol is produced after the process. The quantity of crude glycerol (a byproduct) reached at least 3 million metric tons in 2015 due to the rapid development of the global biodiesel industry [1]. The economic value of crude glycerol is thus rather low. Crude glycerol can be further chemically or physically converted to produce high value-added fuel additives or industrial chemicals [2].

Glycerol acetonide, also known as solketal, is one of the industrial chemicals derived from glycerol through a condensation reaction with acetone. The chemical formula and oxygen content of glycerol acetonide are $C_6H_{12}O_3$ and 36.36 wt%, respectively. Like similar effects of other oxygenate additives of fuels, the high oxygen content in glycerol acetonide may enhance the extent of combustion, improve engine performance, and reduce black smoke or other emissions from the burning of hydrocarbon fuels [3,4]. Solketal has been used as a low-temperature fluidity improver for liquid fuel [5,6]. Its advantages include stable chemical properties and non-pollution of underground water, unlike other oxygenates such as methyl *tert*-butyl ether (MTBE) that permeate soil once they dissolve in water [7]. However, glycerol acetonide has not been applied in the energy field. It was first considered as a combustion improver for diesel fuel in this study.

Solketal is a hydrophile liquid which is immiscible with petroleum-derived diesel fuel [8,9]. The emulsifying method was thus used to prepare nano-emulsions of dispersed solketal droplets in a continuous diesel phase. Adequate surfactant composition is generally required to reduce the surface tension between two immiscible phases of emulsion [10]. Micro-explosions occur when dispersed water or alcohol droplets vaporize and then explode through their enveloping continuous oil phase after absorbing sufficient latent heat from their surroundings. Many smaller fuel droplets were thus produced in the fuel emulsion, so that the surface to volume ratio of the atomized fuel spray increased, leading to a higher burning rate and enhanced combustion efficiency [11].

When the size of the dispersed micelles in the emulsion reduced to less than 100 nm, the emulsion was thermodynamically stable. A transparent or semi-transparent appearance and superior emulsification

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https://doi.org/10.1016/j.fuel.2018.02.091
Received 24 October 2017; Received in revised form 8 February 2018; Accepted 12 February 2018

stability resulted from the formation of nano-sized droplets in the emulsion [12]. In nano-emulsion, many nano-sized droplets dispersed in the continuous phase are produced through various emulsification methods [13]. Microwave is a kind of magnetic wave with high frequency (300 MHz–300 GHz) and low wavelength (0.01–0.30 m). Microwaves transfer energy through radiation, which can reduce energy loss during the transfer process and greatly reduce reaction time. The contact frequency and surface area during various phases of an emulsion can thus be increased via high-frequency molecular microwave rotation [14]. Hence, an emulsion can be formed by adequately controlling the operating power and time of microwave irradiation. Microwave irradiation may therefore alter the physical structure of a nano-emulsion and thus its emulsification characteristics such as stability and mean droplet size in the dispersed phase. Applying glycerol acetonide as a combustion improver for liquid fuel has not been recorded in the literature. Moreover, the emulsification characteristics of nano-emulsions of solketal droplets dispersed within their enveloping diesel fuel by microwave irradiation have not yet been investigated. In this study, nano-emulsions of continuous diesel fuel distributed with nano-sized solketal droplets were prepared using microwave irradiation. The effects of solketal content and emulsification methods on emulsification characteristics were investigated, and the application potential of solketal for successfully preparing micro- or nano-emulsions of diesel fuel was evaluated.

2. Experiment details

The emulsification characteristics of the nano-emulsions prepared using either microwave irradiation or mechanical homogenizing methods were analyzed and compared. The experimental details are described in the following subsections.

2.1. Experimental materials

Ultra-low sulfur diesel (ULSD) with sulfur content less than 10 ppm was provided by CPC Corporation in Taiwan. ULSD was used as the continuous phase of the emulsions in this study. The specific gravity, heating value and kinematic viscosity of the ULSD were 0.83, 43.43 MJ/kg, and 3.62 mm^2/s, respectively. Solketal of 99.8 wt% purity was supplied by Rhodia Company, which is governed by Solvay Group in Belgium. The product serial number of solketal is SL-191 [10]. The solketal, which acted as a combustion improver and dispersed phase of the emulsion fuel in this study, was clear, colorless, non-corrosive and completely soluble in water. Its chemical formula, specific gravity, boiling point, flash point, melting point, and kinematic viscosity were $C_6H_{12}O_3$, 1.07, 191 °C, 91 °C, −26 °C, and 5.32 mm^2/s, respectively [15], as shown in Table 1.

A non-ionic surfactant mixture of Span 80 and Tween 80 (provided by First Chemical Company, Taiwan) was used as the emulsifier to reduce the surface tension among various phases of the emulsions so that the dispersed solketal phase could be more uniformly distributed within the continuous diesel fuel phase. The hydrophile-lipophile balance (HLB) values of Span 80 and Tween 80 are 4.3 and 15.0, respectively, and they are thus respectively classified as lipophilic and hydrophilic surfactants [16]. The combined HLB value of the non-ionic surfactant mixture was adjusted to 10 by controlling the weight proportions of the Span 80 and Tween 80. The weight proportions of the ULSD, surfactant mixture, and solketal in various emulsions are detailed in Table 2.

Table 1
Typical solketal properties in dispersed phase of diesel emulsion [13].

Item	Property
Chemical formula	$C_6H_{12}O_3$
Molecular weight (g/mol)	132.16
State at room temperature	Colorless liquid
Density (g/cm^3)	1.069
Kinematic viscosity (mm^2/s)	5.32

Table 2
Weight proportions (wt%) of solketal and diesel for preparing emulsions with surfactant mixture ranging from 5 wt% to 20 wt% by microwave irradiating or mechanically homogenizing methods.

(a). 5 wt% surfactant mixture					
Solketal (wt%)	1	3	5	7	9
Diesel (wt%)	94	92	90	88	86
(b) 10 wt% surfactant mixture					
Solketal (wt%)	1	3	5	7	9
Diesel (wt%)	89	87	85	83	81
(c) 15 wt% surfactant mixture					
Solketal (wt%)	1	3	5	7	9
Diesel (wt%)	84	82	80	78	76
(d) 20 wt% surfactant mixture					
Solketal (wt%)	1	3	5	7	9
Diesel (wt%)	79	77	75	73	71

2.2. Preparation methods for emulsions

To compare the characteristics of the emulsions, the inputs for the two emulsifying machines of various nominal operating powers were kept unvaried by controlling their operating time. The details of the emulsion preparation using a mechanical homogenizer and microwave reactor are described below.

2.2.1. Nano-emulsions prepared by mechanical homogenizer

A mechanical homogenizer (T50 model, IKA Inc., Germany) was used to prepare the nano-emulsions of various weight compositions of ULSD, solketal, and surfactant mixture, as shown in Table 2. ULSD acted as the continuous phase, and was first mixed in a beaker and stirred with a 15 wt% surfactant mixture of Span 80 and Tween 80 with a combined HLB value equal to 10, using a magnetic stirrer (SP47235-60 model, Barnstead/Thermolyne Inc., U.S.A.) at a speed of 700 rpm. A preset quantity of solketal was then fed into the mixture by a peristaltic pump (Masterflex L/S model, Cole-Palmer Inc., U.S.A.) and stirred by a mechanical homogenizer (T50 model, IKA Inc., Germany) at a speed of 3000 rpm for 300 s to complete the emulsion formation.

2.2.2. Nano-emulsions prepared by microwave reactor

A non-ionic surfactant mixture of preset amounts of Span 80 and Tween 80 was stirred into ULSD by a magnetic stirrer (SP47235-60 model, Barnstead/Thermolyne Inc., U.S.A.). A peristaltic pump (Masterflex L/S model, Cole-Palmer Inc., U.S.A.) was then used to feed solketal into the ULSD/surfactant mixture in a beaker. The beaker was thereafter moved into the irradiating room of a microwave reactor (Ym3101cb model, Teco Inc., Taiwan). The microwave irradiation was then turned on to the entire diesel fuel mixture at a power of 0.1 kW for 30 s to produce the nano-emulsion of solketal droplets dispersed in the continuous phase of ULSD.

2.3. Analysis of emulsification characteristics

An upright fluorescence microscope (BX53 model, Olympus Inc., Japan), Image-Pro plus Version 4.1 analysis software (Media Cybernetics Inc., U.S.A.), an image analyzer (TK-C1380 model, JVC Inc., Japan) and a charge-coupled device were used to observe the