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Emulsification characteristics of three-phase emulsion of biodiesel-in nitromethane-in-diesel prepared by microwave irradiation

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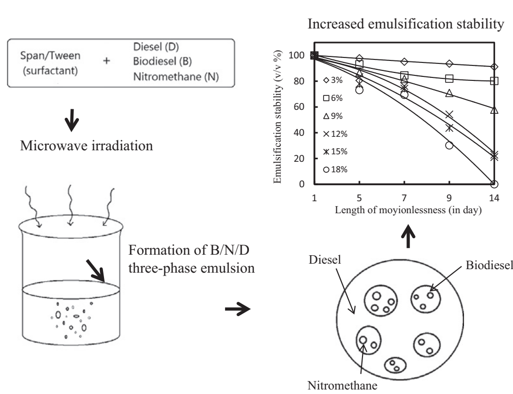
HIGHLIGHTS

- First study to apply microwave irradiation to the formation of three-phase emulsions.
- Emulsions by microwave irradiation have superior emulsification characteristics.
- Emulsions prepared by microwave irradiation have greater emulsification stability.
- Dispersed droplet size of three-phase emulsions is greater than that of two-phase emulsions.
- Emulsions prepared by microwave irradiation feature a more stable droplet size.

GRAPHICAL ABSTRACT



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ABSTRACT

Microwaves, a form of electromagnetic radiation with high frequencies and short wavelengths, are often used for de-emulsification because various emulsion phases are susceptible to separation owing to the intense twisting of polar molecules and abrupt temperature increases caused by microwave vibration. This study was the first to prepare three-phase emulsions of biodiesel-in-nitromethane-in-diesel (B/N/D) with a microwave reactor by capitalizing on effective mass and heat transfer through microwave irradiation. The emulsification characteristics of these three-phase emulsions were compared with those prepared by magnetic stirring, with the same input energy used during the preparation of both sets of emulsions. Nonionic surfactants Span 80 and Tween 80 were used to assist in the emulsions' formation through a reduction in between-phase interfacial tension. The experimental results show that B/N/D three-phase emulsions prepared via microwave irradiation exhibit superior emulsification characteristics to those prepared via magnetic stirring. These superior characteristics include higher levels of emulsion turbidity and emulsification stability and a smaller mean nitromethane droplet size in the dispersed phase. An increase in the mass fraction of the dispersed phase of nitromethane led to an increase in both the number of dispersed droplets and turbidity of the three-phase emulsions in both cases. However, the droplet sizes of the B/N/D emulsions prepared by microwave irradiation were found to be more stable than those prepared by magnetic stirring. Finally, the mean droplet size and temperature of the three-phase B/N/D emulsions were also larger and lower, respectively, than those of two-phase biodiesel-in-nitromethane emulsions of the same composition, regardless of the preparation method.

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1. Introduction

Nitroalkyl compounds that contain one or more nitro-functional groups, such as the radicals of nitrogen oxides (NOx), often exhibit explosive characteristics [1]. They are thus considered to be effective improvers of combustion for petroleum-derived diesel or gasoline [2,3]. The addition of nitroalkyl compounds also serves to break the heavy molecular bonds of liquid fuel, particularly those of residual heavy fuel oil, which features strong attractive forces among its chemical bonds. In other words, more heat might be released during the burning process of a fuel emulsion containing nitroalkyl compounds.

Nitromethane is a representative nitroalkyl compound. The chemical formula of nitromethane is CH_3NO_2, and its molecular weight is 75. It is a colorless liquid that is miscible with water or alcohol but only slightly miscible with petroleum-derived liquid fuels such as diesel and gasoline [4], which implies that when used as an additive to improve combustion, nitromethane is not prone to mixing directly with diesel. The preparation of emulsions of nitromethane dispersed in biodiesel or diesel to maximize the compound's effects in improving the combustion efficiency of liquid fuel is thus of considerable research interest.

As its fuel characteristics are similar to those of diesel, biodiesel is regarded as an excellent alternative fuel [5]. However, owing to the higher oxygen content of biodiesel, internal combustion engines fueled by it generally emit about 10% higher levels of NOx than those fueled by diesel [6,7]. The emulsion of water in diesel has been found to effectively reduce NOx emissions from compression-ignition engines. Therefore, the emulsion of nitromethane in diesel and biodiesel was tested in the study reported herein because of its potential combined advantages of high combustion efficiency and low emission of such pollutants as particulate matter and NOx.

The two-stage emulsification method is generally used to prepare multiple-phase emulsions such as oil-in-water-in-oil in which the dispersed phase separates into an inner phase and outer continuous phase [8,9]. Microwaves are a type of electromagnetic radiation with frequencies in the range of 300 MHz–300 GHz and wavelengths ranging from 0.01 m to 0.3 m. The polar molecules of subject materials exposed to microwave irradiation twist violently, resulting in mutual adherence or movement among the components and thus an abrupt temperature increase in the material [10]. Microwave irradiation has previously been applied to de-emulsification because various emulsion phases are susceptible to separation via the intense twisting of polar molecules caused by microwave vibration. However, the application of microwave irradiation for the preparation of three-phase emulsions has not been reported in the literature. In the study described herein, microwave irradiation was used to prepare three-phase emulsions of bio diesel-in-nitromethane-in-diesel (B/N/D) through a two-stage emulsification method. The emulsification characteristics such as emulsification stability, the mean droplet size of the dispersed nitromethane phase, and emulsion turbidity were analyzed and compared with those of the same emulsions prepared by magnetic stirring to evaluate the application potential of microwave irradiation for the preparation of multiple emulsions.

2. Experimental details

The three-phase emulsions of B/N/D were prepared by the microwave-assisted and magnetic stirring methods. As noted, emulsification characteristics such as emulsification stability and the mean droplet size of the dispersed phase were analyzed and compared. Details of the experimental methods are described in the following.

2.1. Materials for emulsion preparation

Nitromethane of 98 wt.% purity, which is used to improve combustion in three-phase emulsions, was provided by Uni-Onward Co. (Taiwan). The boiling point, flash point, specific gravity, and absolute viscosity (at 25 °C) of the nitromethane were 103 °C, 35 °C, 1.138, and 0.61 mPa s, respectively. Super-low-sulfur diesel (SLSD) was provided by the Taiwan Chinese Petroleum Co. In the second emulsification step, SLSD was prepared as the outer continuous phase, enveloping the dispersed phase of nitromethane containing droplets of the inner phase of biodiesel in the three-phase emulsion. The amount of heat released from burning, specific gravity, and kinematic viscosity of SLSD were 43.429 MJ/kg, 0.834, and 3.615 mm^2/s, respectively. The physical structure of the three-phase emulsion is illustrated in Fig. 1. Finally, a commercial biodiesel made from used cooking oil through strong alkaline transesterification was provided by the Chant Oil Co. (Taiwan). The amount of heat released by burning the biodiesel was 39.62 MJ/kg, 8.8% lower than that released by burning the SLSD. However, the flash point, specific gravity, kinematic viscosity, and acid value of the biodiesel were all higher than those of the SLSD. The fuel characteristics of the dispersed phase (nitromethane), inner phase (biodiesel), and outer continuous phase (SLSD) are presented in Table 1 for comparison purposes.

In this study, Span 80 and Tween 80, non-ionic surfactants provided by First Chemical Inc. (Taiwan), were used to reduce the surface tension between the various phases of the three-phase emulsion in such a way that the dispersed phase in the form of numerous droplets was distributed evenly within the outer continuous phase. The HLB of Span 80 and Tween 80 are 4.3 and 15.0, respectively. The combined HLB of the surfactant mixture could be adjusted by controlling the quantities of these two surfactants in preparing various types of emulsions.

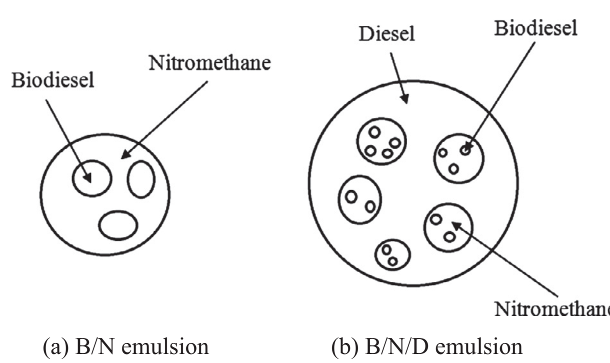

Fig. 1. Physical structure of (a) two-phase emulsion of biodiesel-in-nitromethane (B/N) and (b) three-phase emulsion of biodiesel-in-nitromethane-in-diesel (B/N/D).

Table 1
Fuel characteristics of components of three-phase emulsions.

Property	Nitromethane	SLSD	Commercial biodiesel
Amount of heat release (MJ/kg)	8.618	43.429	39.620
Carbon residue (wt.%)	0.01	0.49	0.20
Kinematic viscosity (mm^2/s)	0.610	3.615	4.274
Specific gravity	1.138	0.834	0.880
Cold filter plugging point (°C)	4	−4	0
Flash point (°C)	32	55	186
Cetane index	–	59.01	45.62