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Rhamnolipid based glycerol-in-diesel microemulsion fuel: Formation and characterization

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HIGHLIGHTS

- RL based diesel microemulsion system was effective on glycerol upgrading.
- Properties of the glycerol-in-diesel microemulsion fuel were comparable to diesel.
- CP and PP of microemulsion fuel were improved by the addition of glycerol.
- Glycerol dispersed in microemulsion fuel acted like an anti-freezing additive.

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ABSTRACT

Microemulsion technology was found to be a promising fuel-upgrading process for glycerol. Biosurfactant rhamnolipid (RL) was successfully tested to obtain nano-scaled glycerol-in-diesel microemulsion (GDM) and glycerol/water-in-diesel microemulsion (G/WDM). These microemulsion fuels were stored at 4 °C without phase separation for over six months. Fuel properties like high heating value (HHV), dynamic viscosity, corrosivity, and thermal decomposition characteristics of GDM and G/WDM were comparable to those of diesel. Thus, the microemulsion fuel may be qualified as commodity fuel like diesel. In addition, the cold flow properties cloud point and pour point of GDM and G/WDM were improved by the addition of glycerol or glycerol/water mixtures. Glycerol—the commonly used raw material for fuel additive production—could be directly introduced into fuel as cold flow property improver by microemulsion technology.

1. Introduction

Glycerol, also known as glycerine or propane-1, 2, 3-triol, is primarily produced during transesterification, saponification, and hydrolysis reaction. It is notably known as a valuable byproduct of biodiesel production. Transesterification in biodiesel production would result in the production of crude glycerol, containing many impurities such as methanol, water, soap, ash, and other organic materials [1,2]. Nearly 18 billion gallons (5.99 million tones) of biodiesel was produced in the USA in 2013, which equated to approximately 132 million gallons (0.63 million tones) of glycerol [2]. The large amount of crude glycerol may induce environmental problem, as it is difficult to be disposed of in the environment. The researches on the application and conversion of glycerol to value-added commodity chemicals, fuels and fuel additives have drawn much attention lately [1,3,4].

Combustion is an advantageous and simple method to make use of glycerol in large amounts as it does not require any purification or processing [5]. However, glycerol is difficult to burn due to several factors such as low energy density, high viscosity, and high auto-ignition temperature [6]. The incomplete combustion from direct burning of glycerol would lead to the emissions of acrolein and carcinogen and the high yield of ash [5–7]. Blending glycerol into diesel or gasoline through emulsification/microemulsification is one of the promising methods to reduce the problems associated with stand-alone glycerol fuel use [2,7]. Emulsion is a thermodynamically unstable but kinetically stable system, which has been

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proven to be a promising fuel upgrading process [8–10]. Glycerol-in-diesel emulsion fuel was produced and tested on a waste oil burner according to the study of Mize et al. [7]. The glycerol-in-diesel emulsion fuel performed well without failure, demonstrating its potential as a fuel for oil burner [7]. In another study, glycerol-in-diesel emulsion was demonstrated to have positive effect on the reduction of unwanted combustion emissions [2]. Oxides of nitrogen and particulate matter emissions were reduced by 5–15% and 25–50% when the glycerol-in-diesel emulsions (prepared at 10 and 20 vol% glycerol phase) were combusted in a naturally aspirated single-cylinder diesel engine [2]. These emission reduction benefits are believed to be offered by the effect of micro-explosion, which was caused by the secondary atomization from the high vapour pressure of the interior liquid [2,11].

Microemulsion is an optically transparent and thermodynamically stable dispersion system that has less risk of phase separation upon long-term storage compared to emulsion system [12]. In addition, microemulsion can be formed spontaneously with low energy consumption and it has nano-metric size dispersed droplets [13–15]. These advantages may qualify the microemulsion technology as a more attractive process than emulsion for glycerol upgrading. However, efficient surfactant should be selected since the formation of microemulsion needs more surfactant than emulsion. Biosurfactant has the advantages of high efficiency, biodegradability, and sustainability compared to synthetic surfactant [16]. Note that biosurfactant rhamnolipid (RL) has been proven to have good performance on microemulsion fuel formation [17,18]. In this study, RL was applied to obtain good performance on glycerol microemulsification.

This study tried to introduce the diesel immiscible glycerol or glycerol mixtures into diesel by microemulsion technology, and provide a novel and environment-friendly glycerol utilization approach with the advantages of energy recovery, cost reducing, and emission reduction.

2. Materials and methods

2.1. Materials

Rhamnolipid was produced by *Phanerochaete aeruginosa* (ATCC 9027, Chinese Type Culture Collection) maintained on *Pseudomonas* agar slants and transferred monthly as described in Ref. [19].

Span 80 (sorbitan monooleate, purity >99%) and Tween 80 (sorbitan monooleate ethoxylate, purity >99%) were purchased from Shanghai Qinxi Chemical Industry S&T Co., Ltd. (Shanghai, China). Glycerol (purity >99%) was purchased from Sigma Aldrich. No. 0 diesel was purchased from a local petrol station in Changsha, Hunan Province, China. All other chemicals were of analytical grade and used as received.

2.2. Glycerol microemulsification

2.2.1. Surfactant screening

Primarily, nonionic surfactants Span 80 and Tween 80 or their mixtures with different hydrophilic and lipophilic balance (HLB) value ranging from 4.3 to 15 were used for glycerol-in-diesel microemulsion (GDM) formation. Table 1 represents the compositions used in the experiment. In each experiment, 10 mL diesel and certain amounts of surfactant and glycerol were added to form the microemulsion system at 25 °C. The solubilization capacity (defined as the mass ratio of the solubilized phase to surfactant (g g^{-1}), e.g. mass ratio of glycerol to the surfactant, or g glycerol/g surfactant) was monitored to optimize the HLB value of the surfactants.

Subsequently, RL with HLB value reported of 22–24 [16] was employed to form the GDM system. Then different concentrations of RL in diesel were evaluated against the solubilization capacities to obtain an optimum RL dosage.

2.2.2. Effect of cosurfactant and model impurities

RL based GDM was also formed with the addition of different alkanols as *n*-butanol, *n*-pentanol, *n*-hexanol, and *n*-octanol to select an optimum cosurfactant. Then the model impurities such as water, methanol, ethanol, and NaCl, which may exist in crude glycerol, were added to assess their influences on the solubilization capacities. Specifically, glycerol/water mixtures with different ratios (w/w, 0–100%) were prepared to monitor the solubilization capacities. Subsequently, the dynamic viscosity of the glycerol/water-in-diesel microemulsion (G/WDM) was measured by a Dynamic Viscosity Analyzer (SNB-2, China). Pour point (PP) was measured by the method described in Section 2.3.

2.3. Microemulsion fuel property characterization

The dynamic viscosity, high heating value (HHV), corrosivity, cloud point (CP), and PP of diesel, glycerol, GDM, and G/WDM were measured. HHV was measured by using a heating value calorimeter (SDACM500, China). CP and PP are cold flow properties of fuel. CP is the temperature at which fuel begins to thicken and become cloudy (the beginning of crystallization) and PP is the temperature at which fuel begins to thicken with no pour in 5 s (the beginning of the operative problems). They were determined by observing the samples to become thicken or cloudy at the decrement of temperature in a Cold Flow Property Tester (SYD-510F1, China). The corrosivity of these fuels was measured by a copper strip corrosion test (CSCT), which was based on the discoloration of a standard copper strip immersed into a sample at 100 °C for 3 h.

A Malvern nanometer particle size analyzer (Zetasizer Nano ZEN3600, UK) was adopted to analyze the droplet size distribution of GDM and G/WDM. In addition, an integrated thermal gravimetric analyzer (EXSTAR, TG/DTA 7300, Japan) with nitrogen atmosphere (purity of 99.99%, flow rate of 100 mL min^{-1}) was adopted for the thermogravimetric analysis (TGA) of RL, diesel, glycerol, and GDM. Each sample was heated from 40 °C to 600 °C with a constant heating rate of 10 °C min^{-1}.

3. Results and discussions

3.1. Formation of glycerol-in-diesel microemulsion

3.1.1. Effect of surfactant

Glycerol and diesel are immiscible in nature with no measurable amount of glycerol or diesel is soluble to each other. But they can soluble to each other by the formation of microemulsion.

Table 1
Surfactant system compositions.

Surfactant composition	HLB value											
	4.3	5	6	7	8	9	10	11	12	13	14	15	22–24
Span 80 (w%)	100	92	84	76	64	56	46	36	28	18	8	0	
Tween 80 (w%)	0	8	16	24	36	44	54	64	72	82	92	100	
Rhamnolipid (w%)													100