



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



Lijian Leng^{a,b}, Xingzhong Yuan^{a,b,*}, Guangming Zeng^{a,b}, Xiaohong Chen^c, Hou Wang^{a,b}, Hui Li^d, Lihuan Fu^{a,b}, Zhihua Xiao^{a,b}, Longbo Jiang^{a,b}, Cui Lai^{a,b}

^a College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

^b Key Laboratory of Environment Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

^c School of Business, Central South University, Changsha 410083, PR China

^d Institute of Bio-energy, Hunan Academy of Forestry, Changsha 410004, PR China

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.

ARTICLE INFO

Article history:

Received 21 September 2014

Received in revised form 15 January 2015

Accepted 18 January 2015

Available online 29 January 2015

Keywords:

Glycerol
Microemulsion
Rhamnolipid
Fuel additive
Diesel

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.

© 2015 Elsevier Ltd. All rights reserved.

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

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 731 88821413; fax: +86 731 88823701.

E-mail address: yxz@hnu.edu.cn (X. Yuan).

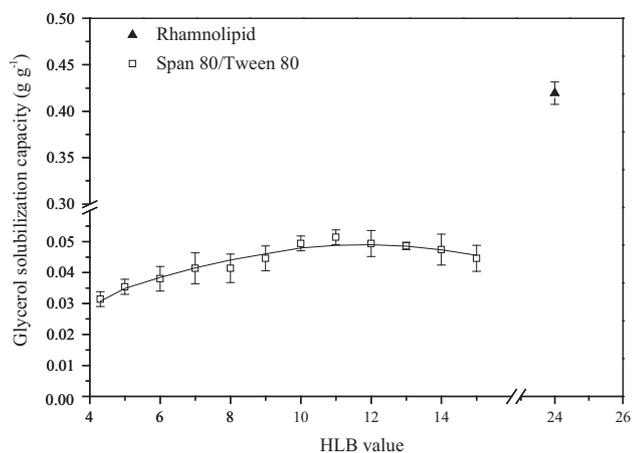


Fig. 1. The effect of surfactant HLB values on glycerol solubilization capacities of the Span 80/Tween 80 mixtures or RL based microemulsion fuels.

Surfactant is required to form microemulsion system. Commonly, a surfactant has a lipophilic or hydrophobic group and a hydrophilic group. HLB value of a surfactant is commonly used to describe the specific polar/non-polar character of the surfactant and the affinity of the surfactant for the oil–water interface. A high HLB value of a surfactant means its super hydrophilic property. Nonionic surfactant Span 80 (HLB = 4.3) and Tween 80 (HLB = 15) mixtures were prepared over a range of HLB values 4.3–15 by adjusting the mixing ratio of the two surfactants. The composition of each mixture is displayed in Table 1.

Upon the addition of surfactant and the formation of GDM, glycerol solubilization capacity was recorded for the selection of an optimum HLB value. As indicated in Fig. 1, the relatively flat region of the plot from HLB 4.3 to 15 indicates that the Span 80/Tween 80 surfactant mixtures were not effective on GDM formation. Nevertheless, the plot played a meaningful role for selecting the optimum surfactant HLB. It is shown in Fig. 1 that surfactant mixtures with HLB values of 10–15 (the higher ones) might have better performance on GDM formation. These phenomena are agree with the previous results that the suitable HLB values for glycerol-in-diesel emulsion formation were 10–12, higher than those for water-in-diesel emulsion [7]. Biosurfactant RL with a higher HLB value of 22–24 was then tested for GDM formation and it showed surprisingly high glycerol solubilization capacity. The glycerol solubilization capacity obtained was 0.42 g g^{-1} (g glycerol/g surfactant), which was almost 10 times higher than those of the Span 80/Tween 80 surfactant mixtures ($0.031\text{--}0.051 \text{ g g}^{-1}$). The carboxylate group gives rhamnolipid its anionic character while the rhamnosyl groups contribute to the bulky hydrophilic component of their structure [16]. The better performance of RL than the Span 80/Tween 80 mixtures on GDM formation was probably due to its particular molecular structure [16] and its superb affinity for the glycerol–diesel interface [7,20].

The glycerol solubilization capacity was used for selecting the optimum RL dosage. As shown in Fig. 2, the mass of glycerol solubilized in diesel microemulsion increased as the increment of RL dosage, while the glycerol solubilization capacity saw a slight increment at the dose range of $0.01\text{--}0.05 \text{ g mL}^{-1}$ and a decrement at the dosage higher than 0.05 g mL^{-1} . Thus, the optimum RL dosage was determined to be 0.05 g mL^{-1} , which is agree with the result reported in Ref. [18].

3.1.2. Effect of cosurfactant

Alkanols such as *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, and *n*-octanol were selected for cosurfactant screening and the

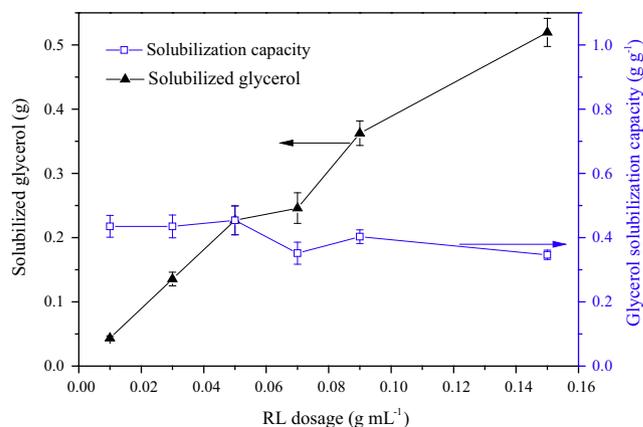


Fig. 2. The effect of RL dosage on glycerol solubilization capacities of the RL based microemulsion fuels.

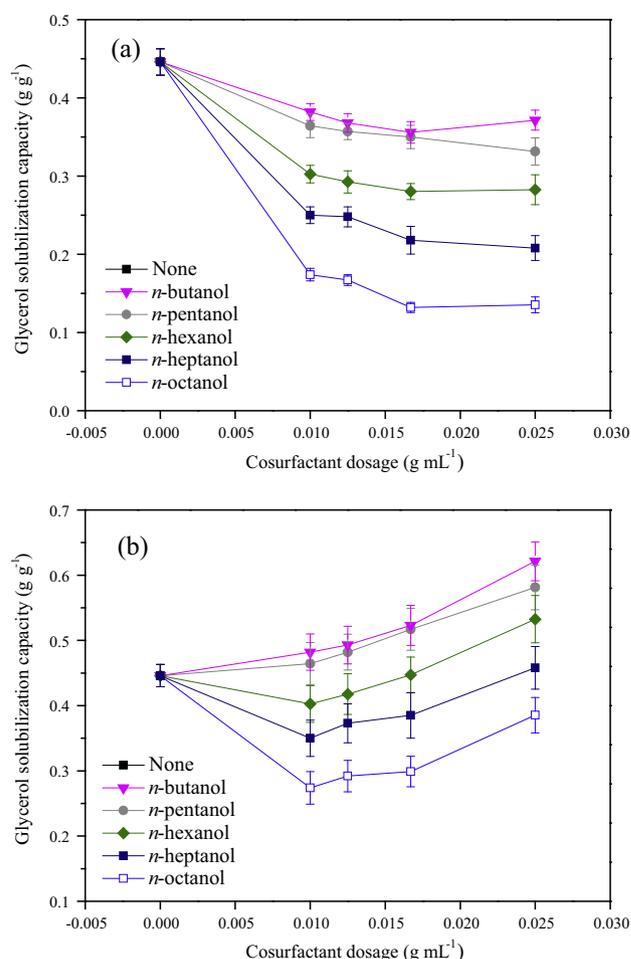


Fig. 3. The effect of cosurfactant on solubilization capacities of the RL based microemulsion fuels with RL at the dose of 0.05 g mL^{-1} ; (a) the monomeric glycerol solubilization capacities and (b) the glycerol mixtures (glycerol/alkanol) solubilization capacities.

results are potted in Fig. 3. As shown in Fig. 3(a), these cosurfactants seemed had negative effect on the GDM formation and reduced the glycerol solubilization performance of RL. The increasing dosage and chain-length of the cosurfactants (alkanols) resulted in the decrement of the solubilization capacity of glycerol. The alkanols probably had been located in the polar phase (acted as

solubilized substances) in competition with glycerol when they were solubilized in the RL based microemulsion. Microemulsion system formed by RL or RL mixture in the absence of cosurfactant had also been reported in many researches [21]. However, as the trends displayed in Fig. 3(b), the glycerol mixture (glycerol/alkanol) solubilization capacity saw an increment as the dosage of alkanols increase. The solubilization capacities of GDM with the addition of *n*-butanol, *n*-pentanol, or *n*-hexanol (at high dose) were higher than that of GDM with no addition of alkanols. Alkanols might preferentially distribute into the polar glycerol phase until the micelles approached swollen and then they might distribute to the glycerol–diesel interface acting like cosurfactants, allowing greater penetration of glycerol or alkanols into the polar glycerol phase.

3.1.3. Effect of the model impurities in crude glycerol

Crude glycerol produced during biodiesel production would contain impurities such as water, NaCl, and methanol when methanol is used as the acyl donor (ethanol when ethanol is the acyl donor). The effects of these impurities on the solubilization capacities of the glycerol mixture are displayed in Fig. 4. As plotted in the figure, these impurities had negative effects on the solubilization of glycerol especially NaCl. But the concentration variation of NaCl (0.1–0.5 mol L⁻¹) did not show obvious negative effect on the solubilization capacity. Stable G/WDM can also be formed at high NaCl concentration. In addition, glycerol was more easily to be emulsified by RL than water, methanol, or ethanol. The monomeric solubilization capacities of water, methanol, or ethanol in the microemulsion systems in the absence of glycerol were obviously lower than those of glycerol or glycerol mixture systems. Water, methanol, and ethanol solubilized in the microemulsion systems might probably have been located in the polar phase in competition with glycerol [22,23]. Additionally, water performed a little better than ethanol and methanol because of its relatively higher solubilization capacity in the RL based microemulsion system (see in Fig. 4 when the percentage of glycerol in water/glycerol mixtures equals to zero).

Although the impurities had negative effects on the solubilization of glycerol, water, ethanol, and methanol mixed with glycerol could efficiently reduce the viscosity of glycerol [24,25]. Upon the formation of G/WDM, the dynamic viscosity of the glycerol/water mixture and the G/WDM were determined and the results are

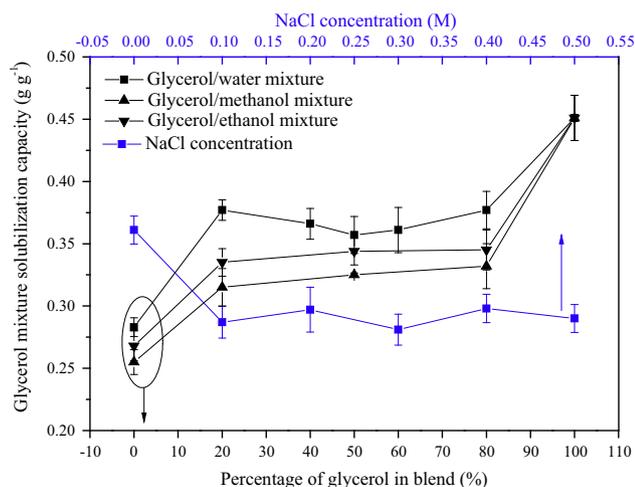


Fig. 4. The effects of model impurities on the solubilization capacities of the RL based microemulsion fuels with RL at the dose of 0.05 g mL⁻¹ (NaCl was added to the glycerol/water mixture (w/w, 50:50) with concentrations ranging from 0 to 0.5 M).

shown in Fig. 5. The water content had a significant impact on the viscosity of the glycerol/water mixture. The dynamic viscosity of the mixture saw a dramatic increase when the content of water was lower than 50% (or content of glycerol higher than 50%), which is in consistent with the result obtained in Ref. [24]. However, the dynamic viscosity of the G/WDM systems with different glycerol/water ratios remained nearly constant (range from 5.83 to 6.06 mPa s), due to that the mixtures solubilized in the microemulsion only took up a small portion (<5% of the total by weight, data not show).

3.2. Characterization of GDM and G/WDM

Diesel, glycerol, WDM, GDM, and G/WDM were selected for fuel property characterization. The dynamic viscosity ($T = 30\text{ }^{\circ}\text{C}$), CP, PP, corrosivity, and HHV were determined and the data were tabulated in Table 2.

The dynamic viscosity, corrosivity, and HHV of the microemulsion fuel systems (WDM, GDM, and G/WDM) were similar to those of diesel and the systems were stored at 4 °C without phase separation for over six months, indicating their good storage stability and great potential to be used as commodity fuels. CP and PP are commonly used indicators for the characterization of the crystallization (cold flow) properties [26,27]. The cold flow properties (CP and PP) of the microemulsion fuel systems were improved by the addition of glycerol or the glycerol/water mixtures, while the addition of water alone had little effect. The CP of both GDM and G/WDM was $-6\text{ }^{\circ}\text{C}$ and PP of them was -13 and $-11\text{ }^{\circ}\text{C}$, respectively. No phase separation was observed during the determination of CP and PP. The CP and PP of both GDM and G/WDM were lower than those of WDM (-3 and $-7\text{ }^{\circ}\text{C}$, respectively) or diesel (-3 and $-6\text{ }^{\circ}\text{C}$, respectively), which could be due to the low freezing point of the added glycerol/water mixtures dispersed in the system [28]. The freezing point of glycerol/water mixture at ratio of 66.7:33.3 could be as low as $-46.5\text{ }^{\circ}\text{C}$ [28] resulting from the ice crystallization inhibition by the hydrogen bonding patterns formed in the solution [29]. The presence of many dispersed materials in the emulsion had been reported to have lower crystal temperature than that of the bulk material (e.g. water-in-oil emulsion, $-39\text{ }^{\circ}\text{C}$ versus bulk water, $-18\text{ }^{\circ}\text{C}$ [30]; and palm oil-in-water emulsion, $2\text{ }^{\circ}\text{C}$ versus bulk palm oil, $21\text{ }^{\circ}\text{C}$ [31]). The smaller the diameter of the dispersed material in the emulsion, the lower the freezing temperature of the system will be [32]. The nano-scaled glycerol or glycerol/water mixtures dispersed in the microemulsion (diameter much smaller than that of the emulsion) could probably

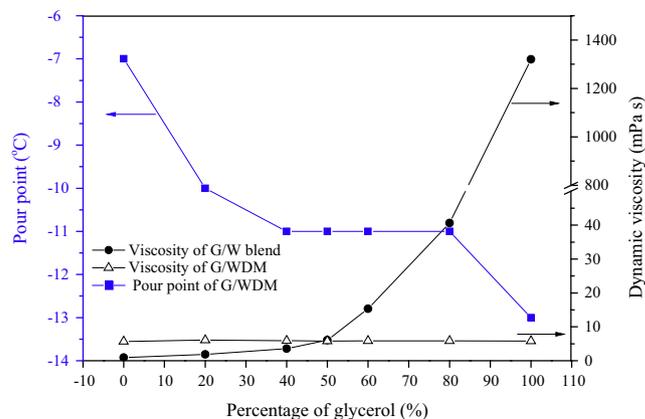


Fig. 5. The dynamic viscosity and pour point of the G/WDM formed with RL at the dose of 0.05 g mL⁻¹ at different glycerol/water (G/W) mixing ratios.

Table 2
Fuel properties of diesel, glycerol, and WDM, GDM, G/WDM.

Item	Dynamic viscosity ($T = 30\text{ }^{\circ}\text{C}$, mPa s)	Mean diameter (nm)	Cloud point ($^{\circ}\text{C}$)	Pour point ($^{\circ}\text{C}$)	CSCT ^a	HHV (MJ kg^{-1})
Diesel	4.8	– ^g	–3	–6	1a	44.3
Glycerol	1320	–	–	–	–	18.5
RMS ^{b,c}	4.9	1.5	–	–	–	–
WDM ^{c,d}	4.9	22.5	–3	–7	1a	43.7
GDM ^{c,e}	5.8	125.6	–6	–13	1a	43.6
G/WDM ^{c,f}	5.7	135.8	–6	–11	1a	43.6

^a CSCT: copper strip corrosion test; 1 = slight tarnish; a = light orange, almost the same as freshly polished strip; b = dark orange.

^b RMS: reversed micellar system with RL at the dose of 0.05 g mL^{-1} .

^c Stored at $4\text{ }^{\circ}\text{C}$ without phase separation in six months.

^d WDM: water-in-diesel microemulsion with RL at the dose of 0.05 g mL^{-1} and water at the dose of 0.28 g/g RL .

^e GDM: glycerol-in-diesel microemulsion with RL at the dose of 0.05 g mL^{-1} and glycerol at the dose of 0.42 g/g RL .

^f G/WDM: glycerol/water-in-diesel microemulsion with RL at the dose of 0.05 g mL^{-1} and glycerol/water mixture (w/w, 50:50) at the dose of 0.36 g/g RL .

^g Not detected.

modify the crystallization behavior of the microemulsion and bring down the CP and PP of the system.

As shown in Table 2, the measured diameter of the reversed micellar system (mixture of diesel and RL in the absent of water and glycerol), WDM, GDM, and G/WDM were in the nano range of 1–200 nm, and thus, the formation of microemulsion was verified. The reversed micellar system had the smallest diameter because there was almost no polar substance in the core of the micelles. The addition of water and/or glycerol increased the diameter of the system, demonstrating that the added water and/or glycerol would probably locate in the core of the micelles.

As shown in Fig. 6, the thermal decomposition characteristics of GDM (the main component was diesel) were similar to those of diesel. There was a mass loss below $100\text{ }^{\circ}\text{C}$ (weight loses of 14.2%) during glycerol decomposition, indicating the existence of water in glycerol. Glycerol has very strong water adsorbing ability and water may probably be absorbed into glycerol upon glycerol usage and storage. Glycerol was almost decomposed at a narrow temperature ranging from $137\text{ }^{\circ}\text{C}$ to $230\text{ }^{\circ}\text{C}$ with the maximum degradation rate (3.64 w\% min^{-1}) appeared at $188.6\text{ }^{\circ}\text{C}$. The decomposition characteristics of diesel after $124\text{ }^{\circ}\text{C}$ were similar to those of glycerol. The maximum degradation rate (2.38 w\% min^{-1}) of diesel appeared at $175.6\text{ }^{\circ}\text{C}$. GDM was a mixture of diesel, glycerol, and RL, therefore the weight loses $<230\text{ }^{\circ}\text{C}$ were mainly attributed to diesel and glycerol decomposition. The weight loses at $230\text{--}310\text{ }^{\circ}\text{C}$ would be ascribed to RL note that RL was almost decomposed at $230\text{--}310\text{ }^{\circ}\text{C}$ with a maximum degradation rate (2.39 w\% min^{-1}) appeared at $253.9\text{ }^{\circ}\text{C}$. The maximum degradation rate (1.53 w\% min^{-1}) of GDM appeared at $175.7\text{ }^{\circ}\text{C}$, meaning that the main component in GDM was diesel. The other component like glycerol and RL did not significantly affect the decomposition of GDM on the whole. However, the maximum degradation rate of GDM was lower than that of diesel, which may because of the formation of microemulsion system. The thermograms of microemulsion obtained had been reported to be different and depended on the amount of solubilized phase in the system [32]. The reduced degradation rate might lead to the reduction of peak combustion temperature and the improvement of atomization of the microemulsion fuel in engine, and further reduce the NO_x emissions [11,33].

3.3. Environmental implications

Although biodiesel is a very good solvent, sometimes it has poorer cold flow properties than petroleum fuels [34]. Biodiesel with poor cold flow properties would usually require the addition of fuel anti-freezing additives like glycerol ethers, acetyl glycerol, and glycerol acetal. It is worth mentioning that glycerol itself was historically used as an anti-freezer for automotive applications

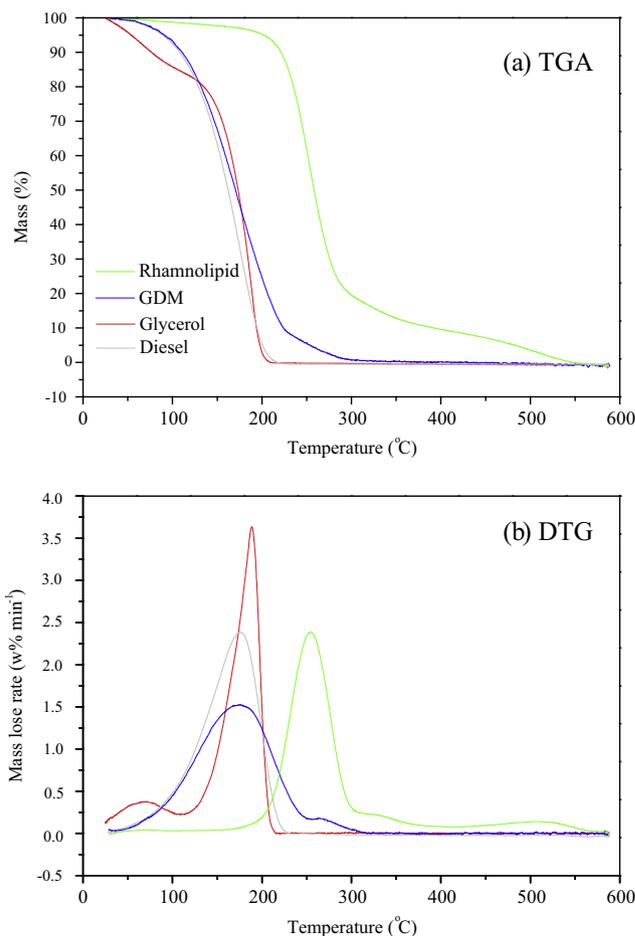


Fig. 6. TGA and DTG curves of RL, diesel, glycerol, and GDM formed with RL at the dose of 0.05 g mL^{-1} , and glycerol at the dose of 0.42 g/g RL .

before being replaced by ethylene glycol because of its relative high freezing point and cost [35]. As the production of less toxic glycerol mounting recently, glycerol can be re-examined for use in automotive applications [35]. Cold flow property improvement results obtained in this study indicate that, glycerol or glycerol/water mixtures can be treated as anti-freezing additive to improve the cold flow properties (e.g. PP) of the emulsion/microemulsion fuel (e.g. biodiesel). Note that glycerol emulsification/microemulsification also has the advantages of direct-energy recovery, unnecessary purification and processing, and emission reduction, RL based glycerol microemulsion fuel could be used as fuel like diesel,

providing a promising way out for the crude glycerol produced in biodiesel production.

4. Conclusions

Microemulsion technology was employed to upgrade glycerol for fuel application. Glycerol or glycerol/water mixture (immiscible with diesel in nature) was solubilized in diesel by forming GDM or G/WDM fuel with the addition of an efficient biosurfactant (RL). The RL based GDM and G/WDM fuel could be formed spontaneously with low energy consumption and had nano-metric sized droplets. They had less risk of phase separation upon long-term storage compared to the emulsion system. In addition, HHV, dynamic viscosity, corrosivity, and thermal decomposition characteristics of GDM and G/WDM were similar to those of diesel. Interestingly, the pour point and cloud point of GDM ($-13\text{ }^{\circ}\text{C}$ and $-6\text{ }^{\circ}\text{C}$, respectively) were improved obviously compared to diesel (-6 and $-3\text{ }^{\circ}\text{C}$, respectively). Glycerol or glycerol/water mixtures could be solubilized in the microemulsion as cold flow property improvers.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China, China (Nos. 21276069, 71431006, and 51408206), the Specialized Research Fund for the Doctoral Program of Higher Education, China (No. 20120161130002), and the Collaborative Innovation Center of Resource-conserving & Environment-friendly Society and Ecological Civilization, China.

References

- [1] Tan HW, Abdul Aziz AR, Aroua MK. Glycerol production and its applications as a raw material: a review. *Renew Sustain Energy Rev* 2013;27:118–27.
- [2] Eaton SJ, Harakas GN, Kimball RW, Smith JA, Pilot KA, Kufflik MT, et al. Formulation and combustion of glycerol–diesel fuel emulsions. *Energy Fuels* 2014;28:3940–7.
- [3] Rahmat N, Abdullah AZ, Mohamed AR. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: a critical review. *Renew Sustain Energy Rev* 2010;14:987–1000.
- [4] Izquierdo JF, Montiel M, Palés I, Outón PR, Galán M, Jutglar L, et al. Fuel additives from glycerol etherification with light olefins: state of the art. *Renew Sustain Energy Rev* 2012;16:6717–24.
- [5] Quispe CAG, Coronado CJR, Carvalho Jr JA. Glycerol: production, consumption, prices, characterization and new trends in combustion. *Renew Sustain Energy Rev* 2013;27:475–93.
- [6] Bohon MD, Metzger BA, Linak WP, King CJ, Roberts WL. Glycerol combustion and emissions. *Proc Combust Inst* 2011;33:2717–24.
- [7] Mize HE, Lucio AJ, Phaner CJ, Pratama FS, Robbins LA, Karpovich DS. Emulsions of crude glycerin from biodiesel processing with fuel oil for industrial heating. *J Agric Food Chem* 2013;61:1319–27.
- [8] Burguera JL, Burguera M. Analytical applications of emulsions and microemulsions. *Talanta* 2012;96:11–20.
- [9] Guo Z, Wang S, Wang X. Stability mechanism investigation of emulsion fuels from biomass pyrolysis oil and diesel. *Energy* 2014;66:250–5.
- [10] Debnath BK, Saha UK, Sahoo N. A comprehensive review on the application of emulsions as an alternative fuel for diesel engines. *Renew Sustain Energy Rev* 2015;42:196–211.
- [11] Kadota T, Yamasaki H. Recent advances in the combustion of water fuel emulsion. *Prog Energy Combust Sci* 2002;28:385–404.
- [12] Lif A, Stark M, Nydén M, Holmberg K. Fuel emulsions and microemulsions based on Fischer–Tropsch diesel. *Colloids Surf A Physicochem Eng Aspects* 2010;354:91–8.
- [13] Balcan M, Mihăilescu FC, Anghel DF, Văcăreșteanu IC, Aricov L, Vasilescu EL. Microemulsion systems containing diesel and colza oil as alternative fuels: phase studies, interfacial tension and solubilization. *Fuel* 2014;117:251–8.
- [14] Attaphong C, Sabatini DA. Phase behaviors of vegetable oil-based microemulsion fuels: the effects of temperatures, surfactants, oils, and water in ethanol. *Energy Fuels* 2013;27:6773–80.
- [15] Attaphong C, Do L, Sabatini DA. Vegetable oil-based microemulsions using carboxylate-based extended surfactants and their potential as an alternative renewable biofuel. *Fuel* 2012;94:606–13.
- [16] Nguyen TT, Youssef NH, McInerney MJ, Sabatini DA. Rhamnolipid biosurfactant mixtures for environmental remediation. *Water Res* 2008;42:1735–43.
- [17] Nguyen T, Do L, Sabatini DA. Biodiesel production via peanut oil extraction using diesel-based reverse-micellar microemulsions. *Fuel* 2010;89:2285–91.
- [18] Zhu R, Liang J, Yuan X, Wang L, Leng L, Li H, et al. The formation of rhamnolipid-based water-containing castor oil/diesel microemulsion and their potentiality as green fuels. *Energy Fuels* 2014;28:5864–71.
- [19] Peng X, Yuan X, Zeng G, Huang H, Wang H, Liu H, et al. Synchronous extraction of lignin peroxidase and manganese peroxidase from *Phanerochaete chrysosporium* fermentation broth. *Sep Purif Technol* 2014;123:164–70.
- [20] Correa NM, Silber JJ, Riter RE, Levinger NE. Nonaqueous polar solvents in reverse micelle systems. *Chem Rev* 2012;112:4569–602.
- [21] Nguyen TT, Sabatini DA. Formulating alcohol-free microemulsions using rhamnolipid biosurfactant and rhamnolipid mixtures. *J Surfactants Deterg* 2009;12:109–15.
- [22] Arpornpong N, Attaphong C, Charoensang A, Sabatini DA, Khaodhiar S. Ethanol-in-palm oil/diesel microemulsion-based biofuel: phase behavior, viscosity, and droplet size. *Fuel* 2014;132:101–6.
- [23] Lif A, Holmberg K. Water-in-diesel emulsions and related systems. *Adv Colloid Interface Sci* 2006;123–126:231–9.
- [24] Longinotti MP, Corti HR. The viscosity of glycerol–water mixtures including the supercooled region. *J Chem Eng Data* 2011;56:1397–406.
- [25] Zhang M, Wu H. Phase behavior and fuel properties of bio-oil/glycerol/methanol blends. *Energy Fuels* 2014;28:4650–6.
- [26] Pérez A, Casas A, Fernández CM, Ramos MJ, Rodríguez L. Winterization of peanut biodiesel to improve the cold flow properties. *Bioresour Technol* 2010;101:7375–81.
- [27] Ramalho EFSM, Filho JRC, Albuquerque AR, De Oliveira SF, Cavalcanti EHS, Stragevitch L, et al. Low temperature behavior of poultry fat biodiesel: diesel blends. *Fuel* 2012;93:601–5.
- [28] Lane LB. Freezing points of glycerol and its aqueous solutions. *Ind Eng Chem* 1925;17: 924–924.
- [29] Dashnau JL, Nucci NV, Sharp KA, Vanderkooi JM. Hydrogen bonding and the cryoprotective properties of glycerol/water mixtures. *J Phys Chem B* 2006;110:13670–7.
- [30] Clause D, Fouconnier B, Gomez JA. Ripening phenomena in emulsions – a calorimetry investigation. *J Dispersion Sci Technol* 2002;23:379–91.
- [31] Thanasukarn P, Pongsawatmanit R, McClements DJ. Impact of fat and water crystallization on the stability of hydrogenated palm oil-in-water emulsions stabilized by whey protein isolate. *Colloids Surf A Physicochem Eng Aspects* 2004;246:49–59.
- [32] Clause D, Gomez F, Pezron I, Komunjer L, Dalmazzone C. Morphology characterization of emulsions by differential scanning calorimetry. *Adv Colloid Interface Sci* 2005;117:59–74.
- [33] Husnawan M, Masjuki HH, Mahlia TMI, Saifullah MG. Thermal analysis of cylinder head carbon deposits from single cylinder diesel engine fueled by palm oil–diesel fuel emulsions. *Appl Energy* 2009;86:2107–13.
- [34] Garcia-Perez M, Adams TT, Goodrum JW, Das KC, Geller DP. DSC studies to evaluate the impact of bio-oil on cold flow properties and oxidation stability of bio-diesel. *Bioresour Technol* 2010;101:6219–24.
- [35] Hudgens RD, Hercamp RD, Francis J, Nyman DA, Bartoli Y. An evaluation of glycerin (glycerol) as a heavy duty engine antifreeze/coolant base. *SAE Tech Pap* 2007-01-4000 2007.