[Research Note]

Physical Properties and Combustion Characteristics of Emulsion Fuels of Water/Diesel Fuel and Water/Diesel Fuel/Vegetable Oil Prepared by Ultrasonication

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Ultrasonic preparation of two-phase water-in-oil (W/O) emulsion fuel was carried out using an ultrasonic apparatus with a rod horn. The effect of the position of the horn tip emitting ultrasound into the sample mixture on emulsion stability was investigated for water (10 vol%)/diesel fuel/surfactant (2 vol%) mixtures. In addition, the effects of ultrasonication time and vegetable oil addition on viscosity, water droplet size and combustion characteristics of the emulsion fuels prepared by ultrasonic treatment were studied for water (5 vol%)/diesel fuel/surfactant (2 vol%) and water (5 vol%)/diesel fuel/vegetable oil (5 vol%)/surfactant (2 vol%) mixtures. The stability of the emulsion fuel significantly depended on the tip position of the ultrasonic horn immersed in the mixture. Both the stability and viscosity of the emulsion increased with sonication time for the first 10 min and then remained constant. The water droplets in the emulsions of water/diesel fuel/surfactant and water/diesel fuel/vegetable oil/surfactant were extremely fine and median diameter of the droplets was about 0.3 μm. The water content in the W/O emulsion fuels was significant in the reduction in soot, NO and NOₓ during combustion.

Keywords
Ultrasound, Emulsion fuel, Emulsion stability, Water droplet size, Vegetable oil, Combustion characteristics

1. Introduction

Recently, biofuels have widely been used around the world, due to the increase in energy demand and greater concerns about energy and environmental issues such as the depletion of fossil fuels and greenhouse warming. Vegetable oils are one of the typical materials of bio fuels. Since vegetable oils have unsuitable properties such as high viscosity and low cetane number, direct use as fuels is difficult without modifications of diesel engines1). In order to improve the physical/chemical properties of fuels, vegetable oils are converted to fatty acid methyl esters (FAMEs), also called “biodiesel fuel,” which can be used as an alternative fuel for diesel engines. Biodiesel fuel is most commonly produced by transesterification reactions of vegetable oils with mono-alkyl alcohols such as methanol in the presence of homogeneous catalyst, but several washing steps following the reaction step are required to remove the catalyst, reactant residues and byproducts from the ester products2). In addition, in the case of use of waste cooking oils containing water as the materials of biodiesel fuel production, the water must be removed from the oils before the transesterification reaction step.

Fuel emulsification is a useful technique to reduce the emissions of nitrogen oxides, particulate materials, smoke and other pollutants during combustion. An emulsion of two immiscible liquids is formed by dispersion of droplets of one phase within the other phase. In a water-in-oil (W/O) emulsion, the emulsion droplets of water are dispersed and encapsulated within the oil. Modification of waste cooking oils containing water into W/O emulsion fuels without removal of the water from the waste oils is considered to allow use of such waste oils as an alternative fuel for boilers or oil heaters without requiring conversion to biodiesel. In general, in order to form a stable emulsion of two immiscible or mutually insoluble liquids, sufficient agitation must be applied to disperse one liquid into the other continuous liquid phase in the presence of an emulsifying agent.

Recently, the high power ultrasonic technique has attracted attention as one of new methods for the synthesis and decomposition of chemical species, the improvement and acceleration of chemical reaction rates, and the preparation of materials3)−6). Ultrasound wave propagation through a liquid causes flow in the same direction as the propagation. This phenomenon is called acoustic streaming. In addition, high power ultrasonic irradiation of a solution leads to formation,
growth and collapse of cavitation bubbles. The implosive collapse of the cavitation bubbles during adiabatic compression causes the formation of microstreaming\(^7\), high-speed microjets and generation of shockwaves in a solution\(^8\)\(^\sim\)\(^10\). The physical effects arising from acoustic streaming, high-speed microjets, microstreaming and shockwaves can contribute to more effective preparation of O/W (oil-in-water) or W/O (water-in-oil) emulsions. Several researchers have investigated the preparation of emulsions\(^11\)\(^\sim\)\(^16\) and synthesis of biodiesel fuel by ultrasonic methods\(^7\),\(^10\).

This study investigated the application of the ultrasonic technique to preparation of two-phase water-in-diesel fuel/vegetable oil emulsion fuels for use in burner combustion systems. The effects of the tip position of an ultrasonic horn immersed in the sample solution and sonication time on the emulsion stability and/or viscosity were investigated in a water/diesel fuel/surfactant mixture. The effect of sonication time on the diameter distribution of water droplets in the emulsion fuels was studied for water/diesel fuel/surfactant and water/diesel fuel/vegetable oil/surfactant mixtures. In addition, the combustion characteristics of the emulsion fuels were investigated and compared with those of diesel fuel and diesel fuel/vegetable oil mixtures without addition of water.

2. Experimental

2.1. Reagents

Diesel fuel supplied to the public was purchased from a gas station. Soybean oil and Span80 (C\(_{24}\)H\(_{44}\)O\(_6\)) were purchased from Wako Pure Chemical Industries, Ltd. Ion-exchange water was employed.

2.2. Ultrasonic Apparatus

Figure 1 shows a schematic diagram of the experimental apparatus. A horn-type ultrasound device (DIGITAL Sonifier® S-250D, Branson Ultrasonics Corp.) was used. The ultrasound frequency emitted from the horn tip of the homogenizer was 28 kHz and electronic input power was 100 W. The cylindrical reaction vessel with a diameter of 100 mm containing the sample mixture solution was immersed in a water bath and the mixture was kept at a constant temperature of 298 ± 1 K. The volume of the mixture was 500 mL and the liquid height in the reaction vessel was about 70 mm.

2.3. Emulsification

Span80 was used as a surfactant to improve the stability of the emulsion. Span80 was added to the water/diesel fuel or water/diesel fuel/soybean oil mixture to surfactant content of 2 vol%. The water content in the mixtures was 5 vol% or 10 vol%. The soybean oil content in the water/diesel fuel/soybean oil mixture was 5 vol%.

2.4. Combustion Test

A stainless steel cylindrical furnace equipped with a commercial burner (SG-S Series, Kato Burner Co., Ltd.) was employed for combustion experiments of diesel fuel, diesel fuel/soybean oil and emulsified fuels prepared by the ultrasonic method. Fuel with swelled air used as the oxide agent was supplied to the furnace. For all combustion tests, the fuel volumetric flow rate was 2 L/min and the fuel equivalence was adjusted to 0.6 by changing the air volumetric flow rate. The fuel was atomized from the atomization nozzle set in the center of the burner, using a pump pressure of 0.7 MPa. The stainless steel cylindrical furnace had an inner diameter of 100 mm and a length of 600 mm. At the outlet of the furnace, a sampling probe was positioned to analyze the exhaust gas. An R type thermocouple (Pt/Pr-Rh 13 %, strand diameter φ 0.1 mm), connected to a temperature recorder (NR-500, NR-TH08, Keyence Corp.) and personal computer, was positioned along the center axis of the furnace to measure the temperature at 9-11 points in the furnace.

2.5. Measurement Techniques

The viscosity of the emulsion prepared by the ultrasonic method was measured with a rotating viscometer (TVB-10W, Toki Sangyo Co., Ltd.). The temperature of the sample during measurement was kept at 288 K and the measurement period was 60 s. The revolution rate of the rotating viscometer was 60 rpm.

The stability of the prepared emulsion was evaluated as follows. The emulsion fuel prepared by ultrasonic treatment was added to the centrifuge vessel and was loaded at 3000 rpm for 15 min using a centrifugal separator. After this centrifugal treatment, the volume of the emulsion phase was determined. Emulsion stability was defined as follows,

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\text{Emulsion stability} \left[\%\right] = \frac{\text{Volume of emulsion phase exiting after centrifugal treatment} \times 100}{\text{Total sample volume before centrifugal treatment}}
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Diameter distribution of the water droplets in W/O emulsion was determined by a laser diffraction apparatus (LA-920, HORIBA, Ltd.). The median diameter \((D_{50})\) was taken as the mean water droplet diameter.

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The specific surface area of the water droplets was calculated based on the assumption that the water droplets were spherical.

The concentrations of chemical species in the exhaust gas during combustion were measured by thermal conductivity detector (TCD) gas chromatography (GC-8A, Shimadzu Corp., and Column WG100, GL Sciences Inc.). The concentrations of NO and NO\(_x\) in the exhaust gas were determined using a NO/NO\(_x\) analyzer. The amount of soot in the exhaust gas was measured with a smoke-tester (Bacharach Inc.). Combustion exhaust gas was removed from the flame tip in the furnace via the sampling tube to trap the soot in the gas on a paper filter. The amount of soot generated during combustion was evaluated based on a reference smoke-scale with 10 levels. Higher levels of the smoke-scale indicate that larger amounts of soot are formed during combustion.

3. Results and Discussion

3.1. Effect of Horn Position on Emulsion Stability

The effect of the tip position of the ultrasonic horn on the stability of the fuel emulsion prepared by ultrasonic treatment for 5 min was investigated for the water (10 vol%)/diesel fuel (88 vol%)/surfactant (2 vol%) system, in which the interface of the two immiscible liquids, diesel fuel and water, was about 5 mm from the bottom of a reaction vessel before ultrasonic treatment. The results in Fig. 2 demonstrate that the stability of the fuel emulsion considerably depends on the position of the ultrasonic horn tip. The highest emulsion stability was achieved for the horn tip set at \(h = 60\) mm, which was far away from the position of the interface before sonication treatment. On the one hand, ultrasonication from a horn tip placed near the interface of immiscible oil and water, at \(h = 5\) mm, is apparently favorable for disturbance of the initial interface, but is considered unsuitable for overall mixing in a vessel due to the steric obstruction of the horn immersed significantly in the solution. On the other hand, down-acoustic streaming generated by ultrasonication from the horn set at \(h = 60\) mm results in smooth convection currents in the solution. Presumably such convection currents are important in sufficient agitation resulting in efficient formation of stable emulsion.

3.2. Water Droplet Size

The emulsion prepared with the ultrasonic horn set at \(h = 60\) mm was subjected to laser diffraction analysis and the median diameter of water droplets in the mixture was determined. Figure 3 shows the time-change of the median diameter of water droplets. Median diameter decreased with longer sonication time and became constant after about 10 min.

3.3. Changes in Viscosity and Emulsion Stability

Figure 4 shows the time-changes in stability and viscosity of the emulsion prepared by sonication treatment at about 298 K. The viscosity increased with sonication time for the first 10 min and then remained constant, and the dependence of stability on sonication time...
also showed a similar tendency. As shown in Fig. 3, a reduction in water droplet size implies an increase in specific surface area of the water droplets in the emulsion. The increase in the specific surface area of water droplets in the solution was probably responsible for the increase in static electric friction of the water phase with the oil phase, resulting in increased viscosity of the emulsion and accordingly improved stability.

Ultrasonication into a sample solution under uncontrolled temperature conditions was performed as shown in Fig. 4. In the first 10 min, the variation of viscosity with sonication time was similar to that under temperature controlled conditions at 298 K. However, the viscosity fell with sonication time after reaching the maximum value under the uncontrolled temperature conditions. Ultrasound energy absorbed in the mixture caused a rise in the temperature of the solution in the absence of the cooling system required to keep the temperature of the solution constant. The higher temperatures probably lead to coalescence of fine water droplets in the emulsion due to a reduction in the surface tension of water. The decrease in the specific surface area of water droplets due to the coalescence is likely responsible for the reduction in viscosity and accordingly the change in emulsion stability.

3.4. Water Droplet Size Distribution in the Water/Diesel Fuel/Soybean Oil/Surfactant System

The change in water droplet size distribution with sonication time was investigated for the water (5 vol%)/diesel fuel/soybean oil (5 vol%)/surfactant (2 vol%) system. The results obtained for sonication times of 2 min and 10 min are shown in Fig. 5. The water droplet size distributions in water (5 vol%)/diesel fuel/surfactant (2 vol%) emulsions are also shown in Fig. 5. For emulsions prepared by ultrasonic treatment for 2 min, the water droplet size distributions were fairly broad. However, the size distributions of water droplets formed in emulsions sonicated for 10 min were narrower and the droplets were smaller. The results in Fig. 5 indicate that the water droplet size distribution of water/diesel fuel/soybean oil/surfactant emulsion is similar to that of water/diesel fuel/surfactant emulsion in the same treatment time, indicating that addition of 5 vol% soybean oil to the water/diesel fuel/surfactant mixture did not affect the water droplet size distribution. However, the viscosity was considerably different between water/diesel fuel/soybean oil and water/diesel fuel emulsion fuels prepared by ultrasonic treatment for 10 min. The viscosity of the water/diesel fuel/soybean oil emulsion fuel was about 8.2 mPa, about twice that of the water/diesel fuel emulsion fuel, chiefly because the viscosity of soybean oil is about 15 mPa and higher than that of diesel fuel.

3.5. Combustion Characteristics

Combustion tests of the high stability-emulsion fuels prepared by sonication were carried out at the fuel equivalent ratio of 0.6 to O2 in air. Figure 6 shows photographs of the filter contaminated by soot in the
exhaust gas during combustion of each emulsion fuel. Combustion tests of diesel fuel and diesel fuel/soybean oil were also performed as shown in Fig. 6. The results demonstrate that the amount of soot generated during combustion of the emulsion fuel is significantly decreased compared with that during combustion of oil with no addition of water. Microexplosion of water droplets in emulsion fuel occurs during combustion and promotes miniaturization of oil fuels, probably leading to effective combustion of the oil due to the increased surface area of the oil easily contacting with O2 in the air.

Figure 7 shows the temperature distribution during combustion in the furnace. During combustion of emulsion fuels of water/diesel fuel and water/diesel fuel/soybean oil, the temperature decreased at the same point in the furnace compared to combustion of diesel fuel and diesel fuel/soybean oil, respectively, due to the high latent heat of water. In particular, the temperature near the jet nozzle during combustion of the emulsion fuel containing vegetable oil was significantly lower, possibly because of an increase in droplet size of the emulsion fuel atomized from the jet nozzle due to high viscosity.

Figure 8 shows the NO and NOx concentrations in the exhaust gas during combustion of diesel fuel, diesel fuel/soybean oil and emulsion fuels. During combustion of diesel fuel/soybean oil as well as diesel fuel emulsion containing water/surfactant agent, the NO and NOx concentrations were lower compared to combustion of fuels without addition of water. As shown in Fig. 7, the presence of water droplets dispersed into oil fuels caused the temperature in the furnace to fall and the lower temperature may contribute to reducing generation of thermal NOx during combustion.

4. Conclusions

The present study demonstrated that efficient ultrasonication is a promising method for preparation of emulsion fuels with high stability and fine water droplets, and the water content of water/diesel fuel and diesel fuel/vegetable oil emulsions prepared by ultrasonic treatment had significant effects in reducing the
amounts of soot, NO and NO\textsubscript{x} generated during combustion.

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要 旨
超音波照射下で調製した水／軽油および水／軽油／植物油エマルション燃料の物理的性質および燃焼特性
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超音波照射による界面活性剤（2 vol%）添加系 W/O エマルション燃料の調製について、ホーン型超音波発振器を用いて検討を行った。水（10 vol%）／軽油エマルション燃料に対して、エマルション安定度に及ぼす超音波発振器のホーン設置位置の影響を調べたところ、安定度が設置位置に大きく依存した。最適なホーン位置で超音波照射した際のエマルション安定度。粘度の経時変化を軽油／水（5 vol%）の条件で調べたところ、両方とも10分間照射時間をともに増加した後、一定値に達した。また、水（5 vol%）／軽油および水（5 vol%）／軽油／植物油（5 vol%）系についてエマルション液滴径分布の超音波照射時間依存性を調べたところ、両方とも相違はほとんどなく、最終的には10〜20 μm 一定の平均液滴径を有したエマルション燃料が調製できた。調製したエマルション燃料の燃焼特性を調べたところ、軽油および軽油／大豆油燃料と比較して、すす、NO\textsubscript{x} および NO\textsubscript{y} の生成抑制が確認された。