Stability of Microemulsion Biofuels and their Characterization

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\textbf{Abstract}

Biodiesel is the renewable and non-polluting alternative energy source derived from vegetable/non-vegetable oils by transesterification method. It is used either individually as fuels or for blending in ethanol or diesel. The use of oxygenated bio-fuels like biodiesel and ethanol in combination with diesel is an effective measure as diesel substitutes. The present research is aimed to study the phase stability of two mixed biodiesels with diesel and proof ethanol (200°, 195°, 190°, 185°, 180° and 175°) and their characterizations. These microemulsions were prepared as B15E2D83, B20E2D78 and B25E2D73 from each proof ethanol at room temperature. Total nine samples of stable microemulsion fuels of 200°, 195° and 190° proof ethanol were selected. These microemulsion fuels were studied for the stability at different temperatures i.e. 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45°C, and their properties such as density, viscosity, flashpoint, cetane number and gross heating values were determined. The study showed that microemulsion fuels of 200°, 195° and 190° proof ethanol were found unstable at 0 and 5°C in the control chamber otherwise; stable at other selected temperatures. The fuel properties of the selected microemulsions were found in the limit of the standard specification except flashpoints.

\textbf{Keywords}

Biodiesel, Microemulsion, Proof Ethanol’s, Properties, Temperatures.

\textbf{Introduction}

Growing population and rapid socio economic development has encouraged the energy consumption across all major sectors of Indian economy. Due to rising in consumption of energy, India is dependent on fossil fuels such as coal, oil and natural gas. These sources are exhaustible in nature and cannot be restored due to their much faster exploitation. The global energy crisis in 1970 prompted many countries to search for alternative energy sources after being vulnerable to crude oil embargoes and shortages. Among liquid fuels, there are mainly two types of biofuel: alcohols (ethanol and butanol) and diesel substitutes (such as biodiesel and hydro-treated vegetable oils). The use of non-edible oils in respect to edible oils is very significant because an increase in demand for edible oils as a food and they are too expensive as compared with diesel fuel. Jatropha and karanj oils can be utilised as biodiesel because these are non-edible oils. \textit{Jatropha curcas} which grows in tropical and sub-tropical climates across the developing world as a feed stock for biodiesel production. They can be used either individually as fuels or for blending in petrol or diesel. The government’s decision of 5% blend of ethanol
in gasoline had been partially successful in years of surplus sugar production and below target when sugar production declined. Presently, the contracted ethanol supply for current fiscal would be just sufficient to meet 2% blending with fuels.

Many researchers (Fernando and Hanna, 2004; Kleinova and Cvengros, 2011; Mehta et al., 2012; Weerachanchai et al., 2009) have investigated that ethanol-biodiesel-diesel microemulsions are stable well below sub-zero temperature and have presented equal or superior fuel properties to regular diesel fuel. Intersolubility of the components of diesel–biodiesel–ethanol system decreases with decreasing temperature and temperatures above 20 °C are not found any problem with phase separation (Kwanchareon et al., 2006).

The stability of ethanol-biodiesel-diesel microemulsions is affected by three factors mainly: temperature, water content and ethanol content (Bhattacharya et al., 2006; Lapuerta et al., 2007). The stability of microemulsions above 8°C is found as the single phase (Torres-Jimenez et al., 2010). Water content in microemulsion affects well on the performance of the diesel engine and carbon monoxide emits more from these fuels (Lif and Holmberg, 2006).

The density, viscosity, heat value and cetane number of microemulsions have the great impact on the injection, atomization, ignition and combustion, and no requirement of technical modifications on the engine side is needed (Fernando and Hanna, 2004; Kwanchareon et al., 2006).

The aim of this research was focused on studying the stability of ethanol–biodiesel–diesel three-component systems at different temperatures along with some basic fuel properties such as density, viscosity, heat value, cetane number and flash point.

Materials and Methods

The different types of proof ethanol were prepared from anhydrous ethanol to develop a microemulsion fuel with biodiesel and diesel. The stability and characterization of microemulsions were determined in the laboratory.

Preparation of the proof ethanol from the anhydrous ethanol

The preparation of the proof ethanol from the anhydrous ethanol was conducted in the laboratory. The concentration of the anhydrous ethanol was 99.9%. The six levels of proof ethanols were prepared as 200°, 195°, 190°, 185°, 180° and 175° from the anhydrous ethanol in the laboratory. 2% ethanol from each proof ethanol was taken to mix with the biodiesel concentrations of 15, 20 and 25% respectively and remaining diesel fuel to formulate the microemulsion of three fuel components. The equal proportional (1:1) quantities of Jatropha and soybean methyl ester were mixed. The three levels of 15, 20 and 25% were selected from the equal mixed biodiesel of both biodiesels. Total eighteen sample fuels were prepared of the three fuel component systems. The prepared sample fuels from the different proof ethanols were left for four days at room temperature for the determination of the stability of the microemulsion fuels.

Those fuels performed the clear, transparent and homogeneous; they were selected to determine stabilities at different temperatures, the fuel characterization and the engine performance evaluation. Based on review and research work requirement, parameters for the study were considered. The sources of variations were selected as three levels of the proof ethanol, three levels of biodiesel concentration and five levels of brake load for the experiment. The experiment was planned
with the full factorial completely randomized design. Three replications were taken for the statistical analysis.

The concentration of ethanol is expressed as the degree proof of ethanol. A proof number represents twice the ethanol concentration. 200° proof ethanol indicates 100 per cent concentration of ethanol and zero per cent of water. For the preparation of 195° proof ethanol, 97.5 ml of anhydrous ethanol was measured through the measuring cylinder and put into the conical flask.

Distilled water 2.5 ml was measured through the pipette of 10 ml having capacity and mixed into the measured quantities of anhydrous ethanol of 97.5 ml. For completely miscibility, this mixture was shaken up to five min. For the preparation of other proof ethnols, similar procedure was adopted. Ethanol proof of 200°, 195°, 190°, 185°, 180° and 175° prepared from anhydrous ethanol.

**Determination of microemulsions stability**

The stability and fuel properties of ethanol–biodiesel–diesel three-component systems were studied by using high speed diesel, different proof ethnols (200°, 195°, 190°, 185°, 180° and 175°) and biodiesel (equal mixed quantity of jatropha and soybean methyl ester). The equal proportion (1:1) of soybean methyl ester (SME) and jatropha methyl ester (JME) was measured through the measuring cylinder and mixed in the conical flask (Ozcanil and Serin, 2011; Sarin et al., 2007). The biodiesel of 15, 20 and 25% were selected from the equal mixed biodiesel of both biodiesels. Anhydrous ethanol (200° proof) and aqueous ethnols (195°, 190°, 185°, 180° and 175° proof) were utilized to formulate the microemulsion fuel with biodiesel and diesel. 2% ethanol from each proof ethanol was taken to mix with the biodiesel concentrations of 15, 20 and 25% respectively and remaining diesel fuel to formulate the microemulsion of three fuel components.

Total sample of microemulsion fuel was prepared as a number of eighteen. All prepared samples of microemulsion fuels were left for four days at room temperature for the stability. At room temperature, biodiesel-ethanol-diesel microemulsions prepared using 185°, 180° and 175° proof ethnols were found unstable, due to more water in these proof ethnols (Bhattacharya et al., 2006). These microemulsion fuels appeared as the turbidity and non-homogeneity for long period at this temperature. These microemulsions were rejected. The microemulsion fuels of 200°, 195° and 190° proof ethnols were found clear, transparent and homogeneous at room temperature. Total number of stable microemulsion fuels of 200°, 195° and 190° proof ethnols was determined as a number of nine samples at room temperature. These microemulsion fuels were selected to study for the stability at different temperatures (0, 5, 10, 15, 20, 25, 30, 35, 40 and 45°C) in the control chambers and their fuel properties.

**Determination of Fuel Properties**

Fuel properties were determined by adopting the ASTM and BIS standard specifications. Density and the absolute viscosity of the selected microemulsion fuels were determined by using the pycnometer and vibro-viscometer according to the standard method. Cetane number, higher heating value and flashpoint of fuels were determined by using the closed type instruments as the Irox diesel, automatic bomb calorimeter and miniflash point respectively.

**Determination of density of fuels**

Cetane number and heating value are related to density. Fuel density influences the efficiency of fuel atomization and combustion
characteristics. Fuel injection systems meter the fuel by volume, the change of the fuel density may influence the Internal combustion (IC) engine output power due to a different mass of injected fuel.

**Determination of viscosity of fuels**

The viscosity has effects on the atomization quality, the size of fuel drop, the injector penetration and the quality of combustion. Too low viscosity can cause leakage in the fuel system. High viscosity causes poor fuel atomization and incomplete combustion, increases the engine deposits, needs more energy to pump the fuel.

**Determination of cetane number for fuels**

Cetane number of fuels was determined by using Irox diesel instrument. The procedure of the calibration with Irox diesel was conducted on n-hexane and then same procedure was followed for the measurement of the cetane number of fuel.

**Determination of gross heating value for fuel**

Heating value is a measure of the heat energy in the fuel and the higher value of heat the more the energy releases after combustion. Heating value of fuel is produced by the internal combustion engine and the specific fuel consumption value that enables the engine to do the useful work.

**Statistical analysis of data**

The statistical data was analysed by using MS excel and SAS software. The experiment was planned with the full factorial completely randomized design. The experiment was conducted in randomised order. The interaction between independent variables was compared for the significance. In statistical analysis, the significant threshold was set at five per cent level of probability for variables.

**Results and Discussion**

Characterization results of fuel properties of diesel, Jatropha methyl ester, soybean methyl ester, mixture of biodiesels, selected microemulsions and proof ethanol were determined and presented.

**Effect of temperatures on stability of selected microemulsions**

Microemulsion fuels of 200°, 195° and 190° proof ethanols were selected to determine for the stability at 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45°C respectively for 24 hours by using the control chambers. The result showed that the selected microemulsions of 200°, 195° and 190° proof ethanols were found to be unstable (Fig. 2) at 0 and 5°C due to low temperatures and excess viscosity of biodiesel. These microemulsions above 10°C were found to be stable. Stabilities for microemulsion fuels of 200°, 195° and 190° proof ethanols at considerable temperatures are shown in figure 1. The stable and unstable stages of microemulsions are indicated by symbols “Circle” and “Star” respectively.

**Fuel properties of microemulsions**

The measured properties as like density, viscosity, flashpoint, cetane number and higher heating values of microemulsion fuels were followed according to ASTM and BIS standard specifications. The densities of microemulsion fuels of 200° and 195° proof ethanols were found within limits as per BIS and ASTM D975 standard specifications. The densities of microemulsion fuels of 190° proof ethanol were found slightly lower as per standard specification. The densities of microemulsion fuels of 200°, 195° and 190° proof ethanols varied as 0.864 to 0.869, 0.855 to 0.859 and 0.847 to 0.849 g/cc respectively.
Table 1: Fuel properties of diesel and selected microemulsions

| Properties → | Density at 15°C (g/cc) | Kinematic viscosity at 40°C (cS) | Flash point (°C) | Cetane number | Gross heat value (MJ/kg) |
|--------------|-------------------------|----------------------------------|------------------|--------------|------------------------|
| Fuels ↓      |                         |                                  |                  |              |                        |
| Diesel       | 0.845                   | 2.93                            | 62               | 51           | 45.2                   |
| 200°proof ethanol microemulsion | B₁₅E₂D₈₃ | 0.864 | 3.15 | 31 | 49.98 | 43.97 |
|              | B₂₀E₂D₇₈ | 0.867 | 3.23 | 36 | 49.9 | 43.66 |
|              | B₂₅E₂D₇₃ | 0.869 | 3.32 | 39 | 49.88 | 43.35 |
| 195°proof ethanol microemulsion | B₁₅E₂D₈₃ | 0.855 | 3.14 | 32 | 50.01 | 43.96 |
|              | B₂₀E₂D₇₈ | 0.857 | 3.23 | 33 | 49.96 | 43.64 |
|              | B₂₅E₂D₇₃ | 0.859 | 3.31 | 34 | 49.91 | 43.33 |
| 190°proof ethanol microemulsion | B₁₅E₂D₈₃ | 0.847 | 3.14 | 30 | 50.03 | 43.95 |
|              | B₂₀E₂D₇₈ | 0.848 | 3.23 | 31 | 49.98 | 43.62 |
|              | B₂₅E₂D₇₃ | 0.849 | 3.30 | 32 | 49.93 | 43.31 |

Fig.1 Stability of microemulsions of 200°, 195° and 190°proof ethanol at different temperatures
The kinematic viscosities of microemulsion fuels of 200°, 195° and 190° proof ethanols were found as 3.15 to 3.32, 3.14 to 3.31 and 3.14 to 3.30 cS respectively. The flashpoints of microemulsion fuels of 200°, 195° and 190° proof ethanols varied as 31 to 39, 32 to 34 and 30 to 32 °C respectively. Main reason is to be lowered flashpoint of proof ethanol. The cetane numbers of microemulsion fuels of 200°, 195° and 190° proof ethanols were found as 49.98 to 49.88, 50.01 to 49.91 and 50.03 to 49.93 respectively. The higher heating values of microemulsion fuels of 200°, 195° and 190° proof ethanols were varied as 43.97 to 43.35, 43.96 to 43.33 and 43.95 to 43.31MJ/kg respectively. Densities, kinematic viscosities, flashpoints, cetane numbers and gross heating values of diesel were found as 0.845 g/cm$^3$, 2.93 mm$^2$/s, 62°C, 51 and 45.2 MJ/kg respectively. Fuel properties (Table 1) of microemulsions were found to be nearer to diesel except flashpoint.

The selected microemulsions of 200°, 195° and 190° proof ethanols were found to be unstable at 0 and 5 °C. These microemulsions of proof ethanols were found to be stable from 10 to 45 °C. Densities, kinematic viscosities, cetane numbers and gross heating values of the selected microemulsions were found within limits of fuel quality standard specifications except flashpoint. Fuel properties of microemulsions were found to be nearer to diesel.

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How to cite this article:
Ramchandra Ram, Atul Kumar Shrivastava, Kunjbihari Tiwari and Patil, D.V. 2017. Stability of Microemulsion Biofuels and their Characterization. Int.J.Curr.Microbiol.App.Sci. 6(11): 675-681. doi: https://doi.org/10.20546/ijcmas.2017.611.080