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Surface tension and rheological behavior of sal oil methyl ester biodiesel and its blend with petrodiesel fuel

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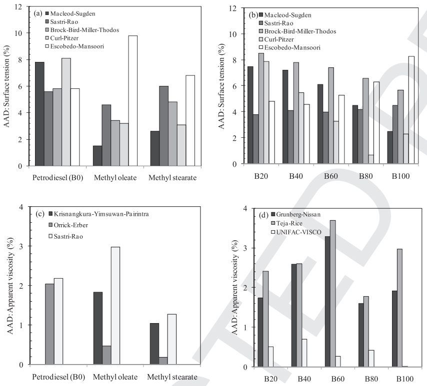
HIGHLIGHTS

- Measurement of surface tension and viscosity of sal oil biodiesel–petrodiesel blends.
- Estimation of surface tension and viscosity of sal oil biodiesel–petrodiesel blends.
- Determination of UNIFAC–VISCO group contribution parameters for biodiesel.
- Viscoelastic properties of sal oil biodiesel–petrodiesel blends.
- Estimation of the generalized Cox–Merz parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

The present paper deals with experimental and theoretical investigation of surface tension, apparent viscosity and viscoelastic properties of sal oil methyl ester biodiesel and its blends with petrodiesel at different temperature. Several methods were used to predict surface tension and apparent viscosity of biodiesel–petrodiesel blends. Satri–Rao method based on the corresponding state predicts surface tension of biodiesel–petrodiesel blends very well, whereas UNIFAC–VISCO group contribution method predicts apparent viscosity of blends very accurately. To predict the apparent viscosity of biodiesel, six unknown UNIFAC–VISCO group interaction parameters were determined and proposed parameters were then used to predict viscosities of biodiesel–petrodiesel blends. The recommendation was given which proportion of sal oil biodiesel and normal diesel was to be mixed to get the proper European standard grade diesel fuel. Viscoelastic properties (i.e., structural stability, storage modulus, loss modulus, complex viscosity and loss tangent) of biodiesel–petrodiesel blends were determined as a function of amplitude, frequency and temperature using parallel plates rotational viscometer in linear viscoelastic range. Finally, generalized Cox–Merz parameters were used to establish the relation between apparent viscosity and complex viscosity of blends.

1. Introduction

Biodiesel is a renewable fuel, which is obtained by transesterification of vegetable oils or other materials, largely comprised of fatty acids of triglycerides, such as animal fats or used frying oils, with methanol/ethanol to give corresponding fatty acid methyl ester/fatty acid ethyl ester [1]. Biodiesel has the advantages of (i) negligible sulfur and aromatic content, (ii) higher flash point, lubricity and cetane number, (iii) maximum biodegradability, (iv) minimum toxicity and (v) reduced emission of carbon monoxide, sulfur dioxide, hydrocarbons, particulate matters, polyaromatics

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and smokes. Besides these advantages, the direct use of biodiesel was limited in diesel engines due to high viscosity and pour point along with reduced calorific value, volatility and oxidation stability of biodiesel [1–3]. In addition, biodiesel is an excellent solvent towards certain elastomeric sealants, which may cause corrosion problems in engine fuel lines. The engine characteristics using diesel blends up to 20% biodiesel are *almost* similar to pure petroleum based diesel fuel (i.e., petrodiesel), whereas higher biodiesel content in biodiesel–petrodiesel blend affects the engine performance adversely [2,3]. Biodiesel from different feedstocks has a different composition of triglycerides and exhibits different physical properties when it is blended with petrodiesel. Surface tension, density and viscosity are considered to be the most important properties of biodiesel–petrodiesel blends that can significantly affect engine performance like fuel injection, spray characteristics, combustion performance, engine wear and pollutant emission [4]. The properties like surface tension, density and viscosity of biodiesel depend on the molecular weight, polydispersity index, structure, number and position of double bonds in fatty acid methyl esters (FAMEs) and operating temperature [5,6]. Long chain FAME molecules with multiple number of unsaturated double bonds allows surface tension to increase, which resists droplet formation causing slower rate of droplet vaporization with insufficient atomization. Density variation in biodiesel results the fluctuation of mass flow rate under given injection condition, which affects the process of atomization. Similarly, the high viscosity of biodiesel reduces fuel atomization efficiency due to the formation of larger droplet during injection resulting poor combustion of fuel, producing black smoke and deposits in the combustion chamber. The increased viscosity of fuel is also responsible to increase fuel injection pressure during engine warm up [2,4]. For the efficient use of biodiesel–petrodiesel blend in diesel engine, it is essential to know surface tension and apparent viscosity (i.e., steady shear viscosity) of biodiesel–petrodiesel blends at elevated temperature. Attempts have been made to predict the surface tension and apparent viscosity of pure FAMEs and mixtures of FAMEs (or biodiesel) at elevated temperature [5–10].

In general, petroleum products (e.g., gasoline, diesel, and etc.) are either Newtonian or non-Newtonian pseudoplastic in nature which is different from viscoelastic liquid [11]. Viscoelasticity plays an important role to control the rheological properties of diesel fuel while injection in the engine. Under given injection pressure, the viscoelastic behavior of the fuel helps to resist the formation of superfine droplets (i.e., mist particles) which results more controlled air–fuel homogeneous blend that helps uniform and complete combustion of fuel with the reduction in the combustion chamber temperature. In addition, visoelastic behavior of petrodiesel with proper additives also helps to improve fuel characteristics, resulting the reduction of emissions of un-burnt hydrocarbons, CO, NOx and particulate matters by improving engine power and reducing in fuel consumption [12]. Till date, viscoelastic properties of biodiesel and its blend with petrodiesel have not been addressed properly at elevated temperature for the rheological characterization.

The present work is focused to investigate and quantify the effect of composition and temperature on surface tension, apparent viscosity and viscoelastic properties of different sal oil biodiesel–petrodiesel blends. For this, biodiesel was synthesized from sal oil using methanol and ion-exchange resin catalyst, and several biodiesel–petrodiesel blends with different blend ratios were prepared for analysis. The surface tension of biodiesel–petrodiesel blends was measured using Kruss K20 Easy dyne tensiometer, whereas apparent viscosity was measured using cup-bob Bohlin Gemini rotational cup-bob viscometer at elevated temperature. Surface tension and apparent viscosity of individual FAME, petrodiesel, biodiesel and biodiesel–petrodiesel blends was predicted using standard prediction methods and predicted results were compared with experimental values to demonstrate the accuracy of the prediction methods. To estimate the apparent viscosity of biodiesel using UNIFAC–VISCO group contribution method, several unknown viscosity group interaction parameters involving structural information of FAME were determined through parameter optimization and the predicted interaction parameters were then used to estimate apparent viscosities of biodiesel–petrodiesel blends at elevated temperature. Viscoelastic properties (i.e., structural stability, storage modulus, loss modulus, complex viscosity and loss tangent) of biodiesel and petrodiesel were measured as a function of amplitude, frequency and temperature using parallel plates Bohlin Gemini rotational viscometer within linear viscoelastic range and the results were compared with biodiesel–petrodiesel blends. Finally, generalized Cox–Merz rule was applied to predict apparent viscosity from complex viscosity.

2. Experimental procedures

2.1. Materials

Biodiesel was synthesized from commercial grade sal oil (*Shorea robusta*) using methanol and INDION 225H acidic solid ion-exchange resin catalyst, and it was composed of *almost* 50:50 mixture of methyl ester of stearic acid and oleic acid [13]. Sal oil (*S. robusta*) oil was collected from a rural area of Ranchi (India) whereas petrodiesel was purchased from local petrol/diesel retailing station of Dhanbad (India). INDION 225H was supplied by Ion Exchange (India) Limited, Ankleshwar (India). Methyl ester of myristic acid, stearic acid and oleic acid (purity >99.0%) was obtained from Sigma–Aldrich (USA).

2.2. Surface tension measurements

Kruss K20 Easy Dyne Tensiometer was used to measure the equilibrium surface tension of individual FAME, sal–biodiesel, petrodiesel and its blend with petrodiesel at different temperatures (313–353 K). The apparatus was calibrated using isobutanol and benzene, while the repeatability of measuring surface tension was tested using methyl ester of myristic acid at regular interval of time. Before conducting experiments, the ring was washed with acetone and heated in an ethanol flame till to red hot. Surface tension reported in this study was the averaged value of five consecutive readings.

2.3. Apparent viscosity measurements

Advanced air bearing rheometer, Bohlin Gemini 2 model GEM-200-913+ROO7721 (Malvern, UK) with stainless steel cup and bob (cup diameter: 19 mm, bob diameter: 17 mm, cup length: 40 mm and bob length: 35 mm) was used to measure the apparent viscosity of individual FAME, petrodiesel and biodiesel–petrodiesel blends under variable shear rate within temperature range of 313–353 K. The gap between the cup and bob from the bottom was 150 μm during the measurement. To measure apparent viscosity, 5.0 ml sample was taken to dip bob into the sample. Shear rate varied from 0.01 to 100 s^{-1} and apparent viscosities for different samples were measured at the steady shear rate. Apparent viscosity reported in this study was the averaged value of five consecutive readings.

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