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Production and Analytical Comparison of Atomization Characteristics for Ternary Blends of Biodiesel

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ABSTRACT:

By the plenty usage of diesel fuel in automobiles, it is necessary to switch over to the alternate fuel such as biodiesel. Generally non edible oils are blended with diesel after the esterification process. But here ternary biodiesel blends with diesel fuel produce almost equal drop size when compared with some binary blends with large quantities of diesel. The ternary biodiesel blends give less amount exhaust emission than the binary blends with diesel. In this work, biodiesel is produced from linseed and rubber seed oil by trans-esterification process and then the fuel atomization characteristics have been determined, The sauter mean diameter of atomization is also computed by analytically. The ternary blends having 90% diesel and 5% linseed biodiesel, 5% rubber seed biodiesel and also 80% diesel, 10% linseed biodiesel and 10% rubber seed biodiesel are observed to give comparatively similar atomization characteristics of diesel.

KEYWORDS:

Ternary blends; Biodiesel; Trans-esterification; Linseed oil; Rubber seed oil

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1. Introduction

Biodiesel can be produced from a great variety of feed stocks. These feed stocks include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, linseed oil, rubber seed oil, sunflower, safflower, coconut) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils). The choice of feedstock depends largely on geography. Biodiesel is miscible with petrodiesel in all ratios. In many countries, this has led to the use of blends of biodiesel with petrodiesel instead of neat biodiesel. It is important to note that these blends with petrodiesel are not biodiesel. Often blends with petrodiesel are denoted by acronyms such as B20, which indicates a blend of 20% biodiesel with petrodiesel. Of course, the un-trans-esterified vegetable oils and animal fats should also not be called “biodiesel” [14]. Although other alcohols such as ethanol may yield a biodiesel fuel with better fuel properties, Methanol is used as the alcohol for producing biodiesel because it is the least expensive alcohol. Often the resulting products are also called fatty acid methyl esters (FAME) instead of biodiesel.

Biodiesel has several distinct advantages compared with petrodiesel in addition to being fully competitive with petrodiesel in most technical aspects:

1. Derivation from a renewable domestic resource, thus reducing dependence on and preserving petroleum and biodegradability.
2. Reductions of most exhaust emissions (with the exception of nitrogen oxides, NOx).
3. Higher flash point, leading to safer handling and storage.
4. Excellent lubricity, a fact that is steadily gaining importance with the advent of low-sulphur petro diesel fuels, which have greatly reduced lubricity. Adding biodiesel at low levels (1-2%) restores the lubricity.

Some problems associated with biodiesel are on its inherent higher price which in many countries is offset by legislative and regulatory incentives or subsidies in the form of reduced excise duties and taxes. The higher price can also be (partially) offset by the use of less expensive feed stocks, which has sparked interest in materials such as waste oils (e.g., used frying oils).

For the trans-esterification process, to give maximum yield, the alcohol should be free of moisture and the FFA content of the oil should be below 0.5%. The absence of moisture in the trans-esterification reaction is important because according to the following equation (shown formethyl esters),

$$R-COOCH_3+H_2O \rightarrow R-COOH+CH_3OH$$
$$(R=alkyl)$$

When the hydrolysis process taken place then the alkyl esters formed due to the trans-esterification reaction gets converted into FFA. Similarly, triacylglycerols are also esters, the reaction of the triacylglycerols with water can form FFA at 32°C and at the same time trans-esterification was 99% completed in 4 hours when using an alkaline catalyst (NaOH or KOH) at greater than or equal to 60°C. When using an alcohol to oil molar ratio of at least 6:1 with fully refined oils, then the reaction was completed in 1 hour and the products obtained are methyl, ethyl or butyl esters. Although the crude oils could be trans-esterified, ester yields were reduced because of gums and extraneous material present in crude oils. Parameters namely 60°C reaction temperature and 6:1 methanol: oil molar ratios have become a standard for methanol-based trans-esterification. Other alcohols (ethanol and butanol) require higher temperatures (75 and 114°C respectively) for optimum conversion [14]. The primary criterion for biodiesel quality is adherence to appropriate standards. Generally fuel quality of biodiesel is influenced by several factors, including the quality of feedstock, fatty acid composition of the parent vegetable oil or animal fat, the production process and other materials used in this process. The properties of biodiesel & diesel are given in Table 1 [2].

Table 1: Properties of biodiesel in comparison with diesel [2]

Fuel properties	Diesel fuel values	Biodiesel values	
	ASTM D975	ASTM D6751	DIN 14214
Density at 15°C (kg/m^3)	850	880	860-900
Viscosity at 40°C (cSt)	2.6	1.9-6.0	3.5-5.0
Cetane number	40-55	Min 47	Min 51
Calorific value (MJ/kg)	42-46	-	35
Acid value (mg KOH/g)	0.062	Max 0.50	Max 0.50
Flash point (°C)	60-80	Min 100-170	>120
Pour point (°C)	-35	-15 to -16	-

The microscopic description is characterized by the content of droplets of diverse sizes and the changes in their special kinetics. For example, the atomization mechanism is responsible for distributing the droplets in the injection process and to a great extent the good distribution of the droplets in relation to their size depend on it. Generally quality of the atomization of a liquid spray can be estimated with the medium diameter of the droplets. A determined medium diameter represents the equivalent diameter that characterizes the entire group of droplets of the spray. Equation 1 establishes the general form based on which all the correlations that determine Sauters medium diameter have been defined[8]. In some processes Sauters medium diameter is used, which represents the diameter of droplets which have the same volume/surface relation in the totality of the spray, which is represented by the following equation:

$$SMD = \sum_{i=1}^{k} D^3 \Big/ \sum_{i=1}^{n} D^2 \quad (1)$$

Where k, n and D are number of volumes of the droplet, number of areas and diameter of the droplet. It must take into account that using medium diameters is very useful to simplify droplet populations existing in an atomizing process. For this reason it is essential to use the distribution of droplet size.

1.1. Linseed oil (Linum usitatissimum)

Linseed oil, scientific name Linum usitatissimum, belongs to the family of Linaceae and the genus Linum which has 100 species. It originated from Mediterranean coastal countries and is cultivated in Canada, Argentina, India and USA. It is an annual species of the Linaceae family, growing to a height of 0.3 to 1m, which is cultivated for the production of textile fiber, seed and linseed oil. In India, it is grown mainly for seeds, used for extracting oil. Under optimum conditions the oil content of linseed seeds varies from 33 to 47%. In India various states have sufficient forest area for the plantation of linseed. Madhya Pradesh leads in yield and acreage, followed by Uttar Pradesh and Maharashtra, Bihar, Rajasthan, Karnataka and West Bengal also grow linseed in large areas. Madhya Pradesh and Uttar Pradesh together contribute to the national linseed production to the extent of about 70%.

India accounts for about 1.9 million hectares, with a seed production of 4.98 lakhs tonnes, the crop in northern India generally gives higher yield than in central and peninsular India. The irrigated crop may yield 1200 to 1500kg per hectare and occupies the third rank among the linseed-producing countries. Linseeds are a source of high quality proteins, soluble fiber and a high content of polyunsaturated fatty acids. They contain 30-40% lipids, 20-25% proteins, 4-8% moisture, 3-4% ash and 20-25% dietary fiber [11]. The chemical composition of linseed oil varies with geographical location and variety. Oils from different sources have different fatty acid compositions. The main fatty acids, which are commonly found in the linseed oil, are listed in Tables 2 and 3.

Table 2: Fatty acid composition of linseed oil [17]

Fatty acids	Contents (%)	Fatty acids	Contents (%)
Palmitic acid	6.58	Linolenic acid	53.21
Stearic acid	4.43	Linoleic acid	17.25
Oleic acid	18.51		

Table 3: Properties of linseed oil [11]

Fuel properties	Values
Density at 15°C(kg/m^3)	893
Viscosity at 40°C(mm^2/s)	26.24
Calorific value(MJ/kg)	39.3
Acid value (mg KOH/g)	0.80
Flash point(°C)	265
Pour point(°C)	-14.65

1.2. Rubber seed oil (Hevea brasiliensis)

Around 91.8 thousand hectare of land of Bangladesh (14.7% of the total planted forest area) is used for rubber plantation from where the rubber seeds can be collected. The productivity of rubber seed oil per hectare per annum is reported as 217kg oil/ha. Taking the data as a basis, the expected annual rubber seed oil production in Bangladesh is 0.02 million MT. Moreover additional rubber plantation can be carried out in the unused lands, which accounts for around 0.32 million hectare. As a potential feedstock, rubber seed oil will add an additional value of energy to the original latex value of rubber plants. Recently, the production of biodiesel from refined (FFA free) rubber seed oil by trans-esterification reaction with methanol using poly (sodium acrylate) supporting NaOH as a water-resistant catalyst has been reported. The main difficulty to produce biodiesel from the crude rubber seed oil is the high free fatty acid (FFA) content in the oil which is approximately 18%. The fatty acid composition and properties of rubber seed oil are summarized in Table 4 and Table 5 [12] respectively.

Table 4: Fatty acid composition of rubber seed oil [12]

Fatty acids	Contents(%)	Fatty acids	Contents(%)
Palmitic acid	10.20	Linolenic acid	16.30
Stearic acid	8.70	Linoleic acid	39.60
Oleic acid	24.60		

Table 5: Properties of rubber seed oil [16]

Fuel properties	Values
Density at 30°C(kg/m$^{3)}$	922
Viscosity at 30°C(mm^2/s)	41.24
Calorific value(MJ/kg)	38.96
Acid value (mg KOH/g)	4
Flash point(°C)	294

2. Production of biodiesel

Surface tension, viscosity and density of non edible oils are the important factors which affect the production of biodiesels. The non edible oils easily adhere to the surface and agglomerate with the impurities to make clogging effect in the surface. Due to this property of the oils it should be treated well before production of biodiesel and the risky factor is their viscosity. It is observed that optimum results can be achieved only when the surface tension and viscosity are low, leading to optimum flowability of biodiesel. Linseed and rubber seed oils have high FFA content therefore the biodiesel derived from those oils have viscosity comparatively similar to the diesel fuel and it gives better atomization characteristics. The reason for the ternary blends are, the linseed oil have low viscosity when compared to rubber seed oil. Therefore blending of those two biodiesels with diesel gives a good economic feasibility.

With methanol, potassium hydroxide was used as a catalyst. Trans-esterification was carried in the following ratio initially for 400ml sample. Raw linseed oil + methanol (25% by volume of linseed oil) + diluted 0.1N KOH solution (2.5% by volume of linseed oil). Volume of Biodiesel obtained and volume of glycerine with impurities are 300ml and 100ml for the given input. Methanol is used as alcohol and the potassium hydroxide is used as a catalyst to produce ruber seed oil blended biodiesel. Trans-esterification was carried in the following ratio initially for a 400ml sample. Raw rubber seed oil + methanol (25% by volume of rubber seed oil) + diluted 0.1N KOH solution (2.5% by volume of rubber seed oil) +10 ml of H_2SO_4. Volume of biodiesel obtained and volume of glycerine with impurities were 220ml and 180ml respectively. Density, surface tension and viscosity of the rubber seed oil, linseed oil and biodiesel were to be determined using the hydrometer, capillary rise method and saybolt viscometer.

3. Data evaluation methodology

Typical mass fractions of fatty acid methyl ester (FAME), which are constituents of biodiesels, are presented in Table 2 and 4. The physical properties of FAMEs and diesel fuel are given in Table 6 [1]. Biodiesels and its blend are the mixtures of FAMEs. One or more biodiesels with petroleum diesel or triglycerides of fatty acids in different mass fractions are having the above said mixtures of FAME. For mixtures, the density of a mixture can be given as [1]

$$\rho_m = \sum_{i=1}^{n} y_i \rho_i \quad (2)$$

Where, ρ_m - density of mixture (kg/m^3) y_i - mass fraction of fatty acid composition of FAMEs ρ_i - density of individual components of mixture (kg/m^3)

Table 6: Physical properties of FAMEs at 80°C [1]

FAME	Density (g/ml) ρ ± 4.3%	Molecular weight (g/mol), M	Parachor [P]	Surface tension (mN/m), γ ± 10%	Kinematic viscosity (cSt), ν
Palmitic	0.82	270.46	739	25.2	2.03
Stearic	0.821	298.51	819.6	25.82	2.53
Oleic	0.838	296.49	807.7	27.13	2.19
Lioleic	0.845	294.48	798.2	27.49	1.92
Linolenic	0.86	292.46	783.9	28.23	1.81
Diesel	0.801	-	-	25.21	1.4

An accurate estimate of surface tension of pure components includes the use of the correlation given by,

$$\gamma^{0.25} = [P](\rho_l - \rho_v)/M \quad (3)$$

The term [P] is a temperature independent parameter known as the Parachor, which is constant for a given molecular structure and relates molecular volume to surface tension of a compound. The terms ρ_l, ρ_v and M are the density of liquid, density of vapour and molecular weight (g/mol) respectively. The vapour density term is negligible at temperatures well below the liquid boiling point. A method to estimate mixture surface tension is presented in Eqn. 3 [1], with negligible vapour pressure for mixtures,

$$\gamma_m = \left[\sum_{i=1}^{n} y_i (\gamma_i)^{0.25}\right]^4 \quad (4)$$

In Eqn. (4), the terms γ_i and γ_m are the surface tension of individual components and mixture respectively, in N/m. As mentioned earlier, biodiesels constitute a mixture of FAMEs in various mass fractions. The viscosity of mixtures is predicted using [1]:

$$In[\nu_m] = \sum_{i=1}^{n} y_i In[\nu_i] \quad (5)$$

Where the terms ν_i and ν_m are the kinematic viscosities of individual fatty acid component and mixture respectively.

The droplet size correlation is most relevant for this study, since it was derived from single-phase dimensional analysis and it correlates viscosity, density, surface tension and operating conditions in a diesel engine. The correlation is [1],

$$SMD = 6156\theta_m^{0.385}\gamma_m^{0.737}\rho_m^{0.737}\rho_A^{0.06}\Delta P_L^{-0.54} \quad (6)$$

In Eqn. (6), ρ_A denotes air density in (kg/m^3) in the combustion chamber and ΔP_L is the liquid fuel injection pressure differential (in bar). The pressure difference between the injection line pressure and gas pressure in the combustion chamber is denoted by ΔP_L. The parameters SMD, θ_m, ρ_m and γ_m, have units of µm, m^2/s, kg/m^3 and N/m, respectively. In this study, the physical properties of the fuels, ρ_A and ΔP_L are within the range used in Eqn. (6). Since the variation of the physical properties of the fuels with SMD is being studied, ρ_A and ΔP_L are kept constant at 8.2kg/m^3 and 200 bar, respectively. Hence, the SMDs obtained from Eqn. (6) provide a representative comparison of atomization characteristics of the different fuels and their blends.

4. Results and discussion

The analytical values obtained for the biodiesels and different proportions of ternary biodiesel blends are presented in Table 7. The variation of density, surface tension, kinematic viscosity and SMD with respect to different biodiesel blends are presented in Figs. 1 to 4. Based on the theoretical relations, the densities of linseed and rubber seed biodiesels were found to be 858kg/m^3 and 884kg/m^3 respectively. The densities are comparatively higher than the density of diesel (850kg/m^3). On making an equivalent density value with diesel, blending was performed. The ternary blend having 80% diesel, 10% linseed biodiesel, and 10% rubber seed biodiesel closely matches with the density of diesel. Derived from the theoretical relations, the surface tension of linseed and rubber seed biodiesels were found to be 26.5mN/m and 27.7mN/m respectively. The surface tension of biodiesels is comparatively higher than the surface tension of diesel (25.2 mN/m). On making an equivalent surface tension value with diesel, blending was performed. The ternary blend having 80% diesel, 10% linseed biodiesel, and 10% rubber seed biodiesel closely matches with surface tension of diesel.

Table 7: Summary of evaluated physical properties of petroleum diesel, biodiesel and ternary biodiesel blends at 80°C

Fuel	Fuel composition (%)	Density (kg/m^3)	Surface tension $\times10^{-2}$ (N/m)	Kinematic viscosity $\times10^{-6}$ (m^2/s)	SMD (microns)
Diesel	100	850	2.52	1.4	21.32
Linseed	100-0	858	2.65	1.93	25.2
Rubberseed	100-0	884	2.76	2.02	27.05
Blend 1	05/05/1990	852	2.54	1.45	21.74
Blend 2	10/10/1980	854	2.56	1.5	22.19
Blend 3	15-15-70	856	2.59	1.55	22.71
Blend 4	20-20-60	858	2.59	1.6	23.06
Blend 5	25-25-50	860	2.61	1.66	23.55

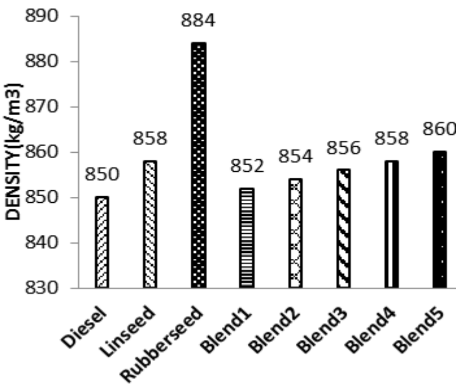

Fig. 1: Variation in density of petroleum diesel, biodiesel and ternary biodiesel blends

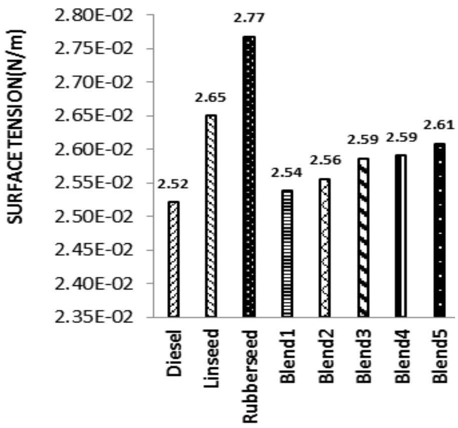

Fig. 2: Variation in surface tension of petroleum diesel, biodiesel and ternary biodiesel blends

Obtained from the theoretical relations, the kinematic viscosity of linseed and rubber seed biodiesels were calculated as 1.93cSt and 2.02cSt respectively. The obtained kinematic viscosity of biodiesels is comparatively higher than the kinematic viscosity of diesel (1.40cSt). The ternary blend having 80% diesel, 10% linseed biodiesel and 10% rubber seed biodiesel is promisingly the best match with kinematic viscosity of diesel. Evaluated from the theoretical relations, the SMD of linseed and rubber seed biodiesels were calculated as 25.20 microns and 27.05 microns respectively. SMD result was comparatively higher than that of the SMD of diesel (21.32 microns). The ternary blend having 80% diesel, 10% linseed biodiesel and 10% rubber seed biodiesel gives similar atomization characteristics of diesel.

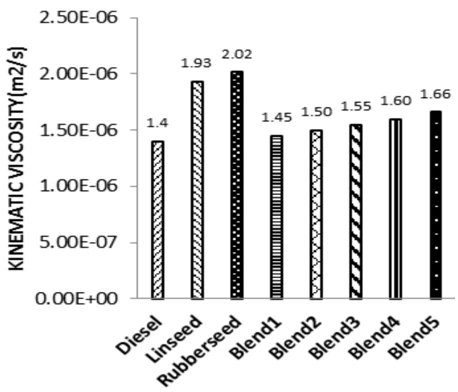

Fig. 3: Variation in kinematic viscosity of petroleum diesel, biodiesel and ternary biodiesel blends

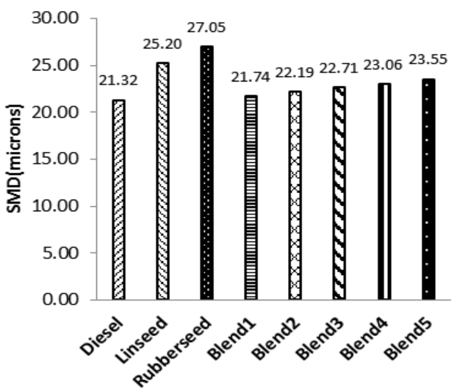

Fig. 4: Variation in SMD of petroleum diesel, biodiesel and ternary biodiesel blends

Blend 1 and Blend 2 gives similar properties while compared with diesel. When comparing the properties of Blend 1 and Blend 2 that gives 0.23% of variation among them. So Blend 2 is selected as a better fuel blend when compared with the Blend 1. It was found that the atomization characteristics gradually increase with increase in blending proportions of biodiesels with diesel fuel. This increase in values could be attributed to the higher viscosity of the pure biodiesels compared with diesel fuel. The higher viscosity is due to the presence of fatty acid compositions. The linseed oil has higher unsaturated fatty acids compared to rubber seed oil and hence has lower viscosity. The viscosity of biodiesels could be reduced by increasing the proportion of methanol: oil ratio during the trans-esterification reaction. The viscosity of ternary blends could be reduced by increasing the proportion of linseed oil, instead of equal proportion that is used in this work.

5. Conclusion

A predictive analytical study and experimental evaluation of the effect of viscosity, density and surface tension at 80°C on atomization characteristics for biodiesels of linseed and rubber seed oils, and five ternary biodiesel blends were performed. The atomization analysis showed that biodiesels of linseed and rubber seed oils have higher drop size compared with diesel. The ternary blends having 80% diesel, 10% linseed biodiesel and 10% rubber seed biodiesel gives atomization characteristics comparatively similar to that of diesel. It was found that the viscosity has the largest contribution on atomization characteristics compared to density and surface tension which together contribute less than 2%. Hence the fuel viscosity should be the first preference of physical property to improve atomization characteristic in an engine. In the future work, the proportions of linseed oil and rubber seed oil based biodiesels could be altered in varying proportions. Performance and emission characteristics of ternary blends could also be studied.

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