



How green the *Jatropha curcas* Biodiesel remains when contaminated with Kerosene?

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Abstract

Biodiesel, an environment friendly and renewable fuel, has emerged as an alternate to conventional diesel fuel. Out of various non-edible oils, *Jatropha curcas* oil (JCO) as a feedstock for biodiesel, has been gaining the attention of various researchers all over the world. However, growing demand for biodiesel has given birth to mal practices like adulteration to lower its cost and degrade the quality. The present study is carried out to purify and characterize *Jatropha curcas* biodiesel (JCB) produced from JCO by transesterification process. The JCB was purified by different methods and characterized for its purity. Its adulteration with kerosene oil has been studied using Gas chromatography, ¹H-NMR spectroscopy (Proton Nuclear Magnetic Resonance), viscosity, density and TGA (Thermo-Gravimetric Analysis). A number of calibration curves and correlations are developed that can be used to find out the extent of adulteration in biodiesel and eventually to know its impact on engine life and associated emissions.

Keywords: Biodiesel, *Jatropha curcas* oil, *Jatropha curcas* biodiesel, Adulteration, Characterization.

1. Introduction

The fast depletion, environmental concerns and exhaustible nature of fossil fuel resources has generated significant interest in the search of eco-friendly and inexhaustible alternative energy sources. In recent years, there has been a spurt of research and development activities for development of liquid biofuels like bioethanol, as a substitute of gasoline and biodiesel, as a substitute of diesel fuel. The present paper is devoted to oil feedstocks like vegetable oils and animal fats that can offer vast opportunities for the production of biodiesel to energize large numbers of diesel engines for transport, industries and commercial activities. Biodiesel is chemically a mixture of methyl/ethyl esters with long chain fatty acids. Vegetable oils include edible and non-edible oil seed crops grown in various parts of the world. To overcome the problem of competition of edible oil markets with food supplies, the interest in non-edible oil resources as a feedstock for biodiesel has grown in recent years. The purification of biodiesel from reaction mixture and its characterization for ensuring purity is the key factor not only for its commercialization and marketability but also in improving the mode of operation and the lifetime of the engine. For this purpose, the biodiesel should meet the specifications set by Indian, European, American standards etc.

Adulteration is the addition of unwanted chemicals in biodiesel to lower/degrade its quality, thereby, reducing the cost. These unwanted substances, called as adulterants, may be intentionally added to more expensive

substances to increase visible quantities and reduce manufacturing cost or for some other deceptive or malicious purpose. It is an unwanted practice and should be seriously checked in order to meet the quality standards of biodiesel/other fuels. The criteria for the addition of adulterants to biodiesel are that these should be miscible with and cheaper than biodiesel. The common adulterants used are kerosene and raw vegetable oils which can lower the cost of biodiesel but degrade its quality that can negatively impact the engine performance with regard to fuel consumption, power output and engine life. Predojevic [1] investigated the influence of different purification methods viz. washing the reaction mixture of transesterification of waste sunflower oils with silica gel, 5% H_3PO_4 and hot distilled water. The results indicated that silica gel and H_3PO_4 treatments gave highest (~ 92%) yield compared to 89% from hot water treatment. Analytical methods like GC, TLC, HPLC, GPC and TGA have been reviewed by Enweremadu and Mbarawa [2] for the characterization of high quality biodiesel from used cooking oil. The biodiesel was also characterized by viscosity, calorific value, cetane number, flash point, cloud and pour point and compared with petrodiesel. Atadashi et al. [3] reviewed the biodiesel separation and purification technologies and reported that the membrane reactor and separative membrane shows great promise for the separation and purification of biodiesel. The authors have also examined the effect of catalysts, FFAs, water content and oil to methanol ratios on the purity and quality of biodiesel. Berrios and Skelton [4] compared the post transesterification purification methods for getting very high biodiesel purity as per European standards (EN 14214). Purification by ion-exchange resins and use of magnesium silicate as solid adsorbent are considered as the methods of interest for the removal of glycerol and soap content. Conceicao et al. [5] reported the thermo analytical characterization of castor oil biodiesel. The GC data indicated a methyl ester content of 97.7% while the best conditions of TG and calorimetric analysis are found in terms of heating rate at $10^\circ C/min$. Rashid et al. [6] studied the base catalyzed transesterification of *Jatropha curcas* seed oil and obtained 94% yield of biodiesel. The GC and ^1H-NMR were used for purity check while the biodiesel stability was studied by TGA as per ASTM D 6751 and EN 14214 standards. Varanda et al. [7] carried out life cycle analysis of biodiesel production from palm oil and waste cooking oil. Liquid-liquid extraction with four theoretical stages was used to separate biodiesel and glycerol. A column of multistage distillation has been used under vacuum to purify the biodiesel. The Electrolyte Non-random two liquids (NRTL) model was used for the neutralization of catalysts and separation of salts formed. Berrios et al. [8] examined the efficiency of removing several impurities in biodiesel from waste cooking oil by adsorption using magnesium silicate and bentonite, liquid-liquid extraction (distilled water, tap water, glycerol) and ion exchange (cation resin). The results indicated that all the purification methods could remove soap, methanol and glycerol effectively but none had an effect on density, kinematic viscosity, FAME content or glyceride content of biodiesel. The different approaches for reducing FFAs in raw oil and refinement of crude biodiesel adopted in industries were reviewed by Leung et al. [9], who described new processes of biodiesel production like Biox co-solvent process that converts triglycerides to esters through the selection of inert co-solvents which generate a one-phase oil-rich system. The foregoing literature reveals that little work is reported on purification and characterization of JCB and no report is available on study related to the adulteration of biodiesel with kerosene as adulterant.

The present study is carried out to characterize *Jatropha curcas* biodiesel (JCB) produced from *Jatropha curcas* oil (JCO) by transesterification process developed in the laboratory of the authors and reported earlier [10]. The JCB was characterized for its purity using different methods. Its adulteration with kerosene oil has been studied using Gas chromatography, ^1H-NMR spectroscopy, viscosity, density, boiling points and TGA. A number of calibration curves are developed that can be used to find out the extent of adulteration of biodiesel and eventually to know the impact on engine life and associated emissions. The properties of JCB were found to deteriorate with the increase in extent of adulteration with kerosene.

2. Materials and Methods

2.1 Chemicals and Materials

JCO was procured from Jatropha Vikas Sansthaan, New Delhi. Chemicals like H_2SO_4 , NaOH, anhydrous Na_2SO_4 , and methanol were of analytical reagent grade and 99% pure. Kerosene was purchased from local market.

2.2 Methods

The experimental work was divided into following sub-sections:

2.2.1 Production of Biodiesel from JCO:

JCO having high free fatty acid (FFA) content of 21.5% was subjected to two step acid-base transesterification process developed by the authors in their laboratory, already reported [10] for the production of JCB. The process of purification of biodiesel is also reported in this paper.

2.2.2 Purity Check of Biodiesel:

The following methodologies were used to analyze the biodiesel sample for its purity:

Gas chromatography (GC): The fatty acid analysis of biodiesel was carried out using a gas chromatograph (Model-Netal) equipped with a flame ionization detector and a capillary column for injecting the samples. The analysis was carried out at a heating rate of 5°C/min from 40° to 230°C using Nitrogen as carrier gas. Quantitative analysis of % FAME was done using European standard EN 14,103:2003 (DIN EN, 1410). The % FAME yield was calculated using Equation (1). Free fatty acids in the samples were determined using stock solution (Methyl heptadecanoate and n- heptane).

$$\% \text{FAME} = ((\sum A - A_{EI}) / A_{EI}) * ((C_{EI} * V_{EI}) / m) * 100 \quad (1)$$

$\sum A$ = Total peak area from the methyl ester in C₁₄ to that in C_{24:1}

A_{EI} = Peak area corresponding to methyl heptadecanoate

C_{EI} = Concentration of the methyl heptadecanoate solution (mg/ml)

V_{EI} = Volume of the methyl heptadecanoate solution (ml)

m = Mass of the sample (mg)

¹H-NMR Spectra of Blends: ¹H-NMR spectrometer (Model- Bruker DRX-600) available at Institute Instrumentation Centre (IIC) was used to analyze the purity of biodiesel sample by operating at 500 MHz and using deuterated chloroform (CDCl₃) as a solvent.

Thermal Analysis of JCB: Thermogravimetric analyzer (TGA) (Model-Perkin-Elmer Pyris 6) available at Institute Instrumentation Centre was used to conduct thermal analysis using alumina pans. The analysis was carried out at a heating rate of 10°C/min from 30° to 330°C in dry air atmosphere of 200 ml/min using 10 mg of biodiesel sample.

2.2.3 Fuel Properties of JCB and Kerosene:

Digital rotational viscosity meter (Model-Brookfield) was used for the measurement of viscosity. A rotational speed was preset and the flow resistance of the sample was measured, i.e., the torque maintaining the set speed was proportional to the viscosity. The viscosity, shear stress and the shear rate was calculated from the torque required, the set speed and the geometry factors of the applied sensor. Density is a measure of the “compactness” of matter within a substance and is defined by the Equation (2).

$$\text{Density} = \text{Mass} / \text{Volume} \quad (2)$$

The standard metric units in use for mass and volume respectively are grams and milliliters or cubic centimeters. Thus, density has the unit grams/milliliter (g/ml) or grams/cubic centimeters (g/cc). For the purpose of experimentation, a digital balance was used for mass measurement and a 50ml graduated cylinder was used for volume measurement of liquid. 50 ml of liquid was added to weighed 50ml graduated cylinder. The density of the liquid was calculated according to Equation (2). The flash point of oil is the minimum temperature at which the oil gives off sufficient vapor to ignite momentarily on the introduction of a flame of standard dimension for a standard period of time, when the oil is heated at a prescribed rate in an apparatus of specified construction and dimensions. As the JCB are known to have higher flash point, therefore, Pensky-Martens apparatus is used for the measurement of flash point. The properties of JCB and Kerosene are reported in Table 1. The quality characteristics of biodiesel produced in this study are in good agreement with ASTM D6751 (American Society for Testing & Materials) and IS 15607 (Indian Biodiesel Standard) specifications and the work of Rashid et al [6].

Table 1: Fuel Properties of JCB and Kerosene

Property (unit)	ASTM D6751	ASTM D6751 limits	IS 15607	IS 15607 limits	JCB	Kerosene
Viscosity (cSt; 40 °C)	ASTM D445	1.9-6.0	IS 1448	2.5-6.0	5.8	1.38
Density (g/c.c at 15°C)	ASTM D4052	-	IS 1448	0.860-0.900	0.862	0.794
Flash point (oC)	ASTM D93	Min of 130	IS 1448	-	174	39
Water and Sediment (Vol%)	D2709	Max of 0.05	D2709	Max of 0.05	0.05	-
Free glycerin (% mass)	D6584	Max of 0.02	D6584	D6584	0.01	-
Oxidative stability of FAME (h)	EN14112	3	-	-	3.3	-
Free glycerol	D6584	Max of 0.02	D6584	Max of 0.02	0.015	-
Total glycerol	D6584	Max of 0.25	D6584	Max of 0.25	0.14	-
Acid value	D664	Max of 0.5	D664	Max of 0.5	0.36	-
Ester content (%)	-	-	EN 14103	Min of 96.5	98.2	-

2.3 Adulteration of JCB with Kerosene

Different blends of JCB were prepared by mixing biodiesel and kerosene in varying proportions and denoted by KBx, i.e., Kerosene Biodiesel blend and x: % of biodiesel in blend.

3. Results and Discussion

The results of various tests are discussed below:

3.1 Fatty Acid Composition

The FA composition as determined by GC, given in Table 2, is comparable with analysis reported in the earlier paper [10]. This indicates that biodiesel is almost pure and contain no impurities of moisture, glycerin, catalysts etc.

3.2 ¹H-NMR Spectra of Blends

¹H-NMR spectra of JCB showed a signal at δ 3.7 ppm which is characteristic of methyl ester protons and is comparable with ¹H-NMR spectral value of pure JCB reported in the literature [6], thereby, indicating the purity of biodiesel prepared. The ¹H-NMR spectra of biodiesel blends were observed and the amplitude of methyl group peak of different blends was noted. The ¹H-NMR Spectra of KB₁₀₀ showed a methyl group (-CH₃) peak at δ 3.7 ppm of higher amplitude (0.41) than that shown by KB₁₀ sample (0.31). The reduction in the amplitude of methyl group peaks from KB₁₀₀ to KB₁₀ sample is attributed to the adulteration of biodiesel with kerosene in varying proportions (Figure 1). The amplitude is linearly increasing with increase in blending ratio of biodiesel/kerosene, indicating that increase in the amplitude of methyl group peak can be used to measure the extent of adulteration in biodiesel i.e. if amplitude of the peak is less; quantity of kerosene is more in biodiesel.

Table 2: Fatty Acid Composition of JCB

Fatty acid	Formula	% Composition of JCB	% Composition [1]
Palmitic acid	$C_{16}H_{32}O_2$ $CH_3(CH_2)_{14}COOH$	14.2	14.1
Palmitoleic acid	$C_{16}H_{30}O_2$ $CH_3(CH_2)_5CH=CH-(CH_2)_7-COOH$	0.7	0.5
Stearic acid	$C_{18}H_{36}O_2$ $CH_3(CH_2)_{16}COOH$	6.5	6.8
Oleic acid	$C_{18}H_{34}O_2$ $CH_3(CH_2)_7-CH=CH-(CH_2)_7COOH$	38.1	38.6
Linoleic acid	$C_{18}H_{32}O_2$ $CH_3(CH_2)_4CH=CH-CH_2-CH=CH-(CH_2)_7COOH$	36.6	36.0
Linolenic acid	$C_{18}H_{30}O_2$ $CH_3(CH_2)_4CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_4COOH$	0.3	0.2
Arachidic acid	$C_{20}H_{40}O_2$ $CH_3-(CH_2)_{18}COOH$	0.2	0.2
Gadolic acid	$C_{20}H_{36}O_2$	3.4	3.6

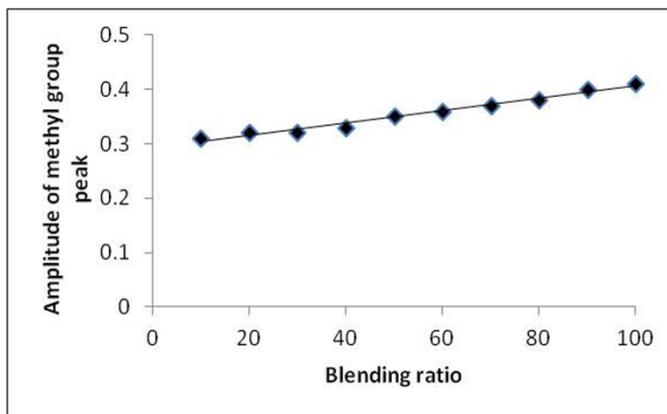


Figure 1: Amplitude of Methyl Group Peak (1H -NMR) of Biodiesel Blends

Based on the above calibration curve (Figure 1), a correlation (Equation (3)) is developed to check the amplitude of the methyl group peak in any unknown adulterated sample of biodiesel blend. The value of the regression coefficient is quite high for Equation (3), thus, indicating the validity of the correlation developed. The correlation can be used to find out the extent of adulteration in unknown samples of biodiesel.

$$A = 0.001b + 0.292 ; R^2 = 0.979 \quad (3)$$

A - amplitude of methyl group peaks; b - blending ratio of biodiesel ; R^2 - Regression coefficient

3.3 Thermal Analysis of Blends

TGA curve of JCB showed a weight loss of approximately 1.7% between 100-150°C, 4.8% between 150-200°C, 16.4% between 200-250°C and 19.4% between 250-300°C. The onset temperature of JCB from TGA curve was found as 113°C. Hence, JCB is thermally stable above its onset temperature without undergoing

considerable weight loss. Table 3 shows the weight loss of biodiesel blends with temperature. The weight loss between 100-150°C is minimum for KB₁₀₀ (1.7%) and maximum for KB₁₀ (36.2%) indicating that the blending of biodiesel with kerosene has an adverse affect on the thermal properties of biodiesel. It is seen that as the proportion of Kerosene is increased in biodiesel (from KB₁₀₀ to KB₁₀), the % weight loss in the lower temperature range (100-150°C) increases and decreases in the higher temperature range (250-300°C). Therefore, the trends of weight losses with successive temperature ranges can be used to assess the extent of adulteration in biodiesel.

Table 3: Percent Weight Loss of Blends with Temperature

Blends	Weight loss (%) with temperature			
	100-150°C	150-200 °C	200-250 °C	250-300 °C
KB ₁₀	36.2	41.6	3.4	3.0
KB ₂₀	35.7	20.9	3.1	6.0
KB ₃₀	34.9	20.1	5.5	6.8
KB ₄₀	34.7	19.4	5.9	10.3
KB ₅₀	20.4	19.0	11.0	11.5
KB ₆₀	21.1	13.6	12.1	12.92
KB ₇₀	13.8	11.5	14.9	14.1
KB ₈₀	7.5	8.2	14.4	15.5
KB ₉₀	4.1	5.4	14.5	16.3
KB ₁₀₀	1.7	4.8	16.4	19.4

Figure 2 shows the plot of onset temperature (°C) of biodiesel blends which indicates that the onset temperature of biodiesel blends decreases from KB₁₀₀ to KB₁₀ , perhaps due to the lower boiling point of Kerosene than biodiesel.

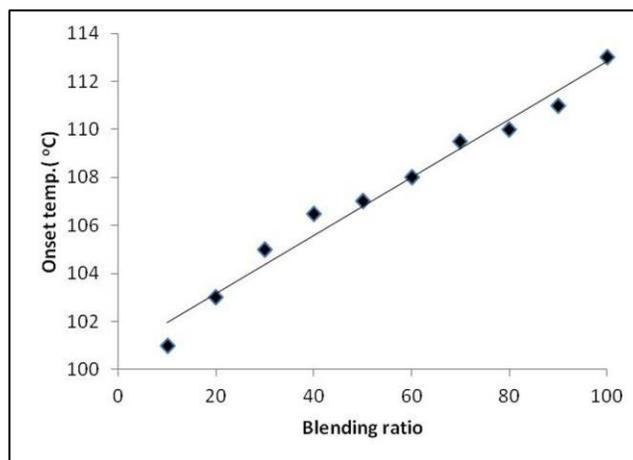


Figure 2: Onset Temperature of Biodiesel Blends

Based on the curve shown in Figure 2, a correlation (Equation (4)) is developed to check the onset temperature of any adulterated sample of biodiesel blend. The value of the regression coefficient is high for the developed correlation, thereby, laying coherence to the equation. The correlation can be effectively employed to determine the thermal behavior of biodiesel blended with kerosene.

$$T_{on} = 0.120b + 100.7 ; R^2 = 0.98 \tag{4}$$

T_{on} - onset temperature of blends in °C

3.4 Viscosity of Blends

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. Figure 3 shows the plot of viscosities of biodiesel blends. The plot can be used as a calibration curve to find out the extent of adulteration in biodiesel on the basis of viscosity. The figure indicates that the viscosity of biodiesel blends decreases from KB₁₀₀ to KB₁₀ due to lower viscosity of kerosene than biodiesel.

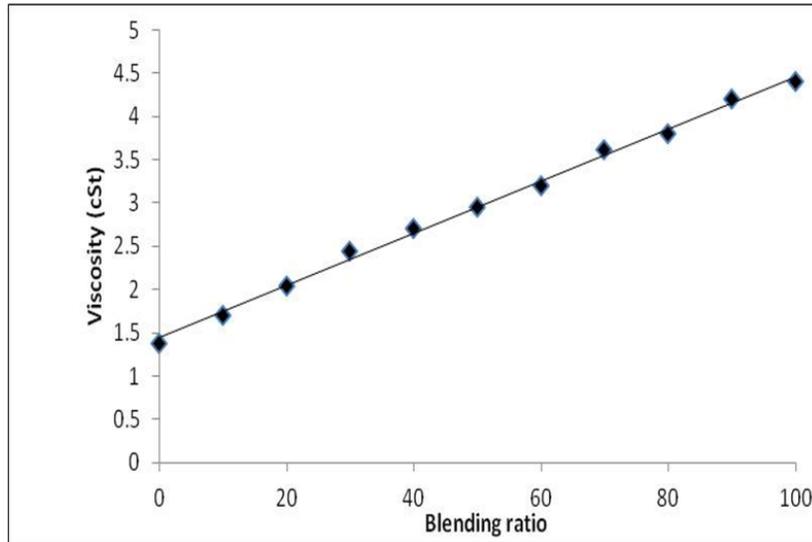


Figure 3: Viscosity of Biodiesel Blends

Based on the curve shown in Figure 3, a correlation (Equation (5)) is developed to measure the viscosity of any adulterated sample of biodiesel blend. The correlation can be used to keep a check on the mal practice of adulteration by finding out the extent of blending of biodiesel with kerosene.

$$v=0.030b+1.441; \quad R^2=0.996 \quad (5)$$

v – Viscosity of blends in cSt

3.5 Density of Blends

Figure 4 shows the plot of density of biodiesel blends that can be used as calibration curve to know the density of unknown adulterated biodiesel sample. The density of biodiesel blends also decreases from KB₁₀₀ to KB₁₀. This is again due to lower density of kerosene than biodiesel.

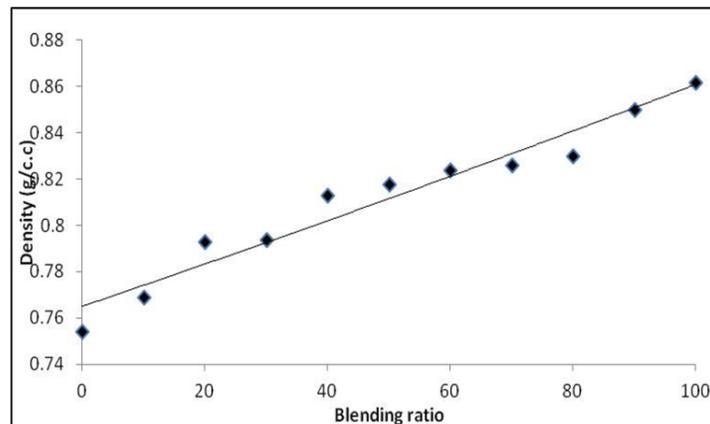


Figure 4: Density of Biodiesel Blends

Based on the curve shown in Fig.4, a correlation (Equation (6)) is developed to measure the density of any unknown adulterated sample of biodiesel blend. The value of the regression coefficient is quite high for correlation, thus, indicating the validity of the correlation developed.

$$\rho = 0.766 e^{0.001b}; R^2 = 0.937 \quad (6)$$

ρ - density of blends in g/c.c

Conclusions

The biodiesel, prepared using the two step transesterification process was purified by usual procedure. Based on the analysis of blends of biodiesel with Kerosene by GC, ¹H-NMR, TGA, viscosity and density, curves and correlations are developed to check the extent of adulteration of kerosene in unknown samples of biodiesel. The study postulates that the regression coefficient (R^2) of correlations has a value above 0.93 indicating their usefulness in curbing the mal practices of biodiesel adulteration. This is the first study of its kind being reported for the first time, which will be helpful in characterizing the biodiesel for its adulteration with kerosene. This would lead to customer acceptance, standardization and quality assurance of biodiesel and its blends in the market. This would also prove to be a boon for biodiesel producing industries by keeping a check on the malicious practice of adulteration and meeting the quality standards of their fuel.

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