

Egyptian Petroleum Research Institute Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp www.sciencedirect.com



FULL LENGTH ARTICLE



Experimental and empirical study of diesel and castor biodiesel blending effect, on kinematic viscosity, density and calorific value

A. Amin^a, A. Gadallah^a, A.K. El Morsi^{b,*}, N.N. El-Ibiari^a, G.I. El-Diwani^a

^a Chemical Engineering & Pilot Plant Department, National Research Centre, 33 El Buhouth St., Dokki, Cairo 12311, Egypt ^b Egyptian Petroleum Research Institute, EPRI, Cairo, Egypt

Received 1 September 2015; revised 2 November 2015; accepted 10 November 2015 Available online 4 January 2016

KEYWORDS

Biodiesel blending; Vegetable oil; Calorific value: Transesterification

Abstract This study aimed to investigate the fuel properties like density, viscosity and calorific value of trans-esterified methyl ester using castor biodiesel and their blends with No. 2 diesel. Empirical correlations are proposed to predict the kinematic viscosity, density, and calorific value for a mixture of castor oil and No. 2 diesel. Kay mixing rule shows a good prediction for the fuel properties under study. Several polynomials are fitted using least square method, and the fitted equations show a good agreement with the experimental data from our study. The developed equations could be used as universal formulas to predict the kinematic viscosity, density, and calorific value for castor oil and No. 2 diesel blend. The equations can be used to optimize the mixing ratio of the castor oil/No. 2 diesel for different applications. Blending of castor oil with No. 2 diesel- in the range of 20% castor oil, will not violate the required specification of diesel engines.

© 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/ licenses/by-nc-nd/4.0/).

1. Introduction

Petroleum based diesel fuels have different chemical structures of vegetable oils and esters. Petroleum diesel contains only carbon and hydrogen atoms, which are arranged in normal (straight chain) or branched chain structures, as well as aromatics configuration. The straight chain structures are preferred for better ignition quality [1]. Diesel fuel contained both saturated and unsaturated hydrocarbons, the latter are

not present in considerable amounts to prevent fuel oxidation problem. Petroleum-derived diesel is composed of 75% saturated hydrocarbons (primarily paraffin's including n-, iso-, and cyclo-paraffins), and 25% aromatic hydrocarbons (including naphthalene's and alkyl benzenes) [2].

Due to the decreasing of oil reserves and the increasing in environmental awareness, it is necessary to look for alternative fuels, which can be produced from available materials. Renewable energy resources are considered the optimal solution to deal with such problem. Biodiesel is defined as mono-alkyl esters of fatty acids derived from trans-esterification of agricultural lipids with short-chain alcohol. Variation in the chemical nature of biodiesel and conventional diesel fuel caused differences in their basic properties, which affect engine

http://dx.doi.org/10.1016/j.ejpe.2015.11.002

1110-0621 © 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute.

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

^{*} Corresponding author.

E-mail address: drakilakamel158@yahoo.co.uk (A.K. El Morsi). Peer review under responsibility of Egyptian Petroleum Research Institute.

performance and pollutant emissions. Biodiesel has higher density, viscosity, cloud point and cetane number, lower volatility and heating value compared to commercial grades of diesel fuel [3–5].

In order to improve the properties of biodiesel, several studies using different types of mixtures have been conducted. One strategy is to use petroleum diesel blends with different types of biodiesel like (sunflower, canola, soybean, cottonseed, corn, waste palm) [6], fish [7], rapeseed, soybean and other seed oils [8], rapeseed [9], and castor [10].

Rehmann and Phadatare [11] show that the blends of Pongamia Pinnata ester oil is a suitable alternative fuel for diesel and could help in controlling air pollution. Experimental studies have revealed that selective amount of biodiesel blends with diesel fuel yielded comparable engine performance similar to diesel [12,13].

In this study, castor seeds are used as a biodiesel source. Castor, *Ricinus communis*, is a non edible oil crop, considered a vital industrial raw material. The castor plant grew uncultivated in large quantities in most tropical and sub-tropical countries [14,15]. The comparison of plantation costs and oil yields of the non edible crops showed that castor is a promising raw material for biodiesel production [16]. Castor oil consisted of triglyceride oil derived from ricin oleic acid, constitutes 90% fatty acids present in the molecule and 10% non-hydroxylated fatty acids, mainly oleic and linoleic acids [15].

Kinematic viscosity and density are considered the key of fuel properties according to diesel and biodiesel fuel standards [2,8]. Due to the presence of ricin oleic acid in castor oil, its viscosity is about 7 times higher than the other vegetable oils [16]. The aim of this study is to investigate the fuel properties like density, viscosity and calorific value of trans-esterified methyl ester using castor biodiesel and their blends with No. 2 diesel.

Also, empirical correlations are correlated based on the experimental results. The developed equations are compared with Kay and Grunberg–Nissan mixing rule.

2. Experimental work

2.1. Reagents and materials

All the chemicals used in the experimental work are of analytical grade. Cultivated castor seeds are procured from Agriculture Research Division, National Research Centre. Commercial grade (of) No. 2 diesel fuel is obtained from local fuel suppliers.

2.2. Oil extraction

The seeds are decorticated to separate kemel and husk. The oil is extracted from the ground seeds in Soxhlet apparatus using either hexane or methanol as solvents. The solvent is collected using a rotary evaporator and the residual oil is dried and weighed. The fatty acid profile of the oil is determined using gas chromatography.

2.3. Transesterification

50 gm of oil is mixed with methanol in which KOH has been previously dissolved in screw-capped bottles. Then hexane is

used as a co-solvent in reaction mixture. Reaction mixture is sonicated in a water bath sonication (Model WUC-D10H, 60 Hz, 230 volts, 665 W, 3 amps). Wave intensity is fixed at 133 W; reaction time is 30 min at room temperature. The reaction mixture is transferred to a separating funnel and allowed to be separated gravitationally. The upper biodiesel layer is dried at 80 $^{\circ}$ C.

2.4. Analysis

The biodiesel is then analyzed to figure out properties such as viscosity, density and calorific value respectively. Density and viscosity measurements are made according to ASTM standard D941 and D445, respectively.

2.5. Blending

The biodiesel produced from castor oil is blended with petroleum diesel oil. The blends are prepared using a beaker, electrical stirrer with a stainless steel propeller at room temperature for 1 h. For example, the blend with a mixture of 30% biodiesel and 70% petroleum diesel is referred to as B30 blend.

3. Results and discussion

3.1. Characterization of castor oil

The oil contained in the seed is about 30% of the total seed weight. The extraction with methanol gives a better oil yield compared to hexane under the same condition due to the presence of ricin oleic acid in castor oil which is soluble in alcohols in agreement with Dasari and Goud [17]. Table 1 shows the composition of the produced castor oil fatty acids as measured using gas chromatography.

The castor oil molar mass is (919.58 gm/mol) determined according to the following relation [18]:

$$MW_{tri} = 3xMW_{acid} + MW_{glycerol} - 3xMW_{(H+OH^{-})}$$

3.2. Blending properties of castor biodiesel with petroleum diesel

Table 2 shows the biodiesel and its blend quality results as a function of castor oil percentage in the mixture. Biodiesel from castor oil was blended in different ratios with petroleum diesel where kinematic viscosity, density and heating value for the blends are investigated experimentally.

Fig. 1 shows that castor biodiesel can be blended up to 20% in the mixture within the accepted standard range of viscosity as shown in Table 3. Fig. 2 shows that castor biodiesel can be mixed with diesel up to 50% without exceeding the standard accepted ratio for biodiesel density. But due to the importance of diesel viscosity specification, the blending ratio shall not exceed 20% in order to maintain the accepted range of blending viscosity as illustrated in Fig. 1.

Fig. 3 shows that the heating value of pure castor biodiesel is comparable to investigated petroleum diesel in this study (46 MJ/kg for diesel compared to 44 MJ/kg for castor biodiesel) so the blending ratio does not have a noticed effect on the heating value of mixture.

Table 1	Gas chromat	ographic an	alysis of	castor o	il fatty acid.
---------	-------------	-------------	-----------	----------	----------------

Eatter a sid	D-1:+:-	Ctonnin .	01-:-	T in state	Timatania	Disimalaia
Fatty acid		Stearic				Kicholeic
	(16:0)	(18:0)	(18:1)	(18:2)	(18:3)	(18.10H)
Wt%	1.45	1.7	8.24	8.50	0.97	79.14
Mw (g/mol)	256	284	282	280	278	298

Table 2Biodies	el and its blend	quality resu	lts.
Biodiesel–diesel %	Kinematic viscosity (mm ² /s)	Density (g/cm ³)	Higher heating value (MJ/kg)
0	2.32	0.8253	45.86
10	2.74	0.8324	45.75
20	3.22	0.8560	45.55
40	5.38	0.8638	45.28
50	6.96	0.8840	45.01
100	15.25	0.9325	44.195



Figure 1 Kinematic viscosity of castor oil-diesel blend.

 Table 3
 Standard specifications for Biodiesel, Diesel [19].

Property	ASTM method	Biodiesel	Diesel
Kinematic viscosity cSt@40°C,mm ² /sec	D445	1.9–6	1.9–4.1
Density at 15 °C, g/cm ³	D941	0.88	0.850
Higher heating value, MJ/kg	D2015	39-43.33	49.65

3.3. Empirical equations

3.3.1. Kinematic viscosity

Using the kinematic viscosity equations proposed by Mejia et al. [20]:

$$\ln \mu_{\text{blend}} = \sum_{i=1}^{k} y_i \ln \mu_i \tag{1}$$

$$\ln \mu_{\text{blend}} = -6.26 + 0.459x + \frac{2283.7}{T} - \frac{35.96x}{T}$$
(2)



Figure 2 Density of castor oil-diesel blend.



Castor oil -diesel blend %

Figure 3 Heating value of castor oil-diesel blend.

$$\ln \mu_{\text{blend}} = -6.63 - 5.44x + \frac{2367.6}{T} - \frac{2230.3x}{T}$$
(3)

where y_i is the volume fraction of component in the mixture for (castor and diesel). *x*: is the volume fraction of castor only in the blend.

A comparison between the experimental data and the above equations prediction had shown that Eq. (1) predicted well the experimental data, as shown in Fig. 4.

While Eq. (2) was modified to fit the experimental data using least square method, Eq. (2) parameters are changed to predict the kinematic viscosity, as shown in Eq. (4). A comparison between the experimental data and the predictions of Eqs. (1) and (4) is illustrated in Fig. 5.

$$\ln \mu_{\text{blend}} = -0.01158 + 1.802x + \frac{296.12}{T} - \frac{0.9998x}{T} \tag{4}$$



Figure 4 A comparison between the experimental data of the kinematic viscosity and the predictions of Eqs. (1)–(3).



Figure 5 A comparison between the experimental data of the kinematic viscosity and the predictions of Eqs. (1) and (4).

Using Eq. (4), the experimental data given in Mejia et al. [20] are predicted to check the applicability of Eq. (4) as a universal equation to predict the kinematic viscosity of any blends of castor and diesel. A reasonable agreement is observed in case of blends kinematic viscosity, as shown in Fig. 6. However for pure diesel and castor oil, a variation is observed due to the difference between data reported in Mejia et al. [20] and the experimental data used to modify Eq. (4).

Another equation is given in [6]:

$$\mu_{\text{blend}} = Ax^2 + Bx + C \tag{5}$$

By minimizing the sum of squared error between Eq. (5) and the experimental values, the best fit is reached when the sum of squared error is minimum by changing the values of the multiplying factors. The multiplying factors that give the best fitting are shown below in Eq. (6). Fig. 7 shows a comparison between the experimental values and Eq. (6) prediction:

$$\mu_{\text{blend}} = 8.61x^2 + 4.36x + 2.32 \tag{6}$$

Fig. 7 shows a good agreement between the kinematic viscosity of the castor oil and No. 2 diesel blend as measured from our experimental study, the literature [20] and the model prediction. Table 4 indicates that Eqs (1), (4), and (6) can predict the kinematic viscosity of the castor-diesel blend.



Figure 6 A comparison between the experimental data of the kinematic viscosity from Mejia et al. [20] and the predictions of Eqs. (1) and (4).



Figure 7 A comparison between the experimental data of the kinematic viscosity and the predictions of Eq. (6).

Table 4Comparison between measured kinematic viscosity incSt and predictions of different equations.

	-		•			
Castor fraction	Experimental data	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (6)
0	2.32	2.32	2.81	2.54	2.54	2.32
0.1	2.74	2.80	2.91	0.72	3.04	2.84
0.2	3.22	3.38	3.01	0.20	3.64	3.53
0.4	5.38	4.92	3.23	0.01	5.22	5.44
0.5	6.96	5.94	3.34	0.004	6.25	6.65
1	15.25	15.25	3.97	8.8E-06	15.38	15.30

3.3.2. Calorific value

Fahd et al. [13] propose the following equation for calculating the calorific value of palm biodiesel and diesel blends:

Calorific value =
$$-6.77 * x + 43.58$$
 (7)

where the calorific value is given in MJ/kg. *x*: is the volume fraction of palm oil in the blend.

By modifying the above equation to fit the data measured for castor and biodiesel blends, the following equation is developed:

Calorific value =
$$-1.693 * x + 45.895$$
 (8)

x: is the volume fraction of castor only in the blend.

Fig. 8 shows a comparison between the experimental results and the prediction of Eqs. (7) and (8) (the fitted form of Eq. (7)) respectively. A good agreement is observed between the experimental results and Eq. (8) prediction.

Using Kay mixing rule for the calorific value, we have developed the following equation, which gives a good fitting with the experimental data as shown in Fig. 9:

Calorific value_{blend} =
$$\sum_{i=1}^{k} y_i$$
 Calorific value_i (9)

where y_i is the volume fraction of component *i* in the mixture for castor and diesel.

Table 5 shows a numerical comparison between the calorific value measured experimentally and the developed equations. Eqs. (8) and (9) can predict well the calorific value of the castor-diesel blend.

3.3.3. Density

Fahd et al. [13] proposed an equation for calculating the density for a mixture according to Kay mixing rule for density.



Figure 8 A comparison between the experimental data of the calorific value and the predictions of Eqs. (7) and (8).



Figure 9 A comparison between the experimental data of the calorific value and the predictions of Eq. (9).

 Table 5
 Comparison between measured calorific value in MJ/kg and predictions of different equations.

Castor fraction	Experimental data	Eq. (7)	Eq. (8)	Eq. (9)
0	45.86	43.58	45.89497	45.86
0.1	45.75	42.903	45.72566	45.6935
0.2	45.55	42.226	45.55635	45.527
0.4	45.28	40.872	45.21774	45.194
0.5	45.01	40.195	45.04843	45.0275
1	44.195	36.81	44.20189	44.195



Figure 10 A comparison between the experimental data of the density and the predictions of Eqs. (10) and (12).

For a mixture of castor bio-oil and diesel, the following equation can be used leading to a good agreement with the experimental data as shown in Fig. 10:

$$\rho_{\text{blend}} = \sum_{i=1}^{k} y_i \rho_i \tag{10}$$

where ρ_{blend} : is the blend density in gm/ml, ρ_i : is the density of component *i* in gm/ml, y_i : is the volume fraction of component (*i*) in the mixture for castor and diesel.

Tesfa et al. [21] used the following expression to calculate the density of the diesel-bio diesel blend in kg/m³at 15.6 °C:

$$\rho_{\rm blend} = 0.2523x + 854.33 \tag{11}$$

where x: is the volume fraction of bio-oil in the blend.

Eq. (11) is a first degree polynomial derived using regression analysis by taking the average slope and the interception. Eq. (11) predictions do not agree with the experimental data measured for the castor and diesel blend since it is developed for rapeseed oil and corn oil biodiesel when mixed with diesel. Eq. (11) is modified to fit the experimental data as shown below to calculate the density in gm/ml:

$$p_{\text{blend}} = 0.108x + 0.8253 \tag{12}$$

ĥ

Fig. 10 shows a comparison between the experimental data and the predictions of Eqs. (10) and (12) respectively. A good agreement between the equation prediction and the experimental data is observed, which can be seen numerically in Table 6. Eqs. (10) and (12) can be used to predict the density of the castor-diesel blend.

Castor fraction	Experimental data	Eq. (10)	Eq. (11)	Eq. (12)
0	0.8253	0.8253	0.85433	0.8253
0.1	0.8324	0.83602	0.854355	0.8361767
0.2	0.856	0.84674	0.85438	0.8470534
0.4	0.8638	0.86818	0.854431	0.8688068
0.5	0.884	0.8789	0.854456	0.8796836
1	0.9325	0.9325	0.854582	0.9340671

4. Conclusions

Castor oil is used as a biodiesel in a mixture with No. 2 diesel. The castor oil is blended with the diesel in limits selected to keep the properties of the produced blend acceptable for diesel users. The kinematic viscosity, density, and calorific value are the properties considered in our study.

Different equations from the literature are used to predict the properties under study. Kay mixing rule shows a good prediction for the properties under study including kinematic viscosity, density, and calorific value. However, different polynomials are used from the literature; the polynomials show a poor fitting for our experimental results. The polynomials are fitted using the least square method, and the fitted equations show a good agreement with the experimental data from our study. In addition, the developed equations are able to predict the experimental data for different experimental studies in the literature. The developed equations can be used as universal formulas to predict the kinematic viscosity, density, and calorific value for castor oil and No. 2 diesel blend.

References

- [1] J. Kapur, S. Bhasin, K. Mathur, Chem. Age India 33 (9) (1982) 475–482.
- [2] M.S. Khan et al, J. Appl. Sci. 15 (2015) 619-625.
- [3] G. Knothe, M. Bagby, T. Ryan III, J. Am. Oil Chem. Soc. 75 (8) (1998) 1007–1013.
- [4] G. Knothe, Fuel Process. Technol. 86 (10) (2005) 1059–1070.
- [5] P. Benjumea, J. Agudelo, A. Agudelo, Fuel 87 (10–11) (2008) 2069–2075
- [6] E. Alptekin, M. Canakci, Renewable Energy 33 (12) (2008) 2623–2630.
- [7] R.M. Joshi, M.J. Pegg, Fuel 86 (1-2) (2007) 143-151.
- [8] S.J. Clark et al, J. Am. Oil Chem. Soc. 61 (10) (1984) 1632–1638.
- [9] C. Peterson et al., Commercialization of Idaho biodiesel (HYSEE) from ethanol and waste vegetable oil. ASAE 1995. Paper No. 956738.
- [10] L. Canoira et al, Renewable Energy 35 (1) (2010) 208–217.
- [11] H. Raheman, A.G. Phadatare, Biomass Bioenergy 27 (4) (2004) 393–397.
- [12] F. Alam et al, Procedia Eng. 49 (2012) 221-227.
- [13] M. Ebna Alam Fahd et al, Renewable Energy 68 (0) (2014) 282– 288.
- [14] D.S. Ogunniyi, Bioresour. Technol. 97 (9) (2006) 1086–1091.
- [15] P.M. Ndiaye et al, J. Supercrit. Fluids 37 (1) (2006) 29-37.
- [16] R.O. Dunn, G. Knothe, J. Oil Chem. Soc. Jpn. 50 (5) (2001) 415–426.
- [17] S.R. Dasari, V.V. Goud, Int. J. Curr. Eng. Technol. 3 (l) (2013) 121–123 (special issue).
- [18] E.A. Ehimen, Z.F. Sun, C.G. Carrington, Fuel 89 (3) (2010) 677–684.
- [19] K. Sivaramakrishnan, P. Ravikumar, Int. J. Eng. Sci. Technol. 3 (11) (2011) 7981–7987.
- [20] J.D. Mejía, N. Salgado, C.E. Orrego, Ind. Crops Prod. 43 (2013) 791–797.
- [21] B. Tesfa et al, Renewable Energy 35 (12) (2010) 2752–2760.