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Novelty of work:

Development of mathematical model for predicting important properties of biodiesel blends.

Evaluation of Rice bran, Sesame and Moringa oils as feasible sources of biodiesel and the effect of blending on their physicochemical properties

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Abstract

Globally, the environmental awareness is driving the research towards energy resources that are more beneficial to milieu. Biofuel is considered as a remarkable option for that. Among the sources of biofuels, vegetable oils are the cheapest, easily available and in enormous quantity. However, some processes are needed to make vegetable oils suitable for engine because of having some detrimental properties. In this study, three potential feedstocks namely; Moringa, Sesame and Rice bran oils are critically investigated as potential sources for biodiesel production. The work was divided into several steps. Firstly, production of biodiesel from the three feedstocks, secondly, measurement of the important physical and chemical properties of biodiesels, and finally development of mathematical equations with the help of polynomial curve fitting method for biodiesel-diesel and biodiesel-biodiesel blends to predict the most important properties such as kinematic viscosity, flash point, calorific value, CFPP of blended biodiesel. The experiment has shown that the three feedstocks can be considered as feasible sources for biodiesel. It is seen from the experiment that biodiesel blends have notable effect on properties, for instance, viscosity of rice bran is improved to 5.1631 mm²/s from 5.3657 mm²/s when mixing

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with sesame biodiesel by 3:1 by volume ratio. It is also improved to 5.0921 mm²/s when mixing with Moringa biodiesel by 3:1 by volume. Moreover, flash point and CFPP of rice bran biodiesel are also improved when mixing with sesame or moringa biodiesel in any percentage.

Keywords: Crude oil, Biodiesel, Physicochemical properties, Biodiesel blends, Mathematical equation.

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1.0 INTRODUCTION

The global concern about the reliability of petro-diesel and their adverse impacts on milieu, the world is converging to renewable sources which are friendly to environment. Currently, more than 80% energy consumption is derived from fossil fuels. Fossil fuels is primarily dominating due to its high combustion efficiency, fuel adaptability and handling facilities ¹. However, the deep concern about fossil fuels is its toxic pollutants generation that linked to the global warming, climate change and even some impasse diseases ². In turn, this phenomenon has promoted biofuels as a prominent source of interest including biodiesel which is one of the prime renewable energy sources.

Among the renewable feedstock such as vegetable oils, animal fats and recycled cooking oil, vegetable oils are found to be promising feedstock for biodiesel because of their availability and large scale production ability. Globally, more than 350 oil-bearing crops are identified as potential source of biodiesel which can be classified as edible and non-edible oil³. Due to the diversity of oil bearing crops, it is a challenge to select the potential sources for biodiesel. Hence myriads of research are ongoing. A number of sources from edible oil are already dominating in several countries. For instance, canola and soybean are used in USA, palm oil in Malaysia, rapeseed oil in Europe etc.³⁻⁵. Sunflower, peanut, coconut, sesame are few other examples of edible oils. Other sources from non-edible oils such as *Jatrapha curcas, Sterculia foetida, Croton megalocarpas, Calophyllum inophyllum,* Karanja, Moringa, Rice bran have attracted considerable attention for biodiesel^{6, 7} because the large usage of biodiesel production from edible oils has incurred a serious concern on food supply.

1.1 Botanical description of Rice bran, Moringa and Sesame feedstocks

Moringa oleifera is the most widely cultivated tree species in the family of *Moringaceae*. It grows throughout most of the tropics and native to sub-Himalayan tracts of north-west India, Africa, Latin America, Pakistan, Bangladesh, and Afghanistan. It is drought tolerant and can survive in arid, harsh and infertile land. The tree can range from 5-10 m in height; sometimes can be even 15 m. The plant starts bearing pods 6-8 months after planting. The seeds are triangular in shape and contains about 35-45% oil by weight ^{1,8-10}.

Rice is the seed of the monocot plants *Oryza sativa* (Asian rice) or *Oryza glaberrima* (African rice). Rice is the most important cereal cultivated in the world which fed more than half of the people of the world. Rice bran is the by-product of rice milling process. Due to the presence of active lipase and high free fatty acid, about 60-70% of rice bran oil production is non-edible. Rice can be grown practically anywhere, even on a steep hill. It contains about 16-32% oil by weight¹¹⁻¹³.

Sesame (*Sesamum indicum* L) is an oil seed herbaceous crop of the *Pedaliaceae* family primarily found in tropical and subtropical areas. It is an annual plant growing 50 to 100 cm tall with opposite leaves 4-14 cm long. The flowers are yellow, tubular with four-lobed mouth. The flower may vary in color with some being white, blue or purple. The tree is originated in Africa, Turkey, India, China, Sudan, Burma, Tunisia, Egypt, Thailand, Mexico, Guatemala, Afghanistan, Pakistan, Bangladesh and etc. The oil content is about 57-63%^{14, 15}.

The pictorial view of the feedstocks is shown in Figure 1.

Figure 1: Feedstocks

1.2 Objectives of this paper

Recently, many studies have been undertaken concerning production, properties of edible and non- edible oils^{6, 16-23}. Some authors have discussed the production of biodiesel from *Moringa oleifera*²⁴⁻²⁶, Rice bran^{12, 27, 28} and Sesame^{14, 29}. However, there is no published report on the comparison of the physic-chemical properties of these feedstocks. Comparative evaluation of properties is inevitable for the maximum usage of biodiesel, optimization of biodiesel blends because research has shown that the blended biodiesel with two or more feedstock provide better performance³⁰⁻³². Therefore, the primary objective of this study is to produce biodiesel from crude rice bran, sesame and moringa oil and analyze critically the physic-chemical properties of rice bran, sesame and moringa biodiesel as potential sources for biodiesel. Then, the biodiesel-diesel, biodiesel-biodiesel blending is suggested to improve some of the main properties such as kinematic viscosity, calorific value, flash point, CFPP and etc. In this paper the polynomial curve fitting method is suggested to predict the properties of blended biodiesel^{6, 33}.

2.0 MATERIALS AND METHOD

2.1 Materials

The crude moringa and sesame oils were purchased from Delhi, India. Rice bran oil was obtained from the local markets of Bangladesh. Other chemicals such as methanol, H_2SO_4 , KOH, Na_2SO_4 , qualitative filter paper of 150 mm size were obtained from Malaysia. Biodiesel production was conducted in the scale of 1L batch reactor.

2.2 Biodiesel production

2.2.1 Production of biodiesel from moringa and rice bran oils

Crude moringa and rice bran oil were poured to a reactor and heated at 60 °C. After reaching this temperature, the oils were reacted with 25% (v/v oil) of methanol and 1% (m/m of oil) KOH. The reaction period was maintained at 60 °C for 2 h and 400 rpm stirring speed. After completion of the reaction, the produced biodiesels were poured in a separation funnel for 12 h to separate glycerol from biodiesel. The lower layer which contained impurities and glycerin was drained off.

2.2.2 Production of biodiesel from sesame oil

2.2.2.1 Esterification process

This process is employed primarily to reduce the acid value of the feedstock prior to the transesterification process. In this process 50% (v/v oil) methanol were reacted with refined sesame oil. 1% (v/v oil) of sulfuric acid (H₂SO₄) were added to the preheated oil at 60 °C for 3 h under 400 rpm stirring speed in a glass reactor. After completing the reaction time the product was poured in a separating funnel to separate the excess alcohol and sulfuric acid. Upper layer containing impurities was separated; the lower layer was taken to a rotary evaporator and heated at 95 °C under vacuum condition to remove ethanol and water content.

2.2.2.2 Transesterification process

This process is same as that in section 2.2.1.

2.2.3 Post-treatment process

Methyl ester in the upper layer from previous process was washed several times with warm distilled water at 55-60 °C to remove impurities and glycerol. Then the upper layer was poured in a control rotary evaporator to eliminate water and methanol. Methyl ester was then dried using Na₂SO₄ and finally filtered using qualitative filter paper.

2.3 Measurement of physic-chemical properties of crude oil and their biodiesel

The physic-chemical properties of crude oils and their biodiesel were tested according to the ASTM method. These properties include kinematic viscosity, density, calorific value, viscosity index, CFPP, cloud point, pour point, flash point and oxidation stability with some non-ASTM properties such as absorbance, transmission and refractive index. **Table 1** shows the test methods and ASTM standard.

2.4 Blending of biodiesel

The blending of biodiesel-diesel and biodiesel-biodiesel was done using a homogenizer at 2000 rpm. The effect of biodiesel blending ratios of 1:1 and 1:3 were studied for some properties. These include kinematic viscosity, calorific value, flash point and CFPP. For this purpose, the polynomial curve fitting method was used to predict the properties of biodiesel-diesel blends and biodiesel-biodiesel blends. Mathematically, a polynomial of order k in X is expressed in the form of: $Y = C_0 + C_1 X + C_2 X^2 + \dots + C_k X^k$ where X is the variable as a function of available data and Y is the predicted value.

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3.0 RESULTS AND DISCUSSION

3.1 Characterization of crude oils

The properties of crude oils are presented in **Table 2**. The finding from the table shows that both sesame and moringa oils possess almost the same kinematic viscosity of 34.087 mm²/s and 32.004 mm²/s, while rice bran possesses the highest viscosity of 52.225 mm²/s. Acid value of rice bran and moringa oil is about 1 mg KOH/g (1.314 and 0.8670), while sesame oil has quite high acid value of 13.56 mg KOH/g. Rice bran oil possesses the highest flash point of 300.5 °C where as moringa and sesame oil have 263.5 °C and 280.5 °C respectively. All the three oil have the same refractive index of about 1.47 whereas sesame possesses the highest absorbance 0.106.

Table 1. List of equipment used in the characterization of fuels

 $n.s. \equiv not specified in ASTM test method$

Table 2. Physicochemical properties of crude oils

 $CRBO \equiv Crude Rice bran oil$ $CMOO \equiv Crude Moringa oleifera oil$ $CSO \equiv Crude Sesame oil$

3.2 Characterization of biodiesels

The measured physical and chemical properties for Rice bran, Sesame and Moringa biodiesel are presented in **Table 3**. The findings show that the kinematic viscosity of Sesame and Moringa

biodiesel satisfy both ASTM and EN standard which are 4.3989 mm²/s and 4.1264 mm²/s however Rice bran oil satisfy only ASTM standard which is 5.3657 mm²/s. Densities of all biodiesels are slightly higher (about 3.5%) than diesel. Calorific values of all biodiesels are about 40 MJ/kg which is around 12% less than diesel. Flash points of the three feedstocks are 174.5, 208.5 and 176.5 °C respectively which also satisfy ASTM and EN standard.

Table 3. Physicochemical characteristics of biodiesel

n.s. \equiv not specified in ASTM test method SME \equiv Sesame methyl ester MOME \equiv *Moringa oleifera* methyl ester RBME \equiv Rice bran methyl ester

3.3 Effect of blending on physico-chemical properties

3.3.1 Effect of biodiesel-diesel blending

In this study, higher heating value, flash point, and CFPP are plotted against kinematic viscosity. Mathematical equation are formed using the polynomial equation with the help of following Figures 2 (a, b and c), 3 (d, e, and f) and 4 (g, h and i). Moreover, the equations are shown in **Table 4 (a)**. The kinematic viscosity, higher heating value, flash point and CFPP can easily be calculated by these equations.

Table 4: Mathematical Equation for various properties of blended biodiesel

Table 4(a): Biodiesel- diesel blends

Table 4(b): Biodiesel-biodiesel blends

3.3.2 Effect of biodiesel-biodiesel blending

In this study, kinematic viscosity, flash point and CFPP were analyzed. Using the following Figures 5 (j, k and l) and 6 (m, n and o), the equations are formed. The equations are shown in **Table 4 (b)**.

3.3.2.1 Effect of biodiesel-biodiesel blend on kinematic viscosity

Blending has a considerable effect on kinematic viscosity. For Sesame-Rice bran biodiesel blend with (3:1) ratio, the viscosity of Rice bran oil has improved from 5.3657 mm²/s to 5.1631 mm²/s. The equation, $Y = -7E-06Z^2 + 0.0105Z + 4.3928$, ($0 \ge Z \le 100$) would help to predict the kinematic viscosity at any percentage of Rice bran methyl ester (Z).

Moreover, for Moringa-Rice bran blend, the kinematic viscosity of Rice bran has also improved from 5.3657 mm²/s to 5.0921 mm²/s. The equation, $Y = -2E-05Z^2 + 0.0147Z + 4.1162$, $(0 \ge Z \le 100)$ helps to predict the viscosity at any percentage of Rice bran methyl ester (Z).

3.3.2.2 Effect of biodiesel-biodiesel blend on flash point

For both Sesame-Rice bran and Moringa-Rice bran, the flash point deflects about 3% from pure Rice bran biodiesel with ratio 3:1 by volume. Flash point is improved to 175.5 °C for Moringa-Rice bran biodiesel, and 198.5 °C for Sesame-Rice bran biodiesel at ratio 3:1 by volume where flash point of Moringa is 176.5 °C, 174.5 °C for Rice bran and 208.5 °C for Sesame biodiesels.

The following equations would able to predict the flash point of Sesame-Rice bran and Moringa-Rice bran biodiesel blends for any percentage of rice bran methyl ester ($0 \ge Z \le 100$).

$$Y = -0.0009Z^{2} - 0.2283Z + 207.23...$$
 (1)
$$Y = 1E - 05Z^{2} - 0.0207Z + 176.47...$$
 (2)

3.3.2.3 Effect of biodiesel-biodiesel blend on cold filter plugging point

The cold filter plugging point (CFPP) can be easily predicted for Sesame-Rice bran and Moringa-Rice bran biodiesel blend by using the following equations (3) and (4) with condition $(0 \ge Z \le 100)$. CFPP of Sesame-Rice bran blended biodiesel has improved to -1 °C at 1:1 ratio by volume where CFPP of rice bran is 2 °C.

 $Y = 0.0001Z^{2} + 0.0406Z - 3.0571..... (3)$ $Y = 0.0005Z^{2} - 0.0057Z - 2.0286.... (4)$

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- (b) (e)
- (c)

Fig 2: Sesame methyl ester-diesel blend (a, b and c)

Fig 3: Rice bran methyl ester-diesel blend (d, e and

(f)

f)

(i)	(j)
(1)	

Fig 4: Moringa methyl ester-diesel blend (g, h,i)

(k) (l)

Fig 5: Sesame-Rice bran biodiesel blends (j, k and l)

(m)

(n)

(0) **Fig 6:** Moringa-Rice bran biodiesel blends (m, n, and o)

3.4 Validation of mathematical equations for biodiesel blends

The equation developed by using polynomial curve fitting method for various biodiesel blend percentages are validated with experimental data shown in **Table 5.** The variation of data is calculated by using **equation** 1^{34} . Viscosity variation with experimental data for each blend is found below 0.5% and not more than 5.5% when it is used for flash point calculation. The variation of CFPP is quite larger, about 20%.

Variation (%) = $\frac{100}{N} \sum_{1}^{N} \left| \frac{Data_{exp} - Data_{equa}}{Data_{exp}} \right| \dots \dots \dots \dots \dots (1)$, N= No. of data;

Table 5: Data comparison for equation validation of various biodiesel blend

4.0 CONCLUSION

Biodiesel is one of the best potential alternatives of petro-diesel because of having profitable benefit though it has some disadvantages such as high kinematic viscosity, density, low volatility and heating value. This article deals with production and characterization of biodiesel from three potential feedstocks viz. rice bran, moringa and sesame oil. Moreover, experimental validation of physicochemical properties of biodiesel-diesel and biodiesel-biodiesel blends is studied. By applying curve fitting method equations are developed for predicting important properties which shows very close fit to experimental data. It will help further research such as optimization of blending percentage, engine combustion and performance and emission analysis.

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Fig 3: Rice bran methyl ester-diesel blend (d, e and f)



Fig 4: Moringa methyl ester-diesel blend (g, h,i)









Fig 6: Moringa-Rice bran biodiesel blends (m, n, and o)

Property	Equipment	Manufacturer	Standard method	ASTM D6751 limit	Accuracy
Kinematic viscosity at 40 °C	SVM 3000- automatic	Anton Paar, UK	D 445	1.9-6.0	± 0.35%
Dynamic viscosity at 40 $^{\circ}C$	SVM 3000- automatic	Anton Paar, UK	D7042	n.s.	± 0.35%
Viscosity Index	SVM 3000- automatic	Anton Paar, UK	D 2270		
Density at 40 °C	SVM 3000- automatic	Anton Paar, UK	D 7042	n.s.	0.0005 g/cm ³
Density at 15 °C	DM40 LiquiPhysics [™] density meter	Mettler Toledo, Switzerland	D 4052		$\pm 0.1 \text{ kg/m}^3$
Flash Point	Pensky-martens flash point - automatic NPM 440	Normalab, France	D 93	130 min	± 0.1 °C
Oxidation stability	873 Rancimat - automatic	Metrohm, Switzerland	D 675	3h min	± 0.01 h
Higher heating value (HHV)	C2000 basic calorimeter - automatic	IKA, UK	D 240	n.s.	$\pm 0.1\%$ of reading
Cloud Point	Cloud and Pour point tester - automatic NTE 450	Normalab, France	D 2500	Report	± 0.1°C
Pour Point	Cloud and Pour point tester - automatic NTE 450	Normalab, France	D 97		± 0.1°C
CFPP	Cold filter plugging point – automatic NTL 450	Normalab, France	D 6371	n.s.	
Acid Value	G-20 Rondolino Automated Titration System	Mettler Toledo, Switzerland	D 664	0.5 max	± 0.001 mg KOH/g

Table 1. List of equipment used in the characterization of fuels

 $n.s. \equiv not specified in ASTM test method$

Property	Unit	CRBO	СМОО	CSO
Kinematic viscosity at 40 °C	mm ² /s	52.225	32.004	34.087
Dynamic viscosity at 40 °C	mPa.s	47.364	29.003	30.905
Density at 15 °C	Kg/m ³	924.3	923.4	923.6
Specific gravity at 15 °C	-	0.9251	0.9242	0.9244
Density at 40 °C	kg/m ³	906.9	906.3	906.6
Kinematic viscosity at 100 °C	mm ² /s	10.393	7.6569	7.6364
Acid value	mg KOH/g	1.314	0.8670	13.56
Oxidation stability	h	4.40	41.75	9.795
Cloud point	°C	0	-7	-3
Pour point	°C	0	-7	-4
CFPP	°C	16	9	44
Higher heating value (HHV)	MJ/kg	39.548	39.868	39.386
Viscosity index	-	192.8	222	202.9
Refractive index	-	1.4718	1.4728	1.4709
Transmission	%T	87.1	85.9	78.4
Absorbance	ABS	0.06	0.066	0.106
Flash point	°C	300.5	263.5	280.5

 $CRBO \equiv Crude Rice bran oil$

CMOO ≡ Crude *Moringa oleifera* oil

 $CSO \equiv Crude Sesame oil$

Properties	Unit	SME	RBME	MOME	ASTM D6751	EN 14214	Diesel
<i>Kinematic viscosity at 40</i> ° <i>C</i>	mm ² /s	4.3989	5.3657	4.1264	1.9-6.0	3.5-5.0	3.1818
Dynamic viscosity at 40 °C	mPa.s	3.8136	4.6581	3.5781	n.s.	n.s.	2.6474
Density at 15 °C	kg/m ³	884.8	886.9	885.8	n.s.	860- 900	849.1
Specific gravity at 15 $^{\circ}C$		0.8856	0.8877	0.8858	n.s.	n.s.	1.2723
Density at 40 °C	kg/m ³	866.9	868.1	867.1	n.s.	n.s.	832.1
Kinematic viscosity at 100 °C	mm ² /s	1.7236	1.9609	1.6655	n.s.	n.s.	1.2723
Oxidation stability	h	1.135	1.61	12.64	>3	>6	58.51
Cloud point	°C	1	0	0	Report	n.s.	3
Pour point	°C	1	-3	-1	n.s.	n.s.	0
CFPP	°C	-1	2	-2	n.s.	n.s.	4
Higher heating value	MJ/kg	39.996	39.957	39.888	n.s.	n.s.	45.315
Viscosity index (VI)		229.0	187	244.9	n.s.	n.s.	133.2
Refractive index		1.4540	1.4541	1.4553	n.s.	n.s.	N/D
Transmission	%Т	86.5	82.4	87.55	n.s.	n.s.	N/D
Absorbance	Abs	0.063	0.08	0.058	n.s.	n.s.	N/D
Flash point	°C	208.5	174.5	176.5	>130	>120	73.5

Table 3. Physicochemical characteristics of bio	odiesel
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n.s. \equiv not specified in ASTM test method

SME \equiv Sesame methyl ester

 $MOME \equiv Moringa \ oleifera \ methyl \ ester$

RBME \equiv Rice bran methyl ester

Table 4: Mathematical Equation for various properties of blended biodiesel

Table 4(a): Biodiesel- diesel blends

Property	Biodiesel blends	Mathematical equation	R^2		Variable
	Sesame-diesel	$y = 1186.3x^2 - 13324x + 75694$	R ²	=	
History harding with a sec	Rice bran-diesel	$y = 288.95x^2 - 4864.4x + 57811$	0.9984	R ²	
Higher heating value vs	Moringa- diesel	$y = 2135.6x^2 - 21284x + 91375$	= 0.998	5	
Kinematic viscosity at 40°C			R ²	=	
			0.9994		X= percentage
	Sesame-diesel	$y = 132.39x^2 - 911.1x + 1642.9$	R ²	=	of biodiesel,
Flash point vs Kinematic	Rice bran-diesel	$y = 26.1x^2 - 182.27x + 394.79$	0.9339	R²	varies from 0 to
viscosity at 40 $^{o}\!C$	Moringa- diesel	$y = 104.91x^2 - 669.72x + 1147.7$	= 0.9	686	100
	Sesame-diesel	$y = -3.2958x^2 + 18.729x -$	\mathbb{R}^2	=	
CFPP vs Kinematic viscosity	Rice bran-diesel	21.881	0.9827	R ²	
at 40 °C	Moringa- diesel	$y = 1.6192x^2 - 14.936x + 35.443$	= 0.9	557	

Table 4(b): Biodiesel- biodiesel ble	nds
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Property	Biodiesel blends	Mathematical equation	R^2		Variable
Kinematic viscosity	Sesame-Rice bran	$Y = -7E - 06Z^2 + 0.0105Z + 4.3928$	R ²	=	Z=
at 40 °C	Moringa-Rice bran	$Y = -2E - 05Z^2 + 0.0147Z + 4.1162$	0.9988		percentage of
	Sesame-Rice bran	$Y = -0.0009Z^2 - 0.2283Z + 207.23$	R ²	=	Rice bran
Flash point	Moringa-Rice bran	$Y = 1E-05Z^2 - 0.0207Z + 176.47$	0.9734	R ²	biodiesel,
CEDD	Sesame-Rice bran	$Y = 0.0001Z^2 + 0.0406Z - 3.0571$	R ²	=	varies from 0
	Moringa-Rice bran	$Y = 0.0005Z^2 - 0.0057Z - 2.0286$	0.9867	R ²	to 100

Blend	Property	Biodiesel	Experimental	Data from	Variation
		blend	data	equation	%
Rice bran + Diesel	Higher heating value	B20	44,206	44279.29	0.14
		B60	42,042	42019.61	
	Flash point	B20	82.5	80.486	3.79
		B60	105.5	102.98	
	CFPP	B20	2	2.469	9.27
		B60	-1	-0.8839	
Sesame + Diesel	Higher heating value	B20	44,291	44256.29	0.13
		B60	42,026	41989.75	
	Flash point	B20	80.5	76	5.45
		B60	95.5	97.278	
	CFPP	B20	4	3.8	19.24
		B60	-1	-1.3882	
Moringa + Diesel	Higher heating value	B20	44,278	44263.7	0.10
		B60	41,995	42031.71	
	Flash point	B20	78.5	76.59	3.99
		B60	96.5	97.49	
	CFPP	B20	3	2.9248	19.30
		B60	1	1.0784	
Sesame + Rice bran Moringa + Rice bran	Kinematic viscosity	B25	4.6421	4.65	0.23
		B50	4.8933	4.9	
	Flash point CFPP	B25	198.5	200.935	0.94 22.76 0.46
		B50	193.5	193.56	
		B25	-2	-1.9796	
		B50	-1	-0.7771	
	Kinematic viscosity	B25	4.4417	4.471	
		B50	4.8216	4.8	
	Flash point	B25	175.9	175.9587	0.03
		B50	175.5	175.45	
	CFPP	B25	-2	-1.8586	
		B50	-1	-1.0636	16.36

Table 5: Data comparison for equation validation of various biodiesel blend