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A review on prediction of properties of biodiesel and blends of biodiesel

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Abstract

The continuous increasing demand for energy and the decreasing petroleum resources has led to the search for alternative fuel which is renewable and sustainable. The quality and efficiency of Biodiesel fuel was found to be more significant than petro diesel. For predicting the properties of Biodiesel, various models were developed using various feed oils and blends, the quality of Biodiesel depends on the type of feed oils. The %ARD values were proposed, which vary with composition of feed oils for a given model in comparison between predicted and experimental data. There is a huge scope in the development of accurate models to predict the properties of Biodiesel and more importantly their blends as they are

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Nomenclature

FAAE	Fatty Acid Alkyl Ester
FAME	Fatty Acid Methyl Ester
CN	Cetane Number
CP	Cloud Point
PP	Pour Point
CFPP	Cloud Filter Plugging Point
N_c	Weighted avg. no. of carbon atoms
N_{DB}	Weighted avg. no. of double bonds
ARD	Absolute Relative Deviation
Greek symbol	
η	Kinematic Viscosity of FAME

1. Introduction

Decline of available oil reserves and more stringent environmental regulations have motivated the global interest in renewable energy sources. Biodiesel is considered as an attractive alternative to replace Diesel fuels. Biodiesel consists of a mixture of fatty acid alkyl esters (FAAE) that can be obtained from vegetable oils or animal fats, mainly by trans-esterification reactions [1]. There are three kinds of catalysts that can be used in transesterification reaction, a strong alkaline catalyst, a strong acid, and an enzyme. The main advantages of using a strong alkali as a catalyst are: less reaction time and lower amount of catalyst required in the Transesterification reaction. It is an attractive alternative fuel which is

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environment friendly as it can be synthesized from edible and non-edible oils which are renewal in nature and which are obtained locally [2].

Edible vegetable oils such as canola and soybean oil in the USA, palm oil in Malaysia, rapeseed oil in Europe have been used for Biodiesel production and found to be good Diesel substitutes. Non-edible vegetable oils, such as Pongamia pinnata (Karanja or Honge), Jatropha curcas (Jatropha or Ratanjyote) and Madhuca iondica (Mahua) have also been found to be suitable for Biodiesel production [3]. Details of oil species for Biodiesel production are given in Table 1.

Table 1. Oil species for Biodiesel Production [2]

Group	Source of oil
Major oils	Coconut (copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower.
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (Acrocomia sclerocarpa), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, (Caryocar brasiliensis seed), pine nut, poppy seed, prune kernel, quinoa, ramtil (Guizotia abyssinica seed or Niger pea), rice bran, tallow, tea (camellia), thistle (Silybum marianum seed), and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall
Other oils	Castor, radish, and tung

The advantages of Biodiesel over Diesel fuel are higher combustion efficiency, higher cetane number and higher biodegradability and less carbon monoxide emissions. Along with the inherent advantages of Biodiesel, the disadvantages of using Biodiesel are worth mentioning. The disadvantages of Biodiesel include slightly higher NOx emissions, cold start problems, lower energy content, higher copper strip corrosion and fuel pumping difficulty resulting from higher viscosity. Currently, Biodiesel is expensive to produce than Diesel, which appears to be the primary factor in preventing its more widespread use. Current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use [2]. These reasons gave rise to the increasing importance of blends of other fuels like Diesel fuel, Bio-ethanol etc with Biodiesel.

Literature reveals that there is great volume of work done in the process design and manufacturing of Biodiesel from various vegetable oils, but there is dearth of experimental data and/or prediction models for thermodynamic properties of feed oils (vegetable oils) and other important properties of Biodiesel. The thermodynamic data needed for a sufficient characterization of the feed oils are requested by the process simulation tools. Infact, these simulation tools use correlations derived by a limited number of data points. The available experimental data in the literature is quite limited [4]. There is a huge scope in the development of accurate models to predict the properties of Biodiesel and more importantly their blends as they are gaining significance with the ever increasing demand of Diesel fuel.

2. Significance of various Properties of Biodiesel

There are various thermodynamic and physical properties of feed oils which are very important for the process modeling and simulation tools. Thermophysical properties of Biodiesel are used for the characterization of Biodiesel and they are also required for the combustion modeling. Physical properties of Biodiesel and their values or range are given below in the Table 2

Table 2. Physical Properties Of Biodiesel[2]

Common name	Biodiesel (bio-Diesel)
Common Chemical name	Fatty Acid Methyl Ester (FAME)
Chemical Formula Range	C14–C24 methyl esters
Kinematic viscosity range (mm^2/s, at 313 K)	3.3–5.2
Density Range (kg/m^3, at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical Appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odour
Biodegradability	More biodegradable than petroleum Diesel
Reactivity	Stable, but avoid strong oxidizing agents

2.1. Thermodynamic Properties

The critical properties, vapor pressure and heat of vaporization of feed oils are very important for the process modeling and simulation studies which can be carried out for various types of feed oils [5]. These include critical Temperature (T_c), critical Pressure (P_c) and critical volume (V_c). There is a dearth of thermodynamic properties for various feed oils as the experimental data is not available because of the decomposition of oils at higher temperature. This gives rise to the growing importance of accurate prediction models for these properties. Many models have already been reported, but a systematic study is not done to evaluate the models for the predictions of various thermodynamic properties.

2.2. Kinematic Viscosity

Viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another. This is a critical property because it affects the behavior of fuel injection. In general, higher viscosity leads to poorer fuel atomization. High viscosity can cause larger droplet sizes, poorer vaporization, narrower injection spray angle, and greater in-cylinder penetration of the fuel spray. This can lead to overall poorer combustion, higher emissions, and increased oil dilution. The viscosity of Biodiesel is typically higher than that of petroleum diesel often by a factor of two. [3],[6-8].

2.3. Density

The air–fuel ratio and energy content within the combustion chamber are influenced by fuel density. In general, densities of Biodiesel fuels are slightly higher than those of petroleum diesel, and increasing the level of Biodiesel blends increases the blend's density. FAME density is strongly affected by the degree of unstauration, with higher unsaturation leading to increased density. It has been reported that Biodiesel density is also affected by chain length, with higher chain length leading to lower fuel density [3],[9-12].

2.4. Cetane Number

Cetane number (CN) is a measure of a fuel's auto ignition quality characteristics. Since Biodiesel is largely composed of long-chain hydrocarbon groups (with virtually no branching or aromatic structures) it typically has a higher CN than petroleum diesel .The CN of pure FAME molecules increases with chain length, but this effect is masked when considering complex mixtures of FAME fuels. On the other hand, the CN of FAME fuels clearly vary with average degree of unstauration. The literature also reports that increasing degree of unsaturation leads to decreasing CN [3], [9-13].

2.5. Cloud Point, Pour Point and Cloud filter plugging point

Two important parameters for low-temperature applications of a fuel are cloud point (CP) and pour point (PP). Cloud point is defined as the temperature below which wax in diesel or biowax in biodiesels form a cloudy appearance. The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines. Pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel. Biodiesel has a higher CP and PP compared to conventional diesel. Cold filter plugging point (CFPP) is the lowest temperature, expressed in 1°C, at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. It is important as in cold temperature countries, a high CFPP will clog up vehicle engines more easily [2], [6], [12].

2.6. Flash Point

Flash point is inversely related to fuel volatility. The biofuel specifications for flash point are meant to guard against contamination by highly volatile impurities – principally excess methanol remaining after product stripping processes [3]. The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. An increase in density from 860 to 885 kg/m^3 for vegetable oil methyl esters or Biodiesels increases the viscosity from 3.59 to 4.63 mm^2/s and the increases are highly regular. There is high regression between the density and viscosity values of vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are irregular [2],[13].

2.7. Heating Value

Due to its high oxygen content, Biodiesel has lower mass energy values than petroleum diesel. As the fatty acid carbon chain increases (for a constant unsaturation level) the mass fraction of oxygen decreases, so the heating value increases [3], [9].

3. Determination of Thermophysical Properties of Biodiesel

The significant properties of Biodiesel are determined by the various tests and methods as per the ASTM specifications. Table 3 gives the standard test methods used for the determination of various properties of Biodiesel.

Table.3 ASTM Standards to determine properties of biodiesel[2]

Property	Test Standard	Reference
Cetane Number	ASTM D 613-05	[9]
Kinematic Viscosity	ASTM D 445-04e	[9]
Density	ASTM D7371-12	[9]
Flash Point	EN ISO 2719	[14]
Cloud Point	ASTM-D 2500-05	[9]
Pour Point	ASTM-D97	[14]
High heating value	ASTM D-240-02	[9]
Cloud Filter Plugging Point	ASTM D6377-05	[9]

4. Prediction of Thermophysical Properties of Biodiesel

There are various methods for the prediction of important Thermophysical properties of Biodiesel. Each model, which is used for the prediction of a given property is dependent on the type of feed oils/animal fats used for the Biodiesel. With the change in the feed source (mainly vegetable oils) the composition of the biodiesel and consequently the properties of the biodiesel changes. The various properties and their details have been compiled in Table 4.

Table 4.Models for the Various Properties of Biodiesel

Property	Name of Model	Model Equation	Requirements for Models	Source of Biodiesel	%ARD*	Reference
Cetane Number	Clement	$CN_{BDF} = \sum_i x_i CN_{FAME,i}$	x_i = wt. fraction of FAME CNFAME = Cetane number of pure FAME CNBDF = Cetane number of Biodiesel	Tallow, Cooking oil, Yellow grease	12.34	[7]
	Gopinath and Nagrajan	$CN_{BDF} = 62.2 + (0.017L) + (0.074M) + (0.115P) + (0.077S) - (0.103O) - (0.279LI) - (0.366LL)$	L = Wt % of Lauric acid methyl ester M = Wt % of Myristic acid methyl ester P = Wt % of Palmitic acid methyl ester S = Wt % of Steric acid methyl ester O = Wt % of Oleic acid methyl ester LI = Wt % of Lenoiec acid methyl ester LL = Wt % of Linolenic acid methyl ester	FAMEs (C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, C18:3)	9.00	[8]
	Yung et. Al.	$CN_{BDF} = 3.930N_C - 15.936N_{DB}$	N_C = weighted avg. no. of carbon atoms N_{DB} = weighted avg. no. of double bonds	Soybean oil	5.66	[6]
	Luis et. Al.	$\emptyset_i = -7.8 + 0.302M_i\text{-}20N$	$\emptyset_i$ = Cetane no. of i^{th} FAME M_i = mol. Wt. of i^{th} FAME, N = no. of double bonds	Beef Tallow, Soybean Oil	5.95	[9]
Viscosity	Allen et. al.	$\ln \mu_m = \sum_{i=1}^{n} y_i \ln \mu_i$	μ_m = Mean viscosity of mixture μ_i = Viscosity of pure component 'i' y_i = Mass fraction of component 'i'	Coconut oil, Palm oil, Rapeseed oil, Peanut oil, Soybean oil, Canola oil	8.04	[10]
	Ceriani et. al.	$\ln \mu_i = \sum_i N_k \left[A_{1k} + \frac{B_{1k}}{\left(\frac{T}{K}\right)} - C_{1k} \ln\left(\frac{T}{K}\right) - D_{1k}\left(\frac{D}{K}\right) \right]$	N_k = No. of groups k in a molecule i M = Component mol. Wt. A_{1k}, B_{1k}, C_{1k}, D_{1k} = Obtained from the regression of the experimental data.	FAME (Not given in literature)	7.62	[11]

	Chang and Liu	$\eta = 0.235N_C - 0.699N_{DB} - 3.648$	η = Viscosity of FAME N_C = weighted avg. no. of carbon atoms N_{DB} = weighted avg. no. of double bonds	Palm oil, Olive oil, Peanut oil, Rapeseed oil, Soybean oil, Sunflower oil, Grape oil, Almond oil, Corn oil	7.60	[12]
	Yung et. al	$\eta = 0.235N_C - 0.468N_{DB}$	η = Viscosity of FAME N_C = weighted avg. no. of carbon atoms N_{DB} = weighted avg. no. of double bonds	Soybean oil	5.45	[6]
	Luis et. al.	$\ln \eta_i = 12.503 + 2.496 \ln M_i - 0.178N$	η = Viscosity of FAME N_C = weighted avg. no. of carbon atoms N_{DB} = weighted avg. no. of double bonds	Beef Tallow, Soybean Oil	2.57	[9]
Density	Luis et. al.	$\rho_i = 0.8463 + \frac{4.9}{M_i} + 0.0118N$	ρ = Density of FAME M_i = mol. Wt. of i^{th} FAME, N = no. of double bonds	Beef Tallow, Soybean Oil	N.A.	[9]
Higher Heating Value	Luis et. al.	$\delta_i = 46.19 - \frac{1794}{M_i} - 0.21N$	δ = Higher heating value M_i = mol. Wt. of i^{th} FAME, N = no. of double bonds	Beef Tallow, Soybean Oil	N.A.	[9]
Flash Point	Yung et. al.	$T_f = 23.362N_C + 4.854N_{DB}$	T_f = Flash Number of Biodiesel N_C = weighted avg. no. of carbon atoms N_{DB} = weighted avg. no. of double bonds	Soybean oil	1.81	[6]
Cloud Point	Yung et. al.	$CP = 18.134N_C - 0.790U_{FAME}$	N_C = weighted avg. no. of carbon atoms U_{FAME} = Composition of FAMEs in Biodiesel	Soybean oil	1.10	[6]
	Sarin et. al.	$CP = 0.526P_{FAME} - 4.992$	P_{FAME} = Content of Palmitic acid methyl ester	Palm oil, Jatropha oil, Pongamia oil	1.05	[15]
Pour Point	Yung et. al.	$PP = 18.88N_C - 1.000U_{FAME}$	N_C = weighted avg. no. of carbon atoms U_{FAME} = Composition of FAMEs in Biodiesel	Soybean oil	1.43	[6]
	Sarin et. al.	$PP = 0.571P_{FAME} - 12.24$	P_{FAME} = Content of Palmitic acid methyl ester	Palm oil, Jatropha oil, Pongamia oil	1.56	[15]
Clod filter plugging point	Yung et. al.	$CFPP = 18.019N_C - 0.804U_{FAME}$	N_C = weighted avg. no. of carbon atoms U_{FAME} = Composition of FAMEs in Biodiesel	Soybean oil	0.83	[6]
	Sarin et. al.	$CFPP = 0.511P_{FAME} - 7.823$	P_{FAME} = Content of Palmitic acid methyl ester	Palm oil, Jatropha oil, Pongamia oil	0.88	[16]
Vapor Pressure	Antoine Equation	A,B,C = Antoine Constants T = Temperature in Kelvin (K)	A,B,C = Antoine Constants T = Temperature in Kelvin (K)	Soybean oil, Rapeseed oil, Tallow	Not Reported	[17]
	Ceriani et. al.	$\ln P_{i,vp} = \sum_k N_k \left[A_{1k} + \frac{B_{1k}}{T^{1.5}} - C_{1k} \ln(T) - D_{1k}(T)\right] + \left[M_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T^{1.5}} - C_{2k} \ln(T) - D_{2k}(T)\right)\right]$	$P_{i,vp}$ = Vapor Pressure (Pa) T = Temperature (K) N_k = Number of groups k in the molecule M_i = Component molecular weight Q = Correction Term A_{1k}, B_{1k}, C_{1k}, D_{1k} = Ceriani constants obtained from the regression of the experimental data.	Soybean oil, Rapeseed oil, Tallow	Not Reported	[17]

* Percentage ARD is calculated by

$$\% \text{ ARD} = \frac{1}{N} \sum_i^N \left| \frac{X_{exp} - X_{cal}}{X_{exp}} \right| \times 100$$

Where X_{exp} = Experimental value
X_{cal} = Calculated value
N = Number of experimental value

5. Biodiesel Blends

Biodiesel is used as a fuel in the form a blend with the Diesel fuel (Fossil fuel). The Biodiesel can be blended in any percentage. Biodiesel blends from 2% to 20% can be used in most diesel equipment with no or minor modifications. For example blend 'B20' refers 20 volume percent of Biodiesel is present [10]. The properties of the blend change with the amount of fuel blended with the Biodiesel and hence there is a need for the development of suitable models for the prediction of various properties of the blends.

Table 6 give the various models reported in literature for the prediction of viscosity and density of Blends of Biodiesel. The models for the other properties of Biodiesel do not exist and this gives rise to scope for the development of models for the others such as cetane number, flash point, fire point and vapour pressure.

Table 6.Models for the Properties of Biodiesel Blends

Property	General Equation	System	Correlation Constant				% ARD	Reference	Remark
			A	B	C	D			
Density	$\rho = A+BT+CT$ ρ = Density T = Temperature in K V= %Volume	Biodiesel(1) + ULSD(2)	1.043	5.1666×10^{-4}	-7.1063×10^{-4}	-	0.02	[4]	T he maximum % ARD values (6%) reported for the given systems is very much acceptable.
		Colza Biodiesel(1) + Coconut Biodiesel (2)	1.089	1.5245×10^{-4}	-7.4641×10^{-4}	-	0.04	[4]	
		Soybean Biodiesel(1) + Coconut Biodiesel (2)	1.0911	1.6021×10^{-4}	-7.5233×10^{-4}	-	0.06	[4]	
		Cotton Biodiesel(1) + Babassu Biodiesel (2)	1.0974	0.7248×10^{-4}	-7.5094×10^{-4}	-	0.04	[4]	
	$\rho_{cal} = A + B \cdot r_{mix} + C \cdot T + D \cdot T \cdot r_{mix}$ ρ_{cal} = density (kg/m^3) r_{mix} =Blending ratio of biodiesel (%), T=Fuel temperature (°C).	methyl ester of soybean(1) + ULSD(2)	845.762	0.41871	-0.7011	5.844×10^{-4}	R^2= 0.998	[21]	"R^2" is very much close to unity, hence model fits well the experimental data.
Viscosity	$\eta = \exp\left(A + BT + CT + D \cdot VT2\right.$ η = Viscosity T = Temperature V = % Volume	Biodiesel(1) + ULSD(2)	-4.6529	1.2943×10^{-3}	1775.2	805.9	2.10	[4]	Six correlations were developed the reported one fits the best to the given system.
		Colza Biodiesel(1) + Coconut Biodiesel (2)	-4.47	1.81168×10^{-3}	1735	397.5	2.17	[4]	
		Soybean Biodiesel(1) + Coconut Biodiesel (2)	-4.4834	1.9318×10^{-3}	1739.4	276.1	2.13	[4]	
		Cotton Biodiesel(1) + Babassu Biodiesel (2)	-4.5961	1.431×10^{-3}	1808.9	139.5	2.24	[4]	
		Commercial Biodiesel(1) + Low sulfur Petrodiesel(2)	-6.2378	3.8163×10^{-3}	2276.9	28.5	1.74	[4]	
		Methyl Oleate(1) + Low sulfur Petrodiesel(2)	-6.0587	2.3162×10^{-3}	2224	-202.9	2.41	[4]	
		Soybean Biodiesel from Growmark(1) + Diesel(2)	-4.7126	3.3833×10^{-3}	1788.7	-122.2	2.87	[4]	
		Soybean Biodiesel(1) + Diesel(2)	-4.6927	2.9419×10^{-3}	1782.2	250.1	3.25	[4]	
		Genetically Modified Soybean Biodiesel(1) + Diesel(2)	-4.6767	3.0099×10^{-3}	1772	332.8	2.63	[4]	
		Yellow Grease Biodiesel(1) +Diesel(2)	-4.6942	1.8303×10^{-3}	1781.8	476.2	3.01	[4]	

$\eta = \alpha \cdot exp\left(\frac{-T}{\beta}\right) + \gamma$		A	β	Γ	-	R^2		
	B100	10.120	40.843	0.972	-	0.998	[21]	Based on the "$R^{2"}$ values the reported models fit the data very well.
	B60	8.544	46.872	0.830	-	0.999	[21]	
	B40	6.726	53.791	0.767	-	0.994	[21]	
	B20	6.103	53.441	0.635	-	0.995	[21]	
	D100	5.052	50.495	0.654	-	0.997	[21]	

Blending bio-ethanol with Diesel fuels is an alternative to incorporate a renewable fraction in vehicle fuels which is receiving growing attention for its economic and environmental advantages. The generalized practice in Europe of including some Biodiesel content in the commercial Diesel fuel has even enhanced the interest of the ethanol blends as a consequence of the wider range of stability when Biodiesel is added. However, one of the main concerns is related to the loss of lubricity caused by the presence of ethanol [18], [19].

Blends of Biodiesel with butanol have also been reported in the literature. These blends were tested for physical stability and various fuel properties conforming to ASTM standards. Subsequently engine performance and emission tests were conducted with each blend. Observations revealed the blends to be thermally and physically stable, and they showed good resemblance to the properties of Diesel, with the exception of flash point only [20].

Summary

In this paper, emphasis has been given on the Biodiesel, as a potential and sustainable substitute for petro diesel. Due to the dearth of experimental data for the various thermodynamic properties of feed oils and other important properties of Biodiesel, there is a need to develop accurate model for the prediction of various properties of Biodiesel and its Blends.
For each property, various models have been proposed, which are specific to the type of feed oil. The %ARD values for each model for a given property varies and it is not to justify the best prediction model as the model equation have been proposed for different type of FAAE.

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