

FATTY ACID PROFILING AND COMPOSITION IN BIODIESEL AND BIOFUELS

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INTRODUCTION

Before discussing biodiesel, we must know about biofuels and, more commonly, fuels. Fuel is nothing but a combustible matter used to maintain fire, such as coal, wood, oil, or gas, to create heat or power. These days it is used as an energy source for engines, power plants, or reactors. We already know that the earthly atmosphere gets affected by the production and usage of conventional fuels. To avoid such contingencies, the concept of biofuels is being introduced nowadays. Also, before knowing about biofuels, we must remember that the production of fuels takes a good amount of time and most of the natural processes creating fuels are too slow. Biofuels are special fuels that are produced over a very short period from biomass. According to US Energy Information Administration, the word biofuel is reserved for liquid or gaseous fuels. Now, it will be easier for us to jump to our topic with this fable background in our hands. Biodiesel is just another form of diesel fuel coming from plants or animals and consists of long-chain fatty acid esters. In other words, it is produced using domestic procedures and is majorly a renewable fuel whose manufacturing is possible using vegetable oils, animal fats, etc. Why biodiesel? Well, there are numerous reasons for its wide acceptance. The most important ones are -

1. It is the most diverse planet on earth.
2. It has been scientifically proven as a carbon reducer.
3. It is a simple solution with a proven performance.
4. It is one of the major job creators and economic drivers.

Another critical aspect of biodiesel and fuels is the storage problems. The oxidative stability of biodiesel fuel is a crucial factor in determining the allowable storage time for biodiesel fuel. The iodine number can be used to estimate the oxidative stability of the fuel before any

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stabilizers are added. Typically, biodiesel fuels can be stored for up to 6 months without problems. Depending on the production methods, the color varies from golden to dark brown. It's slightly miscible with water and has a high boiling point and low vapor pressure. The flash point of biodiesel exceeds 130 °C (266 °F), significantly advanced than that of petroleum diesel which may be as low as 52 °C (126 °F). More specifically, biodiesel refers to a family of products, called alkyl esters of fatty acids, made from vegetable oils or animal fats in combination with alcohol such as methanol or ethanol.

BIODIESEL AND BIODIESEL PRODUCTION METHODS

Biodiesel is a diesel engine¹ alternative fuel made from a variety of sources, including palm, soybean, and mahua oil, animal fats, and waste cooking oil.²⁻¹¹ **Table 1** shows the various feedstocks for biodiesel production and displays the numerous feedstocks used to make biodiesel.^{5,12,13} Saturated and unsaturated fatty acids¹⁴ are found in equal amounts in vegetable oil. Biodiesel is made up of FAME, which is created when vegetable oils are trans-esterified with methanol, ethanol, and other alcohols. Biodiesel is a promising replacement for fossil diesel¹⁵ because of its feature. Alkyl ester structures^{16,17} in biodiesel synthesis govern parameters including cold flow, oxidation stability, viscosity, cetane number, calorific value, and lubricity. Cold biodiesel Because both depend on the proportions of saturated and unsaturated fatty acids contained in the oil^{16,18-21}, flow behavior and oxidation stability have opposing features.

- **TABLE-1**

Name of feedstocks for biodiesel production-^{5,12,13}

Edible feedstocks	Non-edible feedstocks	Animal fats or waste	Waste or recycled oil
Amaranth	Rubber seed tree	-	-
Rice bran	Karanjaor	Yellow grease	-
Wheat germ	Orange	-	-
Opium poppy	Nagchampa	-	-

Palm	Jojoba	-	-
Olive	Cottonseed	-	-
Pistachia Palestine	Mahua	-	-
Sesame seeds	Tobacco seed oil	-	-
Grape seed	Halophytes and Xylocarpus moluccensi	-	-
Coriander seed	Linseed	-	-
Rice bran	Sea Mango	-	-
Tea (camellia)	milk bush	-	-
Safflower oil	Kusum	-	-
Coconut	Pongamia	Chicken fat	-
Corn	Neem	By-products of the refining of vegetable oils	-
Sunflower	Jatropha	Tallow	-
Borneo tallow nut	Deccan hemp	-	-
Prune kernel	Algae	-	-
Tallow	Rubber seed	-	-
Peanut	Karanja or Honge		

- **METHODS OF PRODUCTION OF BIODIESEL: -**

Biodiesel Production Methodologies Biodiesel technological advancements are constrained by specific biodiesel features, such as cold flow behaviour.²² Direct usage and blending, thermal cracking (pyrolysis), esterification, trans-esterification, and micro emulsion^{23,24,25} is some of the ways used to make biodiesel. Trans-esterification of animal fats and vegetable oils is the most prevalent of these processes.²³

- **TRANS-ESTERIFICATION PROCESS: -**

Direct transesterification cannot be used because vegetable oils have high acid values (greater than 4 mg KOH/g oil). Before the process, several processes are required, including pre-treatment, esterification, trans-esterification, and a fine post-treatment process. If the acid value of the vegetable oil is less than 4 mg KOH/g oil, trans-esterification can be done immediately.²⁶

- **PRE-TREATMENT PROCESS:**

Crude oil is exposed to rotary evaporation and heated to 95 °C in under an hour to remove moisture content.

- **PROCESS OF ESTERIFICATION:**

Before transesterification, the esterification process is performed to lower the acid value of the biodiesel feedstock. Crude oil is put through an esterification reaction in this procedure, Crude oil is allowed to react in a flask for acid-catalyzed esterification with 50% (v/v) of alcohol (methanol or ethanol) and 1% (v/v) H₂SO₄. The reaction mixtures are stirred for 3 hours at a speed of 400 rpm while being kept at a minimum temperature of 60 °C. The product is transferred to a separating funnel once the primary phase of acid esterification is finished, and any excess methanol and contaminants that have moved to the upper layer are withdrawn. To separate the methanol and water from the esterified oils, the lowest layer of the product is heated at 90 °C for 60 min. The substance is then utilized for trans-esterification.²⁶

- **PROCESS OF TRANS-ESTERIFICATION:**

Trans-esterification is a biodiesel production method that involves combining animal fats or vegetable oils with alcohol (either ethanol or methanol) to produce esters and glycerol.^{8,27,28,29} After applying a catalyst²⁷, the reaction rate improves. These catalysts might be homogeneous, like NaOH, KOH, and NaOCH₃, or they can be heterogeneous, like NaOH, KOH, and NaOCH₃. MgO, CaO, Na, and K³⁰⁻³² are examples of heterogeneous minerals. Esters and

glycerols, as well as mono-, di-, and triacyl-glycerols, catalysts, and soaps make up the final reaction mixture. After the trans-esterification reaction,³³ the biodiesel glycerol is separated.

- **POST-TREATMENT PROCESS:**

To remove glycerol content and contaminations, the trans-esterification product is washed with distilled water at a temperature of more than 65 °C. The biodiesel is next treated to rotary evaporation to remove any remaining water and methanol/ethanol. Finally, Na₂SO₄ is used to absorb moisture, after which the product is filtered and collected.²⁶

Benefits of this method: -

1. Biodiesel fuel has nearly identical properties to normal petroleum diesel fuel.
2. BDF has a cheap production cost.
3. This strategy is appropriate for industrialized production.
4. High conversion efficiency.

Limitations of this method: -

1. Low levels of free fatty acids and water are necessary.
2. BDF can be neutralized and washed due to pollution concerns.
3. Separation of the reactive product is difficult.

- **OILS ARE USED DIRECTLY AND BLENDED: -**

Vegetable oils (VOs) used directly in diesel engines have several inherent flaws. Although this technology has only been investigated in recent decades, the use of vegetable oils for other reasons has been practiced for over a century. To overcome the viscosity concerns due to the secondary viscosities of vegetable oils in compression ignition engines,^{34,35} crude vegetable oils can be combined directly and alternately weakened with diesel fuel. Clean vegetable oils were found to have the same energy consumption as diesel fuel. However, gum development during storage or cold weather^{27,34} may be caused by fatty acid polymerization, oxidative stability, and poor cold flow behavior of vegetable oils. Vegetable oils have a lower cetane number (32-40) and heating value (39-40MJ/kg) than diesel fuel.^{36,37} When compared to diesel

fuel, VOs have a very high kinematic viscosity (30-40cSt at 38oC) and flash point (over 200oC). The viscosity and volatility of VOs can be improved by blending 181 and heating them. However, because the molecular structure does not alter, polyunsaturated behavior does not change as well.^{34,35,38} The use of 183 VOs in diesel engines necessitates significant engine modifications, such as changes to piping and injector development materials, as well as the addition of a heat exchanger and an additional fuel tank to the fuel system.³⁹ Otherwise, engine running times are reduced and maintenance costs are increased due to increased wear, resulting in an increased risk of engine failure.⁴⁰ Direct or blended VOs, on the other hand, are incompatible with direct or indirect injection diesel engines.^{41,42} To tackle the challenges caused by high fuel viscosity, micro-emulsification, pyrolysis, and trans-esterification have been used as solutions.⁴²

Advantages:

1. It is simple to use and does not necessitate additional production costs.

Drawback:

1. The fundamental issue with this technique is its high viscosity, which results in poor fuel atomization.
2. Low volatility qualities are associated with a high flash point.
3. Issues with storage and CFP
4. The main issues include high carbon deposits, scuffing of the engine liner, and injection nozzle failure.
5. The engine fuel system must be modified, which is why it is costly.

• HYDROTREATED VEGETABLE OIL (HVO) -

For developing biobased diesel fuels, also known as renewable diesel fuels, hydrotreating vegetable oils provides an alternative to esterification. Hydrotreated Vegetable Oil (HVO) can be made from vegetable oils such as rapeseed, soybean, and animal fat, among others, using a three-step process: first, pre-treatment of the oils; then hydrotreatment of the oils⁴³⁻⁴⁵ to remove metals, N₂, and other impurities; and finally, isomerization to absorb any remaining impurities in the oils^{46,47} chemical reaction, where the oils and hydrogen (triglycerides) are reagents.

HVAC is a paraffinic chemical mixture. However, the cetane number is high (75 to 95), although the density is low (770 to 790 kg/m³). The heating value of HVO^{46,48-50} is approximately identical⁴⁶ to that of diesel fuel^{46,51,52} and the stability is good.

Advantages:

1. The properties of the fuel are nearly identical to those of diesel fuel.
2. When it comes to stability, NO_x emissions, the tendency to dilute engine oil, and winter conditions, HVO outperforms ester-type biodiesel (FAME).

Limitations:

1. HVO has low torque and engine performance at high speeds compared to FAME, as well as low total energy.⁵³
2. Any remaining impurities in HVO will cause the catalysts to deactivate prematurely.⁴⁶

- **INFLUENCE OF FAME ON COLD FLOW PROPERTIES (CFPS) AND OXIDATION STABILITY (OS) OF BDF: -**

FAME's effect on the oxidation stability and cold flow characteristics of BDF Fatty acid methyl esters and CFPs and OS of BDFs^{54,55} is connected. CFP is dependent on the length of the fatty ester chain, whereas OS is dependent on polyunsaturated fatty esters.⁵⁶ The unsaturated fatty acid methyl ester is beneficial for CFP, but saturated fatty acid methyl ester⁵⁷ is favorable for OS. In comparison to short-chain and unsaturated fatty compounds, long-chain and saturated fatty compounds^{58,59} have a higher melting point (MP), which leads to crystallization at higher temperatures. Investigated how the physical characteristics of vegetable oil biodiesel were affected by fatty acid chain length and unsaturation degree (UD). CFPP was decreased with a UD increase from saturated to the monounsaturated fatty acid ester's lower melting point and the reduction in CFPP that resulted, UD was increased when saturated fatty acid ester was used as the starting point. Reduced polyunsaturated fatty esters increase OS. linolenic acid (one bis-allylic position at C-11), as well as linolenic acid (two biallelic positions at C-11 and C-14), and numbers such as methyl oleate, methyl linoleate, and methyl linoleate, are examples of double bond locations and numbers that affect the autoxidation of UNSFAE. The OS of BDFs^{58,60} is influenced by the large amounts of methyl/ethyl esters found in most BDFs, such as oleate, linoleate, or linoleate.

- **EFFECT OF BIODIESEL PRODUCTION ON COLD FLOW BEHAVIOURS: -**

Cold flow characteristics are connected to biodiesel production processes. Made biodiesel from oils of corn, sunflower, soybean, peanut, and other seeds by transesterification and thermal cracking. Following ASTM criteria, they checked the biodiesel for thickness, CFPP, and cementing point. The findings showed that, in contrast to catalytic cracking biodiesel, the pour point for trans-esterified biodiesel increases significantly while the pour point for CFPP falls. According to the study, cold temperatures have an impact on how biodiesel is produced. Using the trans-esterification method with short-chain monohydric alcohol, Dunn⁶¹ produced biodiesel. Small amounts of minor components, including saturated mono-acylglycerols and free steryl glucosides, were produced during this process. These substances have high liquefaction and poor solubility characteristics, which enable them to create dense residues that block fuel filters in cold climates and have an adverse effect on OS. Improved the operability of biodiesel in cold climates by using biobutanol as alcohol during the trans-esterification of rapeseed oil and frying oil to improve the low-temperature behavior, such as CP, PP, and CFPP Improved the behavior of biodiesel's cold flow and oxidation stability by producing it from canola oil and SBO using thermal cracking. A significant impact on cold flow behavior and other biodiesel features was found to be caused by the quality and composition of the raw material. Browning vegetable oil is converted into biodiesel through low-temperature behavior, which is governed by Physico-chemical properties. BDF was created through transesterification utilizing feedstock that had large levels of saturated long-chain fatty acids with high melting points, however, it tended to have fairly subpar cold flow behavior. As a result, biodiesel presents several challenges when used in engines in cold climates.

CLOUD POINT (CP) AND POUR POINT (PP) -

Cloud point is the second crucial factor for the low-temperature use of fuel (CP). "Cloud point (CP)" is the temperature at which fuel begins to appear cloudy as a result of the development of hardened wax. Wax in diesel or bio wax in biodiesel causes the oil to thicken and clog fuel injectors and filters in engines. The temperature at which there is enough wax present to gel the gasoline to the point where it can no longer be pumped is known as the pour point. In comparison to biodiesel, conventional diesel has a lower (better) cloud point and pour point. The cloud point of biodiesel is between 262-289 K, whereas the cloud point of diesel is between 17 and 8 °C. In addition, although biodiesel has a pour point between 258 and 286 K, diesel

has a pour point between 36 and 30 °C. Due to their molecular interactions, double bonds have a big impact on crystallization. Unsaturated compounds crystallize more slowly than saturated ones because the spatial architecture of molecules with double bonds prevents the aggregation of molecules at lower temperatures. Unsaturated methyl oleate melts at 19 °C, stearic acid melts at 39 °C, and methyl linoleate is solid at 35 °C. Because they are more saturated than rapeseed and soybean esters, which have average pour points of 4 °C and -10 °C and cloud points of 0 °C and 5 °C, respectively, the palm methyl esters have poor cold flow qualities with a cloud point of 14 °C and PP of 10 °C⁶² Double bonds in the middle of the carbon chain lead to lower cloud points than double bonds near the extremities of the carbon chain, according to Rodrigues et al.⁶³. Additionally, compared to molecules with longer carbon chains, those with shorter, linear carbon chains that have a stronger van der Waals attraction can crystallise at lower temperatures.

- **CLOUD POINT AND POUR POINT PREDICTION MODELS-**

- a. Thermodynamic-based models-**

Unfortunately, the majority of models that have been created are only useful for mixed mixtures. Pure biodiesel or pure FAME models are quite rare. According to Imahara⁶⁴, the cloud point is a temperature based on the thermodynamic equilibrium between a compound's solid and liquid states, and the equilibrium conditions may be calculated from the equality of each component's fugacity in each phase. They discovered that independent of the makeup of unsaturated esters, the cloud point of biodiesel could only be determined by the quantity of saturated fatty acid methyl esters. With this model, it is possible to estimate the cloud point of biodiesel with a maximum variance of 1.83 per cent for samples that contain a lot of saturated chemicals. To predict the cloud point from the carbon number of biodiesels, Lopez et al.⁶⁵ used the same method to characterize the phase equilibrium of fatty acids and to construct a set of equations for melting points and melting enthalpies. Only binary mixes, or mixtures having two saturated substances, have been evaluated using this approach, and the results have shown reasonable consistency. However, as unsaturated fatty compounds have lower melting points than saturated ones, the cloud point in both of the aforementioned thermodynamic-based models is determined by the quantity of saturated compounds rather than unsaturated esters. As a result, the predictions of these models for biodiesel including unsaturated fatty acid esters show a significant variance.

b. Molecular structure-based models-

Previous studies have demonstrated that the features of low-temperature flow are influenced by the attractive forces between the molecules, which decrease with the presence of double bonds. In contrast, the values of cold flow characteristics increase as a result of intermolecular forces, which rise with chain length. In other words, as the degree of saturation and carbon chain length grow, so do the values of low-temperature flow characteristics. As a result, several models have been created and associated with the composition of total unsaturated FAMEs in biodiesels as well as the weighted-average number of carbon atoms. A set of semi-empirical models for low-temperature flow characteristics based on biodiesel composition were presented by Sarin et al.^{66,67}. Each cold flow property was given two sets of prediction equations (CP, PP, and CFPP). One is depending on how total unsaturated FAMEs are composed (UFAME). The other, which is used in most vegetable-based biodiesel, is based on the structure of palmitic acid methyl ester (PFAME), which is the main component of saturated FAME. However, for biodiesel comprising both saturated and unsaturated components, the predictions of these models produce a significant discrepancy. Su et al.⁶⁸'s conclusion were that the quantity of unsaturated esters and the weighted-average number of carbon atoms were the primary determinants of the cloud and pour points. These equations' predictions for biodiesel including both saturated and unsaturated fatty acid esters exhibit reasonable errors. Bolonio et al.⁶⁹ created similar models for the cold flow characteristics of fatty acid ethyl esters (FAEE). These models, which were built using 11 different types of pure biodiesel, had dismal R² values for cloud and pour point, respectively, of 0.89 and 0.76.

c. Composition based model-

The other three ways include comparing the cloud and pour points to how saturated and unsaturated fatty acid methyl esters are distributed in biodiesel. Fairly speaking, none of these models could provide a valid forecast because of the small set of experimental data that they were based on. This makes the output of the developed model untrustworthy. These biodiesels had 1.7–13wt% unknown.

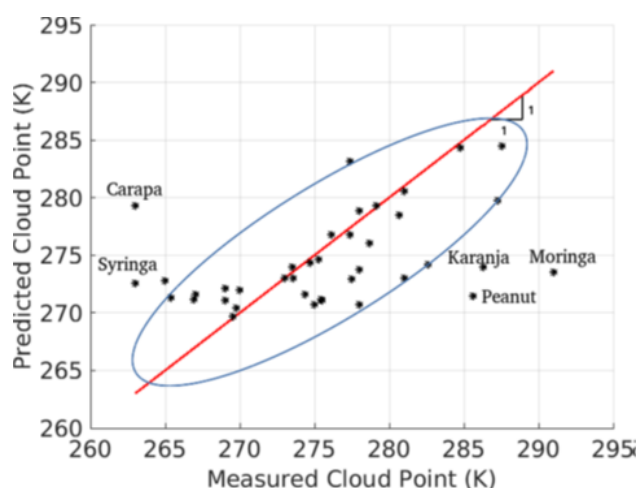


Fig. . Cloud point prediction and experimental data for all studied biodiesel.

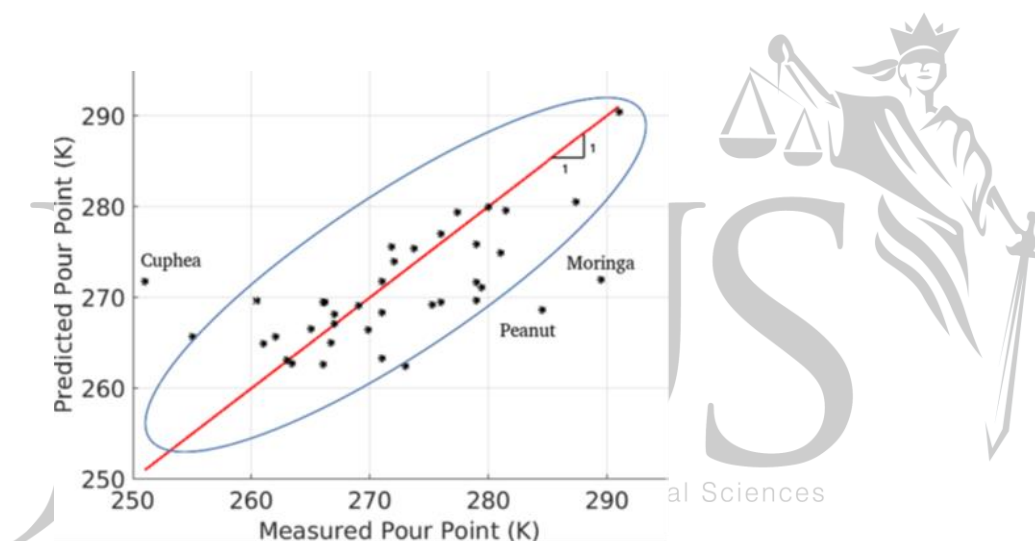


Fig. Pour point prediction and experimental data for all studied biodiesel.

COLD FILTER PLUGGING POINT (CFPP)-

The temperature at which fuel filters clog due to solidified or gelled gasoline components is specified as CFPP t. CFPP is less progressive than CP, but some researchers believe it is a better indicator of low-temperature operability. The CFPP of biodiesel can be determined using the ASTM standard D6371-05¹²⁵, a standard test technique for determining the CFPP of sample fuels. Fuel samples are pipetted under vacuum circumstances and chilled with a 1 °C

temperature determination in this approach. The experiment is then repeated until wax crystals and fuel filter blockages are seen.

COLD FILTER PLUGGING POINT PREDICTION MODELS:

- **Composition-based model-**

Long-chain saturated fatty acids have a significant impact on CFPP, whereas unsaturated esters have no effect. As a result, the CFPP of biodiesels is typically proportional to the chain length saturated factor (LCSF). Ramos et al.⁷⁰ generated a good correlation ($R^2=0.96$) based on this concept. Because the melting values of unsaturated esters are substantially lower than those of saturated esters, they are not included in the model. Unsaturated molecules function as solvents, dissolving saturated esters and causing them to precipitate under the effect of warmth. Sarin⁷¹ proposed another model in which simply the concentration of palmitic acid, the major saturated ingredient in most biodiesel samples, was taken into account.

This model is based on the fatty acid composition of 20 distinct palm biodiesel blends with jatropha and Pongamia having palmitic acid ranging from 0-45 per cent with a 1.03 per cent variance. However, in biodiesel, when other saturated chemicals are predominant, the variance might reach up to 7%. The melting temperatures of saturated compounds and their mass fraction can also be used to calculate LCSF. To the best of the authors' knowledge, two models based on the melting point of saturated fatty acids are available. Wangetal recommended one⁷² used the fatty acid content of woody biodiesel, which took into account the carbon chain length of C14:0-C20:0.

Sarin et al.⁷⁰ developed the alternative model after analyzing the FAME composition of 21 different biodiesel blends with carbon chain lengths ranging from C18:0-C24:0 and discovering a favorable link between the concentration of palmitic acid methyl ester and CFPP. However, the melting point differences for both models were reported to be roughly 9-10%.

- **Molecular structure-based models-**

According to various publications, biodiesel rich in long-chain saturated methyl esters has the highest CFPP, while unsaturated chemicals have a marginally beneficial effect

on biodiesel CFPP. In the various models that have been proposed. The CFPP of biodiesels is related to the concentration of unsaturated chemicals as well as the length of the carbon chain. As previously stated, the existence of double bonds lessens the attractive forces between molecules, resulting in lower CFPP values. A comparable concept exists for Fatty Acid Ethyl esters (FAEE).

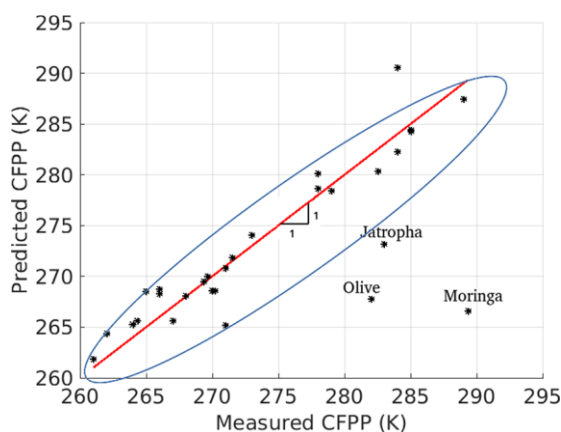


Fig. 1. CFPP prediction and experimental data for all studied biodiesel.

Fig. Depicts the CFPP experimental data as well as the current work's regression results. The proposed regression model's RSME and (MAPE per cent) about the experimental data is 5.72 K. (1.11 per cent)

HIGHER HEATING VALUE:

The Higher Heating Value (HHV or δ) or the gross or energy calorific value is the amount of heat released during the combustion of a unit quantity (1 gram) of fuel to produce H₂O and CO₂ at its initial temperature. This attribute describes the energy content of fuels and, as a result, their efficiency.⁷³ As the number of carbon atoms (chain length) in the fuel molecules increases, the calorific value increases and also increases as the ratio of carbon and hydrogen to nitrogen and oxygen increases. However, at lower molecular chain lengths (from C₈ to C₁₄), the increase is more significant than at longer carbon chains (from C₂₀ to C₂₂). As the number of double bonds increases the heating value of fatty acid methyl esters and biodiesel decreases. The degree of unsaturation had a greater impact on heating values than the length of the carbon chain. For each increase in the degree of unsaturation of FAMEs, the higher heating

value is reported to decrease by around 0.21 MJ/kg.⁷³ The selection of compounds with the highest and lowest HHV is a little perplexing because the manner of HHV presentation in the literature varies: some papers provide higher heating values, others lower values and still others merely report heating values. In general, the heating value of petrol-diesel is roughly 12% higher than that of biodiesel, with 46 MJ/kg versus 39.57–41.33 MJ/kg. Furthermore, the heat content of vegetable oil is around 88 per cent that of diesel. A number of models can accurately predict higher heating values. The most trustworthy predictions could well be made using the model published by Channiwala based on the relevant combustion reaction and another model developed based on the fatty acid compositional profile of FAME⁷⁴. Other models' output is confined to certain substances such as saturated fatty acids. HHV is one of the physical attributes of biodiesel that can be achieved from individual HHV of FAMES when suitable mixing criteria are followed using the proper mixing rule. There are several prediction models for estimating the HHV for vegetable oil and vegetable oil-based biodiesel fuel available in the literature⁷⁵⁻⁷⁸. These models are-

MODELS BASED ON COMBUSTION REACTION:

The first category of HHV prediction models is based on C, H, S, and N combustion reactions to CO₂, H₂O, SO₂, and NO₂. One of them is Channiwala's model⁷⁸. This model is based on 225 data points, and its deviation is 1.45–3 per cent. This model was used by Fassinou et al.^{79,80} to predict HHV in canola oil, crude soybean oil, palm oil, and waste cooking oil. They obtained results with greater than 97 per cent accuracy⁸⁰. The authors presented a similar model based on the relevant combustion reactions for biodiesel and vegetable oil HHV using their fatty acid composition. Their correlation was within a deviation range of 0.2–3.87%. This type of model is also useful for other oil-based fuels⁷⁵.

MODELS BASED ON THE PHYSICAL PROPERTIES OF BIODIESEL:

The first equation was proposed by Demirbas et al.⁷⁶ based on the saponification (SV) and iodine values (IV) of biodiesel and vegetable oil. They also proposed two correlation models for the HHV of vegetable oil as a function of its densities and viscosities in another paper. Later that year, they used the same strategy to discover new correlations between vegetable oil and biodiesel. Their new density models failed to produce reasonable predictions. However, predictions based on density, viscosity, iodine, and saponification values have an accuracy of less than 4.5 per cent in predicting biodiesel HHV. There is also one model for HHV of pure

fatty acid methyl ester in this category, which comes with the mixing rule of higher heating value. This model produced reasonable predictions with a 2 per cent deviation in Demirbas et al.⁷⁶ works.

MODELS BASED ON MOLECULAR WEIGHT OR ELECTRON NUMBER:

Kharasch and Sher⁸¹ reported HHV of many classes of organic compounds based on the number of valence electrons present in the molecule for the first time in 1925. However, all saturated and unsaturated FAMES were not included in their model. Therefore, based on Kharasch's idea, Freedman [10], developed different equations for both the saturated and unsaturated FAMES and FAEEs as a function of several valence electrons using linear regression. The models were nearly similar with a deviation of -0.5% to 0.44% and -0.35% to 0.62%, respectively.

They also presented other models based on the carbon number of acid chains and molecular weight⁸². Other researchers have created models based on the carbon chain and molecular weight. The coefficient difference between these models and those presented by Freedman is due to unit differences. Verduzco et al.⁷³ developed an empirical correlation to estimate FAMES' higher heating value as a function of unsaturation and molecular weight. This model agreed reasonably well with the experimental data. When the mass and mole fractions were used in the mixing rule, the average absolute deviation between experimental and predicted HHV was about 1.92 per cent. Fassinou⁸³ discussed in another work that the HHV of the neat compounds must be determined with the highest accuracy experimentally to obtain a reasonable prediction mode. To evaluate the basic experimental data, Fassinou⁸³ developed and evaluated some new models based on experimental data reported by Knothe, Sadrameli, Freedman, and Demirbas⁷⁶. They obtained the maximum deviation of 18.39%, 4.83%, and 5.17% based on the experimental results reported by the mentioned authors, respectively.

COMPOSITION-BASED MODEL :

Sanli et al.⁸⁴ provided the most recent and only model for predicting cetane number based on biodiesel composition. This model was developed using 35 different samples with varying ratios of saturated (from C14:0 to C22:0) and unsaturated (C18:1, C18:2, and C18:3) compounds and produced precise results with an average deviation of 0.37 % and a maximum deviation of 1.38 %.

LOW-TEMPERATURE FLOW PROPERTIES OF BIODIESEL (CP, PP AND CFPP)-

Method of Sarin et al. According to this method, correlations depend on the content of palmitic acid methyl ester (P_{FAME} , wt. %) that include:

$$CP = 0.526P_{FAME} - 4.992 \quad (0 < P_{FAME} < 45) \quad E77a$$

$$PP = 0.571P_{FAME} - 12.24 \quad (0 < P_{FAME} < 45) \quad E77b$$

$$CFPP = 0.511P_{FAME} - 7.823 \quad (0 < P_{FAME} < 45) \quad E77c$$

Correlations based on the complete unsaturated material of FAME (U_{FAME} , wt. %) include:

$$CP = -0.576U_{FAME} + 48.255 \quad (0 < U_{FAME} < 84) \quad E78a$$

$$PP = -0.626U_{FAME} + 45.594 \quad (0 < U_{FAME} < 84) \quad E78b$$

$$CFPP = -0.561U_{FAME} + 43.967 \quad (0 < U_{FAME} < 84) \quad E78c$$

Methods of Young et al [15]

$$CP = 18.13N_c - 0.790U_{FAME} \quad E79a$$

$$PP = 18.880N_c - 1.000U_{FAME} \quad E79b$$

$$CFPP = 18.01N_c - 0.804U_{FAME} \quad E79c$$

$$DU = MUFA + (2 \times PUFA) \quad E80a$$

The LCSF was estimated using Eq.80b. This factor was directly used to calculate CFPP in Eq.80c. These factors are related to chain saturation and length of FAMEs.

$$LCSF = (0.1 \times C16) + (0.5 \times C18) + (1 \times C20) + (1.5 \times C22) + (2 \times C24)$$

E80b

$$CFPP = (3.1417 \times LCSF) - 16.477 \quad E80c$$

$$CP(K) = 299.6y_{C16:0} + 378.5y_{C18:0} + 266.5y_{C18:1} + 265.2y_{C18:2}$$

Where $y_{C16:0}$, $y_{C18:0}$, $y_{C18:1}$, $y_{C18:2}$ = Mass percentage in biodiesel

$$CP(^{\circ}C) = -40.278 + 0.514C_{16:0} + 0.6364C_{18:0} + 0.38363C_{18:1} + 0.35362C_{18:2} \\ + 0.26341C_{18:3} - 0.58623C_{22:1}$$

$$PP(^{\circ}C) = -30.324 + 0.667C_{16:0} + 0.4065C_{18:0} + 0.11791C_{18:1} + 0.23225C_{18:2} \\ + 0.7162C_{18:3} - 0.48149C_{22:1}$$

$$CFPP_{..}(^{\circ}C) = 1.7556 \times LCF - 14.772$$

$$LCF = \sum (MP_n \times C_n) / 100$$

$$CFPP_{..}(^{\circ}C) = 8.9243LCSF - 19.325$$

$$LCF = MP_{C18:0}C_{C18:0} + MP_{C20:0}C_{C20:0} + MP_{C22:0}C_{C22:0} + MP_{C24:0}C_{C24:0}$$

$$CFPP(^{\circ}C) = -103.47 + 7.30N_C - 0.59U_{FAEE}$$



	Myristic C14:0	Palmitic C16:0	Palmitoleic C16:1	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Arachidic C20:0	Gadoleic C20:1	*b C20:2	Behenic C22:0	Erucic C22:1	Nervonic C24:0	FP	CP	CPPP	PP	References
Feedstocks																		
1 Bitter Almond	10.3			3.9	33.9	46	4.8	0.2						135.1	-4			-7 KiveleandHuan2015
2 Carba	26.15			8.75	53.4	10.95								99.25	-10	11		Sajjadi,AbdulRaman,andArandyan2016
3 Cardifina	0.08	5.59		0.04	2.54	16.45	14.6	35.88	1.15	13.53	1.69	0.57	2.5	94.84	3	-3		-7 Hoekmanetal.2012
4 Cuphea viscosissima	4.7	18.2		3.5	46.9	22.8	2.3	0.6					0.6	100	-9.6			-22 Sajjadi,AbdulRaman,andArandyan2016
5 Euphorbia lathyris		6.16		1.98	79.83	4.16	5.31		0.5			0.2		98.14		-11		Sajjadi B, Raman AAA, Arandyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renew. Sustain. Energy Rev. 2016;63:62-92.
6 Forsythia suspense		5.65		1.99	18.68	72.89	0.79							100	5			Jiao J, et al. Biodiesel from Forsythia suspense ([Thunb.] Vahl (Oleaceae)) seed oil. Bioresourc Technol 2013;143:653-6.
7 Idesia polycarpa		15.6		6.5	1.18	5.5	70.6	1.1						100.48	-4	-2		Sajjadi B, Raman AAA, Arandyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renew. Sustain. Energy Rev. 2016;63:62-92.
8 Jatropha	1.4	14.62		1.47	7.36	41.43	35.42	0.2	0.3					102.2	4	2	3	Dunn2010
9 karanja		8.86		5.94	56.12	16.39		3.18	2.4	4.86		1.93		99.68	13.3	-7	6.4	Sajjadi,AbdulRaman,andArandyan2016
10 Linseed		4.81		0.3	2.9	19.76	17.34	54.88						99.99	-2	-8		Udomsapetal.2008
11 Syringa	0.1	10		1.5	3.5	21.9	64.09	0.39	0.2	0.24				101.92	-10			Sajjadi B, Raman AAA, Arandyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renew. Sustain. Energy Rev. 2016;63:62-92.
12 Sour plum		22.4		7.3	16.4	45.9		6.49						93.34				Sajjadi B, Raman AAA, Arandyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renew. Sustain. Energy Rev. 2016;63:62-92.
13 Tobacco		9.91		1.07	3.94	14.31	69.08	2.44						100.75	-7.8	-5		Sajjadi B, Raman AAA, Arandyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renew. Sustain. Energy Rev. 2016;63:62-92.
14 Terminalia atappa		31.65		4.95	31	30.4	1.7							99.7		12		Chakraborty M, Baruah DC, Konwer D. Investigation of terminalia (Terminalia belerica Roxb.) seed oil as prospective biodiesel source for North-East India. Fuel Process Technol 2009;90(12):1435-41. [234]
15 Terminalia belerica		28.66		0.5	7.3	35.16	23.53		0.2	2.6				97.95	5			Chakraborty M, Baruah DC. Investigation of oxidation stability of Terminalia belerica biodiesel and its blends with petrodiesel. Fuel Process Technol 2012;98:51-8. [235]
16 Zanthoxylum bungeau		12.48		7.79	1.26	33.18	23.28							77.99	-6			[235] Sarin R, Sharma M, Khan AA. Terminalia belerica Roxb. seed oil: a potential biodiesel resource. Bioresourc Technol 2010;101(4):1380-4.
17 Neem	16.5			19.35	44.15	18.1	0.3							98.4	14.4	11		Yang F-X, et al. Studies on the preparation of biodiesel from Zanthoxylum bungeanum Maxim Seed Oil. J Agric Food Chem 2008;56(17):7891-6.
18 NigerCO	9.2			10.1	9	71.7								100	4			Food Chem 2008;56(17):7891-6.
19 Polongga	0.09	16.25		2.5	19.23	40.13	20.01	1.18	0.47	0.36		0.42	2.6	101.82	11.7	9.5	8.43	Sajjadi,AbdulRaman,andArandyan2016 C
20 Rice bran	0.43	16.2		2.32	42.43	34.58	1.55	0.55						98.08	5	0	-1	Sajjadi,AbdulRaman,andArandyan2016
21 Milkweed		10.7		6.4	32.8	42.5	1							93.4	2.23			Udomsapetal.2008
22 Nahar	1.5	10.82		13.29	57.95	14.42		0.9	2.92					101.8	6.1			2.23 review on properties of edible and non-edible
23 Putranjiva roxburghi	0.03	9.11		12.81	52.32	22.75	0.85	2.02	0.15	0.12	0.02	0.15		100.4				-1.2 Sajjadi,AbdulRaman,andArandyan2016
24 Rubber	1.1	10.27		9.75	23.9	42.93	12.85							100.8	3.1			-7 review on properties of edible and non-edible

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