

# Experimental study on the effects of feedstock on the properties of biodiesel using multiple linear regressions

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## EXPERIMENTAL STUDY ON THE EFFECTS OF FEEDSTOCK ON 1 THE PROPERTIES OF BIODIESEL USING MULTIPLE LINEAR 2 **REGRESSIONS** 3 Aulia Qisthi Mairizal<sup>1,2</sup>, Sary Awad<sup>1\*</sup>, Cindy Rianti Priadi<sup>2,3</sup>, Djoko M. Hartono<sup>2</sup>, Setyo 4 S. Moersidik<sup>2</sup>, Mohand Tazerout<sup>1</sup>, Yves Andres<sup>1</sup> 5 6 7 <sup>1</sup>GEPEA, UMR-CNRS Department of Energy System and Environment (DSEE) IMT 8 Atlantique, Nantes 44300, France 9 <sup>2</sup>Environmental Engineering Study Program, Department of Civil Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia 10 <sup>3</sup>Tropical Renewable Energy Center (TREC), Faculty of Engineering, Universitas Indonesia, 11 Depok 16424, Indonesia 12 \* Corresponding author: sary.awad@gmail.com 13 **Abstract**. Biodiesel is a very promising alternative fuel that has its place in the future energy 14 mix. The dependence of fuel properties on fatty acids profile will influence the choice of 15 feedstock or appropriate treatment that it should undergo in order to respect biodiesel standards. 16 The objective of this study is to find models that predict biodiesel's viscosity, density, flash 17 point, higher heating value, and oxidative stability based on saponification value, Iodine value 18 and the polyunsaturated fatty acids content of feedstock. Biodiesel samples were produced from 19 20 seventeen different blends of oils. Multiple linear regressions were used to obtain models. High 21 accuracy prediction was obtained for density and higher heating value with prediction errors < 5%, a very good accuracy was obtained for viscosity with error < 10% and flash point and 22 oxidative stability were predicted with a fair accuracies (error < 15%) which indicates a good 23 correlation level with IV, SV and Polyinsaturations but it also reveals that other parameters 24 could also interfere and should be taken in consideration to reach acceptable accuracy. 25

- 26 Keywords: Iodine Value; Saponification Value; polyunsaturated fatty acid, Multiple linear
- 27 Regressions

## 28 1. Introduction

The increasing energy demand, combined with declining global environmental conditions has led to a shift towards utilization of more sustainable sources of energy. This shift signifies that energy of the future may be highly dependent on sources that are environment-friendly but highly variable. Biodiesel is a renewable alternative fuel that is biodegradable and has similar properties with conventional diesel fuel [1]. Many researchers have identified biodiesel as a good alternative fuel with high potential since it has a good balance in terms of environmental, economic development and technical availability. As the demand of alternative fuels keeps rising, biodiesel holds a lot of promise for future of transportation [2]. Biodiesel is defined as the mono alkyl esters of fatty acids derived from vegetable oils or animal fats. Biodiesel could be produced from a large variety of feedstock. The most common feedstock used for biodiesel production comes from vegetable oils and animal fats that are mostly composed from triacylglycerol (TAG). In general, the TAG of vegetable oils and animal fats are composed of different combinations of fatty acids (FA) having a wide variety in terms of physical and chemical properties [3]. The main sources of properties variations are attributed to the degree of unsaturation (it might be expressed in terms of iodine value) and the carbon chain length (it might be expressed in terms of saponification value) [4] Making mathematical correlations between feedstock composition from a side and quality parameters on the other side, with a reasonable accuracy, could have several benefits on scientific plan. For example, it could be a good estimation of the ability of a feedstock to produce a good quality of biodiesel before undergoing time and money consuming characterization by only using simple tests. At the same time, it could help to determine appropriate treatment strategies of feedstock to improve biodiesel properties. These treatments could be as simple as mixing two types of oil or advanced as hydrogenation [5] where a good balance between saturated/unsaturated fatty acids is needed in order to meet norms. At the same

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time, correlations could reduce the number of variables that could be used to define a biodiesel in combustion engines simulations. Several studies have demonstrated the influence of fatty acids methyl esters (FAME) profile on biodiesel properties. Allen et al. (1999) [6] proposed a quadratic model to predict viscosity from fatty acid composition. Ramírez-Verduzco et al. (2012) [7] developed a correlation to estimate cetane number, viscosity, density and higher heating value as a function of iodine value (IV) and molecular weight. Pinzi et al. (2011) [8] proposed a mathematical model for low calorific value, kinematic viscosity, flash point, cetane number and cold filter plugging point with the independent factors of IV and carbon chain length. Ramos et al. (2009) [9] predicted cold filter plugging point (CFPP) using chain length and saturation factor, while Yuan et al. (2017) [10] presented the relation between CFPP and FAME. Sarin et al. (2010) [11] performed a mathematical model for oxidation stability as a function of unsaturation degree and palmitic acid content. Lapuerta, et al. (2009) [12] reported the estimation of cetane number of biodiesel as a function of iodine value and number of carbon atoms. All works found in literature dealt with unsaturation level using IV, but no one has investigated the effect of mono and polyunsaturated fatty acids balance (PU/MU) on the characteristics of biodiesel. Thus, the present work aims to introduce new correlations that include, besides SV and IV, the PU/MU ratio as an independent parameter in order to predict viscosity, density, flash point (FP), higher heating value (HHV), and oxidative stability (OS) with fair precisions. To do so, wide ranges of IV, SV and PU/MU profiles were investigated. The IV ranged from  $(0 - 148 g_{12/100goil})$ , SV ranged from  $(188-265 g_{KOH/goil})$  and PU/MU ranged between (0 - 3.87). Those ranges were reached by using blends of seven different types of feedstock. A multiple regression analysis was carried out in order to determine correlations and analysis of variance (ANOVA) was derived in order to study the significance of correlations.

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- All the oils were characterized by gas chromatography-mass spectrometry (GC-MS) to find the
- fatty acid methyl ester (FAME) profile and then tested according to European biodiesel standard
- 79 EN 14214.

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#### 2. Materials and Methods

- 81 2.1. Raw Materials
- 82 Seven different types of oil were used during this study. Sunflower oil, peanut oil, hydrogenated
- coconut oil, hydrogenated copra oil, beef tallow, rapeseed oil and walnut oil. These types of oil
- were purchased from local stores in Nantes, France. Methanol and potassium hydroxide were
- purchased from Sigma Aldrich Company.
- 86 2.2. Transesterification Process
- 87 The biodiesel production was carried out with transesterification process by using an alkali
- catalyst KOH and methanol in a 1 L flat bottom flask. The process was accomplished under the
- 89 following conditions: 6:1 methanol/oil molar ratio, 400 rpm rotational speed, 50 °C reaction
- 90 temperature, 1 wt.% catalyst dosage based on oil weight, and a reaction time of 2 hours.
- 91 At the end of transesterification process, the samples were left overnight to settle the phase
- 92 separation between glycerol and crude methyl ester. Then, the lower layer containing the
- 93 glycerol and other impurities was removed. After that, the crude methyl ester was washed a few
- 94 times with warm distilled water at 50°C until the pH of last washing water became neutral. The
- 95 residual water and methanol in the mixture were separated from biodiesel product with rotary
- evaporation under vacuum at 40°C for 1 hour. Finally, the yield of biodiesel was measured at
- 97 this step and after that, samples were characterized.

#### 2.3. Blend Preparation

- Feedstock (7 different types of oil) were chosen carefully in order to present a wide range of SV and IV and different balances between monounsaturated and polyunsaturated fatty acids.
- 101 Then blends were prepared from binary and ternary mixes of produced biodiesel.
- 102 2.4. Analyses and Instruments
- To determine the FAME profile from various feedstock, 25 mg biodiesel samples were injected into a gas chromatograph Perkin Elmer Clarus 680 equipped with a flame ionization detector to obtain the chromatogram and peak integration report. Iodine value was calculated using the following expression developed by Knothe (2002) [13]:

$$IV = 100 \times \sum \frac{(\% FA) \times 253.81 \times db}{MW}$$
 (eq 1)

- 108 Where, *IV* is the iodine value of the oil, db is the number of double bonds per FA molecule,
- 109 MW is the molecular weight of each fatty acid and % FA is percentage of each fatty acid in oil.
- 110 The calculation was also conducted to determine the saponification value of each biodiesel
- produced, where SV is the saponification value of the oil, with the equation 2 [13]:

$$SV = 100 \times \sum \frac{(\%FA) \times 56.106}{MW}$$
 (eq 2)

- 113 Biodiesel Characterization
- 114 HHV analysis was carried out following the ASTM D3180 Standard, using Parr 6200
- 115 Calorimeter The results were expressed in MJ/kg with a relative error of 0.25%. OS was
- determined with PetroOxy device following the ASTM D7525 standard.
- Densities of different samples were measured at 15°C using a pycnometer M50T (850 900 g/l)
- with a precision of 1 g/l. While an AND vibro viscometer was used to measure the dynamic
- viscosity at 40°C, then kinematic viscosity was obtained by dividing it by the density. The
- relative error of kinematic viscosity was estimated to 3%.
- 121 Flash point was measured using a PENSKY MARTENS NPM440 device with a precision of
- 122 1°C.

## 2.5. Statistical analysis

A multiple regression analysis was conducted in order to describe the relationship between each of the independent variables (SV, IV and PU/MU) and the dependent variables of the samples (characteristics matrix). Moreover, ANOVA was performed for each regression in order to determine its significance and the significance of each parameter. Finally, correlations were tested by plotting predicted data versus experimental results. Models were then compared to experimental data found in the literature.

### 3. Results and Discussion

3.1. Fatty Acid Methyl Ester Profile (FAME)

result was also reported by Giakoumis (2013) [14].

The fatty acid profile of different methyl esters is summarized in Table 1. The present work shows that biodiesel derived from sunflower oil was very rich in unsaturated acids. Based on experimental results, it contains high amounts of linoleic acid (C18:2) and oleic acid (C18:1). Their fractions are 60 % and 29% respectively. Rapeseed oil has also high amount of monounsaturated acids, which achieved 62 %, consisting mainly of oleic acid (C18:1). Both sunflower and rapeseed oils are the most common used feedstock in biodiesel production in EU.

The biodiesel derived from walnut oil has the highest percentage of polyunsaturated fatty acids with 56 % linoleic acid (C18:2) and 11.3% of linolenic acid (C18:3). Beef tallow is composed of a high variety of fatty acids with high concentrations of palmitic (33.72%) and stearic (18.9%) acids which were the highest among the other investigated biodiesel samples. The same

- Peanut oil is also one of the interesting feedstock to investigate since its profile covers very long carbon chains reaching C24. Both methyl esters from hydrogenated coconut oil and hydrogenated copra oil represent a short carbon chains compared to other feedstock (from C6 to C16).
- 3.2. Correlations between biodiesel properties and independent parameters
- 151 The study was carried out using a set of 17 experimental points (7 oils and 10 blends), covering
- wide ranges of SV, IV and PU/MU ratio. The characteristics of experimental points are listed
- in table 2.
- 154 These data were used to obtain wanted correlations using multiple linear regressions and results
- are listed in table 3, while ANOVA is listed in table 4.
- 156 *3.2.1. Density*
- In general, density of biodiesel (860-900 kg/m<sup>3</sup>) is slightly higher than that of petroleum diesel
- 158 (820-845 kg/m<sup>3</sup>). Density has an important role, especially during the fuel injection, since a
- higher fuel density will lead to a higher fuel mass injection in the engine. Therefore, the energy
- 160 content within the combustion chamber and the engine performance are highly influenced by
- fuel density [1].
- In the US, there is no specification for biodiesel density, but in European biodiesel standard,
- EN 14214, it is mentioned that the acceptable range of density lies between 860-900 kg/m<sup>3</sup>
- while in Indonesian National Standard (SNI 7182:2015) the range of density lies between 850-
- 165 890 kg/m<sup>3</sup>. The main reason behind this limitation is to avoid the significant amount of
- polyunsaturated fatty acids in the fuel [15].
- Based on the experimental results presented in table 2, the densities from all investigated
- biodiesel samples, range from 862.9 kg/m³ to 877.6 kg/m³ with an overall average value of
- 870.9 kg/m<sup>3</sup>. The results show that all examined methyl esters meet both the EU and Indonesian
- standards specifications. Highest density (877.6 kg/m³) was registered for biodiesel derived
- from walnut oil. This amount resulted from its high content of unsaturated fatty acids (84.7%)

with a high balance of polyunsaturated fatty acids (PU/MU = 3.87). This result is in line with the investigations led by Ramírez-Verduzco et al. (2012) [7] that biodiesel rich in unsaturated compound such as linoleic acid (C18:2) and oleic acid (C18:1) will have a higher density.

As it is listed in table 3 a model's fit between density as a function of IV, SV and PU/MU ratio was developed and showed high coefficient of determination ( $R^2$ = 95.4%) using a quadratic model. The relative error between measured and predicted data was lower than 0.3%, as it is shown in Figure 1. Lowest *p*-values were found for IV, IV² and IV\*SV which reflects the strong correlation between the degree of unsaturation with the value of density, which seems to be more significant than the carbon chain length and the balance between mono- and polyunsaturated fatty acids. Nevertheless, including PU/MU into the correlations have decreased standard error from 6 kg/m³ to 1.52 kg/m³ and increased the significance of the correlation. Giakoumis (2013) [14] reported that density would increase with increasing unsaturation degree. This is in line with study led by Ramírez-Verduzco et al. (2012) [7] that density is directly proportional with degree of unsaturation with the additional increase of density 0.00118 g/cm³ for each additional double bond.

In figure 1, the model was also compared to the data from literature, it can be noticed that the maximum relative deviation between experimental data and predicted values was around 2.2% while the majority of points lie between the  $\pm 2\%$  relative error limits. It could also be noticed that all data reported by Giakoumis et al. [14] and Yuan et al. [10] lie under the Y=X line, which means that the model tends to underestimate the density values. Taking into account the low error margin, this could be related to the methods used for density measurements and the apparatus related errors.

## 3.2.2. Higher Heating Value

Heating value is an important fuel property since it defines the amount of energy that will be released during FAME combustion in the engine. The heating value is also known as the heat

of combustion and could be divided into two types as lower heating value (LHV) and higher heating value (HHV). Both are the measurement units to indicate the heat of combustion when the fuel is burned completely. It is expressed as a unit of energy released per quantity of the fuel (MJ/kg). LHV is deduced from HHV by subtracting the heat of vaporization of water formed during combustion. The HHV could be explained as a function of hydrogen content, carbon content and oxygen content with equation performed by Demirbas (1998) [16]. There is no specific limit of higher heating value mentioned in European biodiesel standards, US ASTM D 6751-08 and Indonesian National Standard (SNI 7182:2015). However, due to its significant oxygen content (10-12% w/w) [14], it is generally expected that the energy content of biodiesel will be lower than diesel fuel [1, 7, 17]. As a result, higher fuel injection rates are required, when engines are fuelled with biodiesel, in order to deliver power outputs similar to those obtained with diesel fuel [8, 14]. The results of this study show, as illustrated in Table 2, that saturated biodiesel, derived from coconut oil, present a HHV of 38.43 MJ/kg and the most unsaturated methyl esters, derived from walnut oil, recorded 39.6 MJ/kg. The highest SV of hydrogenated oils leads to a higher concentration of oxygen, which reduces the HHV. In the present work, the prediction of HHV was made as a function of SV and IV. The result of the ANOVA analysis showed the best model that fits the experimental result was a linear model with  $R^2 = 76\%$ . The values of experimental HHV and calculated ones are compared in Figure 2, and they present a maximum relative error lower than 1.3%. Furthermore, the p-value of SV demonstrates a strong influence on HHV. The negative sign in SV coefficient is in line with the earlier study by Demirbas (1998) [16] that demonstrated that the decrease in SV will increase ratios of carbon and hydrogen to oxygen in fuels and increase the specific heat of combustion. However, the positive sign of IV coefficient means that HHV is increasing with unsaturation, which is in contradiction with the study of Ramírez-Verduzco

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et al. (2012) [7] that showed HHV will decrease by 0.21 MJ/kg for each double bond in FAME molecule. In fact, when IV increases, that means that the H/C ratio will decrease, leading to a decrease in HHV. However, the energy content decrease due to the replacement of two hydrogen atoms by a double bond in a molecule is very low. Thus, the final result could be more influenced by other parameters such as the combustion efficiency in the calorimetric bomb. So the lowest viscosity of unsaturated FAME could enhance mixing with air during sample combustion and counterbalance the effect of energy content of hydrogen present in saturated FAME.

- Although the low R<sup>2</sup> recorded for the HHV, the comparison of the present model to other researchers works showed that the maximum error was lower than 5%, with 86% of literature data lying below 3% relative error, which reflects a good accuracy of the model.
- 233 *3.2.3. Viscosity*

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- Viscosity is a key biodiesel property, since it indicates the ability of a material to flow [17] and
- has a strong relation with the behavior of fuel injection [18]. High viscosity of fuel will lead to
- poor atomization and large droplet sizes of the fuel spray which leads to operational problems
- [3]. European biodiesel standard EN 14214 has set an acceptable range of viscosity from 3.5 -
- 5.0 mm<sup>2</sup>/s, while US ASTM D 6751-08 accepts 1.9 6.0 mm<sup>2</sup>/s and Indonesian National
- 239 Standard (SNI 7182:2015) accepts 2.3 6.0 mm<sup>2</sup>/s.
- As can be seen in Table 2, the viscosity values of all examined feedstock range from 2.63 to
- 4.75 mm<sup>2</sup>/s. The result is higher than the viscosity of common diesel fuel (1.3-2.4 mm<sup>2</sup>/s), due
- to the large molecular mass and chemical structure of biodiesel [1].
- Based on the experiments, methyl esters from hydrogenated coconut and copra oils have the
- lowest viscosity (2.63 mm<sup>2</sup>/s). The outlier's value of viscosity from coconut oil was also found
- by Giakoumis (2013) [14]. The reason behind this is that low values of kinematic viscosity are

obtained from biodiesel having short fatty acid chains [19]. In fact, the carbon chains found in methyl esters from hydrogenated oils went until C16 (palmitic acid).

On the other hand, the highest value of viscosity was recorded for methyl esters derived from peanut oil (4.75 mm<sup>2</sup>/s). This high viscosity comes from the high content of long carbon chains FAME. The higher unsaturated-levels biodiesel will have lower values of viscosity. In the present work, viscosities of biodiesel from different feedstock were measured at 40°C and correlated to SV, IV and PU/MU. As shown in figure 3, the correlation found can predict viscosity with a fair accuracy, where the observed relative error was lower than 6%.

Furthermore, the *p*-value of SV demonstrates that it has higher influence on viscosity than IV and that the PU/MU ratio has negligible effect. The result is in line with the earlier studies that demonstrated that viscosity increases with the increase of carbon chain length [16, 20]

The comparison of viscosity model to data from literature shows that the maximum deviation is around 12% and around 90% of inspected data points lie between the  $\pm 10\%$  relative error lines. It is to be noted that most of the references cited viscosities values with measuring errors exceeding 10% of measured values and which were excluded from comparisons. Taking in counts the fair error of prediction, the present model can be reliable for biodiesel viscosity prediction of FAME mixtures.

#### 3.2.4. Flash Point

Flash point is defined as the minimum temperature of the fuel at which its vapors ignite in presence of air and a heat source [21]. The minimum limits of flash point are 100°C, 120°C and 130°C for SNI 7182:2015, EN 14214 and ASTM D 6751-08 respectively. These requirements were set in order to ensure that the produced biodiesel has been purified from the excess methanol that could decrease the flash point [18]. This high flash point of biodiesel has advantages in terms of storage and fire hazard perspectives.

The flash points of biodiesel samples examined in the present work ranged from 124°C to 181.5°C. All the results from table 2 show that the biodiesel produced from different feedstock have met EU, US and Indonesian biodiesel standards.

Further study was conducted to propose mathematical prediction of flash point as a function of IV, SV and PU/MU ratio. The best fit was found for a  $3^{rd}$  degree model as listed in Table 3 with coefficient correlation  $R^2 = 95.7\%$ . The FP values predicted are compared to the measured ones in Figure 4. The correlation found for this biodiesel property is fair since the maximum relative error found is less than 7.5%. The results of this model were also compared to literature data after filtration. In fact, all literature data that have standard deviations >10% were excluded from the comparison. As it can be seen in figure 4, the maximum deviation between experimental data and model prediction was lower than 15%, with 75% of compared data lying between  $\pm 14\%$  lines. This relatively high error could be referred to the fact that fatty acid composition is not the only parameter that influences the flash point as claimed by Kumar (2017) [22].

#### 3.2.5. Oxidative Stability

Oxidative stability is one of the major issues for fuel storage. Generally, oxidation of fuels occurs during storage under aerobic conditions. Earlier studies demonstrated that there is a link between oxidation stability and the number of double bonds in FA structure [14, 18] that makes biodiesel susceptible to degradation in the presence of oxygen [22]. Other factors also can influence the oxidative stability as acid value, peroxide value, the presence of air, metals, heat, light or pressure, and also polymer content [23]. However, the rate of oxidation could be slowed down by adding antioxidants.

European norm EN 14214 has set the minimum value of oxidative stability for biodiesel to 293 8 hours by using the Rancimat method, while in US biodiesel standard US ASTM D 6751-08 294 the minimum level is 3 hours, and 8 hours for Indonesian National Standard SNI 7182:2015. 295 The PetroOxy method, used in this work, has the advantage of accelerating the oxidation 296 process which reduces drastically the time needed to achieve the analysis. Several studies have 297 298 reported correlations between PetroOxy number and Rancimat number, but there is still some divergence between results. For example, by fitting the results of the present study to models 299 suggested by Botella et al. [24] and Neumann et al. [25], deviations reaching 240% were 300 observed. Thus, in the present work, it was opted to correlate PetroOxy number to oil 301 302 characteristics directly. The oxidative stabilities of biodiesel samples examined in the present work covered a wide 303 range lying between 6.23 – 108 minutes. For example, the methyl esters from walnut oil, 304 sunflower oil and rapeseed oil which are rich in unsaturated fatty acids have the lowest oxidative 305 stabilities, around 6.2 min. From the experiments, it could be seen that there is a correlation 306 307 between unsaturated compounds content in methyl esters and oxidation. This is in line with 308 Shahabuddin et al. (2012) [26] that reported the oxidative stability will decrease with increasing degrees of unsaturation. 309 On the contrary, saturated fatty acids such as those contained in coconut oil and copra oil are 310 way more stable, with the PetroOxy numbers reaching 108 minutes. 311 312 Further study was conducted in order to investigate the relation between PU/MU ratio with oxidation stability. The study of oxidation stability as a function of IV and PU/MU ratio was 313 investigated. The SV was not included as an independent variable since the relation between 314 oxidative stability and SV was found very weak. A 3<sup>rd</sup> order model resulted in a correlation 315

coefficient R<sup>2</sup> of 94.1%. Figure 5 represents the predicted values of OS using the quadratic model compared to measured ones and as it can be shown, the maximum error was around 13%. Based on the *p*-value from ANOVA analysis, it was confirmed that the PU/MU (PU/MU and (PU/MU)<sup>2</sup> terms) is the most influencing factor on the oxidative stability, which points out the effects of polyunsaturations on the OS [27]. This observation comes in line with Kumar's work [22] who reported that not only the presence of double bonds influences the rate of oxidation, but also their position. Karavalakis et al. (2010) [28] also showed that polyunsaturated FAME are more susceptible to oxidation degradation than monounsaturated, because of the number of reactive bis-allytic, that is why polyunsaturation is more prone to autoxidation.

The value of R<sup>2</sup> and the relatively high deviation (13%) between experimental measurements and predicted OS values could be explained by the fact that the oxidative stability is very sensitive to other parameters such as moisture content, peroxide value, acid value, glycerides content, etc. More parameters need to be investigated in order to get accurate prediction of this fuel characteristic.

#### 4. Conclusion

In the present work, multiple linear regressions were used to predict biodiesel viscosity, density, flash point, higher heating value and oxidative stability as a function of Saponification value, Iodine value and Polyunsaturated/Monounsaturated fatty acids balance (PU/MU). The Investigations were carried out using seventeen blends derived from seven different oils. The results showed good correlations for all parameters, excluding flash point and oxidative stability. High accuracy was obtained for density and higher heating value, a very good one for viscosity and a fair prediction was obtained for Flash Point. Adding PU/MU as an independent parameter increased accuracy and correlation coefficients for prediction models.

#### 339 References

- Mahmudul, H., Hagos, F., Mamat, R., Adam, A., Ishak, W., & Alenezi, R. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines A review. Renewable and Sustainable Energy Reviews 2017;72:497-509.
- Antolín, G., Tinaut, F., Briceno, Y., Castaño, V., Pérez, C., & Ramírez, A. Optimisation of biodiesel production by sunflower oil transesterification. Bioresource Technology 2002;83: 111-4.
- 346 [3] Knothe, G., Gerpen, J., & Krahl, J. The Biodiesel Handbook. Champaign, Illinois: AOCS Press;2005.
- 348 [4] Saraf, S., & Thomas, B. Influence of feedstock and process chemistry on biodiesel quality. 349 IChemE 2007;85(B5):360-4
- Fattah, I. R., Kalam, M., Masjuki, H., & Wakil, M. Biodiesel production, characterization, engine performance, and emission characteristics of Malaysian Alexandrian laurel oil. RSC Adv., 2014,4, 17787-17796.
- Allen, C., Watts, K., Ackman, R., & Pegg, M. Predicting the viscosity of biodiesel fuels from their fatty acid ester composition. Fuel 1999;78:1319-26.
- Ramírez-Verduzco, L., Rodriguez-Rodriguez, J., & Jaramillo-Jacob, A. Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. Fuel 2012;91:102-11.
- Pinzi, S., Leiva, D., Arzamendi, G., Gandia, L., & Dorado, M. Multiple response optimization of vegetable oils fatty acid composition to improve biodiesel physical properties. Bioresource Technology 2011;102:7280-8.
- Ramos, M. J., Fernández, C. M., Casas, A., Rodríguez, L., & Pérez, Á. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresource Technology 2009;100:261–8.
- 363 [10] Yuan, M.-H., Chen, Y.-H., Chen, J.-H., & Luo, Y.-M. Dependence of cold filter plugging point 364 on saturated fatty acid profile of biodiesel blends derived from different feedstocks. Fuel 365 2017;195:59-68.
- 366 [11] Sarin, A., Arora, R., Singh, N., Sarin, R., & Malhotra, R. Blends of biodiesels synthesized from non-edible and edible oils: Influence on the OS (oxidation stability). Energy 2010;35:3449-53.
- Lapuerta, M., Rodríguez Fernández, J. L., & Mora, E. F. Correlation for the estimation of the cetane number of biodiesel fuels and implications on the iodine number. Energy Policy 2009;37:4337–44.
- 371 [13] Knothe, G. Structure indices in FA chemistry. How relevant is the iodine value? JAOCS 2002;79(9):847-54.
- 373 [14] Giakoumis, E. G. A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of unsaturation. Renewable Energy 2013;50:858-78.
- 375 [15] Knothe, G., & Razon, L. F. Biodiesel fuels. Progress in Energy and Combustion Science 2017;58:36-59.
- 377 [16] Demirbas, A. Fuel properties and calculation of higher heating values of vegetable oils. Fuel 1998;77:1117-20
- 379 [17] Atabani, A., Silitonga, A., Badruddin, I. A., Mahlia, T., Masjuki, H., & Mekhilef, S. A 380 comprehensive review on biodiesel as an alternative energy resource and its characteristics. 381 Renewable and Sustainable Energy Reviews 2012;16:2070–93
- Hoekman, S. K., Broch, A., Robbins, C., Ceniceros, E., & Natarajan, M. Review of biodiesel composition, properties and specifications. Renewable and Sustainable Energy Reviews 2012;16:143-69.
- Gopinath, A., Puhan, S., & Nagarajan, G. Theoretical modeling of iodine value and saponification value of biodiesel fuels from their fatty acid composition. Renewable Energy 2009;34:1806-11.
- 387 [20] Demirbas, A. Relationship derived from physical properties of vegetable oil and biodiesel fuels. 388 Fuel 2008;87:1743-8.
- 389 [21] Bajpai, D., & Tyagi, V. Biodiesel: Source, Production, Composition, Properties and Its Benefits. 390 Journal of Oleo Science 2006;55(10):487-502.
- 391 [22] Kumar, N. Oxidative stability of biodiesel: causes, effects and prevention. Fuel 2017;190:328-50.
- 392 [23] Knothe, G. Some aspect of biodiesel oxidative stability. Fuel Processing Technology

393 2007;88:669-77.

- 394 [24] Botella, L., Bimbela, F., Martin, L., Arauzo, J., & Sanchez, J. L. Oxidation stability of biodiesel 395 fuels and blends using the Rancimat and PetroOXY methods. Effect of 4-allyl-2,6-396 dimethoxyphenol and catechol as biodiesel additives on oxidation stability. Frontiers in chemistry 397 2014;2(43):1-9.
- 398 [25] A. Neumann, T. Jebens, V. Wiembicki, A Method for Determining Oxidation Stability of Petrodiesel, Biodiesel, and Blended Fuels, American Laboratory 2008; 40(4): 22-26. Available online at: http://www.americanlaboratory.com/914-Application-Notes/34716-A-Method-for-Determining-Oxidation-Stability-of-Petrodiesel-Biodiesel-and-Blended-Fuels/
- 5 Shahabuddin, M., Kalam, M., Masjuki, H., Bhuiya, M., & Mofijur, M. An experimental investigation into biodiesel stability by means of oxidation and property determination. Energy 2012;44:616-22.
- 405 [27] Saluja, R. K., Kumar, V., & Sham, R. Stability of biodiesel A review. Renewable and Sustainable 406 Energy Reviews 2016;62:866-81.
- 407 [28] Karavalakis, G., Stournas, S., & Karonis, D. Evaluation of the oxidation stability of diesel/biodiesel blends. Fuel 2010;89:2483–9.

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412 413	Figures Captions
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419	

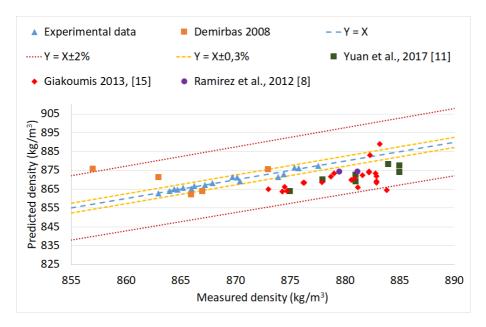


Figure 1: Predicted versus measured density plot

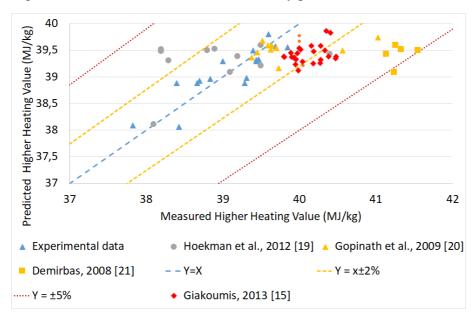


Figure 2: Predicted versus measured HHV plot

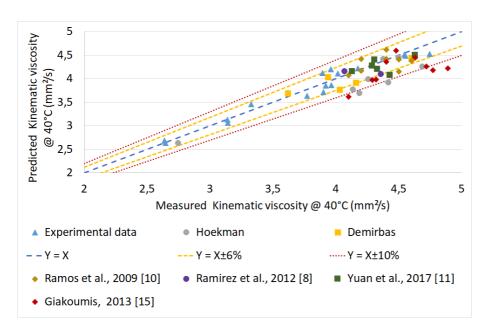


Figure 3: Predicted versus measured Viscosity plot

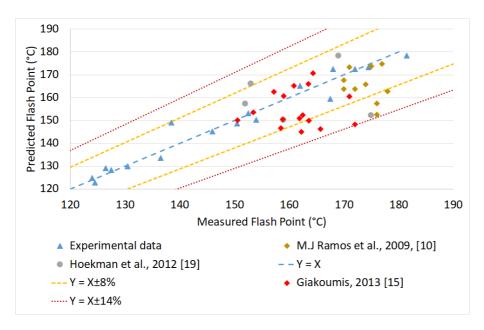


Figure 4: Predicted versus measured Flash point plot

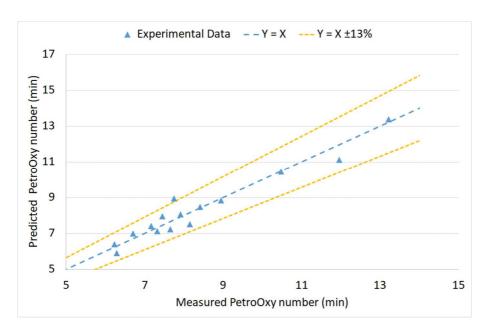


Figure 5: Predicted versus measured Oxydative stability

**Table 1**Fatty Acid Composition (wt.%) of different types of oils

Carbon Chain	C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C18:3	C18:2	C18:1	C18:0	C20:1	C20:0	C22:0	C24:0
Molecular Weight	116	144	172	214	242	270	292	294	296	298	324	326	340	382
Formula	C7H <sub>12</sub> O	$C_9H_{16}O_2$	$C_{11}H_{20}O$	$C_{13}H_{26}O$	$C_{15}H_{30}O$	$C_{17}H_{34}O$	$C_{19}H_{32}O$	$C_{19}H_{34}O$	$C_{19}H_{36}O$	$C_{19}H_{38}O$	$C_{21}H_{42}O$	$C_{21}H_{42}O$	$C_{23}H_{44}O$	$C_{25}H_{50}O$
	2		2	2	2	2	2	2	2	2	2	2	2	2
Sunflower Oil						6.5%		60.0%	29.0%	4.3%				
Peanut Oil						9.4%	18.0%		65.0%	3.6%			1.0%	1.6%
H.O. Coconut Oil	1.4%	8.5%	6.8%	50.3%	18.5%	8.2%				6.2%				
H.O. Copra Oil		3.8%	10.3%	54.5%	17.8%	7.5%				6.1%				
Rapeseed Oil						4.2%	8.4%	22.0%	60.0%	1.6%	2.1%			
<b>Beef Tallow</b>					4.3%	33.7%		0.8%	34.7%	18.9%	0.5%			
Walnut Oil						5.5%	11.3%	56.0%	13.8%	3.0%	3.6%	1.1%		

Table 2

Properties of biodiesel from various feedstock and mixtures

Parameter	IV	SV	PU/MU	Viscosity at 40°C	Density at 15°C	Flash Point	OS (Petrooxy)	Higher Heating Value
Unit	<b>g</b> I2/100g	<b>g</b> 12/100g	-	mm²/s	kg/m <sup>3</sup>	°C	min	MJ/kg
Feedstock								
Sunflower	134.981	200.29	2.07	3.96	875.78	174.5	6.3	39.69
Peanut	107.88	197.08	0.28	4.75	874.43	168	8.95	39.4
HO Coco	0.00	265.22	0	2.64	866	162	103.47	38.43
HO Copra	0.00	263.35	0	2.64	864.39	154	108.89	37.83
<b>Beef tallow</b>	33.19	192.96	0.024	4.55	862.94	172	13.22	39.2
Rapeseed	118.70	196.21	0.49	4.55	875.39	181.5	6.7	39.85
Walnut	147.95	188.40	3.87	3.97	877.58	152.5	6.23	39.6
Mixture 1	53.53	223.72	0.24	3.90	864	130.5	11.97	38.67
Mixture 2	36.49	217.83	0.39	3.62	864.69	127.5	10.48	39.29
Mixture 3	77.62	224.43	1.03	3.77	867.22	124	8.15	39.31
Mixture 4	62.83	226.54	2.49	3.14	870.43	126.5	7.92	38.4
Mixture 5	80.16	226.43	2.14	3.33	865.22	124.5	7.45	38.84
Mixture 6	73.85	226.93	3.81	3.14	866.22	146	7.32	38.7
Mixture 7	99.27	206.70	0.45	4.17	869.74	167.5	8.42	39.47
Mixture 8	63.75	197.40	0.59	3.89	867.88	150.5	7.75	39
Mixture 9	99.41	207.07	0.77	4.02	873.88	138.5	7.2	39.44
Mixture 10	84.38	204.21	1.23	3.92	870.14	136.5	7.65	39.44

**Table 3**Summary of Models Developed to Predict Biodiesel Properties

Quality parameter	Units	Equation Model	$\mathbb{R}^2$	Standard error
Density	kg/m <sup>3</sup>	993 -0.899.IV -1.091.SV + 78.87.PU/MU + 32.5E-4.IV.SV – 0.189.IV.PU/MU-0.29.SV.PU/MU+28.4 E-4.IV² + 22.95E-4. SV²+0.22.(PU/MU)²	95.4%	1.52 kg/m <sup>3</sup>
Higher Heating Value	MJ/kg	41.76 + 0.0045.IV – 0.0139.SV	76%	0.29 MJ/kg
Viscosity (at 40°C)	mm²/s	9.152 + 0.00572.IV - 0.0245.SV - 3.522.PU/MU - 1.37.E-5.IV.SV + 0.00533.IV.PU/MU + 0.013.SV.PU/MU	95.5%	0.17 mm²/s
Flash Point	°C	$-11749 - 4.364.IV + 173.76.SV - 8.07.PU/MU + 0.0276.IV.SV - 0.418.IV.PU/MU - 0.0149.SV.PU/MU - 0.0249 IV^2 - 0.833 SV^2 + 17.718 (PU/MU)^2 + 0.00016IV^3 + 0.00131SV^3 - 1.8135(PU/MU)^3$	95.7%	8°C
Oxidative Stability	mn	$15.157 - 0.0169.IV - 10.284.PU/MU + 0.0214.IV.PU/MU + 0.00084.IV^2 + 4.54.(PU/MU)^2 - 5.37E-6.IV^3 - 0.688 (PU/MU)^3$	94.1%	0.7 mn

**Table 4** ANOVA of regressions

	SSR	SSE	SST	MSR	MSE	F	Significance F	Max Relative error	Average relative error
Density	337.9	16.18	354.095	37.545	2.312	16.24	6.7E-4	0.27%	0.084%
Higher Heating Value	3.558	1.111	4.67	1.78	0.085	20.880	8.85E-5	1.26%	0.61%
Viscosity at 40°C	5.8	0.27	6.09	0.027	0.97	35.4	3.57E-6	6.15%	2.7%
Flash Point	5701.8	256.2	5958.029	475.15	64.05	7.41	0.033	7.6%	1.85%
Oxidative Stability	54.15	3.35	57.5	0.48	7.74	16.16	7.9E-4	13.12%	4.4%