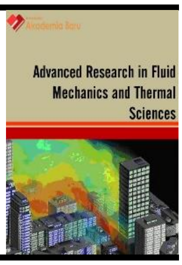
Journal of Advanced Research in Fluid Mechanics and Thermal Sciences 54, Issue 1 (2019) 191-203

Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Relationships Derived from Physical Properties of Waste Cooking Oil / Diesel Blends and Biodiesel Fuels

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ARTICLE INFO

Article history:
Received 9 September 2018
Received in revised form 22 November 2018
Accepted 12 December 2018
Available online 12 February 2019

ABSTRACT

The aim of this study is to estimate mathematical relationships of vital fuel properties that are heating value, density, pour point, cloud point, flash point and viscosity of waste cooking oil/diesel blends and biodiesel fuels. The origin of both waste cooking oil (WCO) and biodiesel (BD) are from palm oil to keep the uniformity of this study. To find the fuel properties, experimentation methods are carried out to acquire data for each blend sample. The samples of blends prepared are ranging from 10% to 100% for both waste cooking oil and biodiesel blend with diesel respectively. From the data of fuel properties obtained, graphs of each fuel property against percentage of blends are plotted. Using Microsoft Excel, mathematical equation for each fuel property for WCO/Diesel and BD/Diesel blends are produced with their respective coefficient of determination denoted as R^2. The results have shown that the properties of the fuel mainly have polynomial relationships. The equations produced are important because fuel properties are prerequisite as input data for research regarding engine combustion diagnostically and in prediction. From the results obtained, it was also determined that BD blends are of better fuel characteristics than WCO blends because of the positive effects of transesterification.

Keywords:
Waste cooking oil (WCO), Palm oil biodiesel (BD), basic properties, mathematical relationships

1. Introduction

Diesel is a very useful and incredible fuel with diverse use and applications. However, diesel fuel is at increasing demand in the global state alongside with the petroleum demand. Besides that, the usage of petroleum when it is at its high demand is actually costly since it is a limited source. With this apparent global energy issue and crisis, scientists have been working towards developing alternate source of energy that is more economical and sustainable in the ecology system of the earth. One of the options for alternative fuel that is often turned to these days is the waste cooking oil. Biodiesel on the other hand is also another alternate source that is too a well-known solution towards petroleum dependency. In addition, biodiesel is renewable and has a positive and less

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damaging impact on the environment and yet it could be a good substitution of diesel as an engine fuel thus reducing the demand of fossil fuel which is very limited source to cope with the global use. Instead of using crude oil, biodiesel is made from vegetable oils or animal fats.

Biodiesel is a liquid fuel that is also chemically known as mono-alkyl esters of long chain fatty acids. Biodiesel is given its name because it is made up of variety of ester based oxygenated fuel produced from renewable biological resources [1]. As for the production of biodiesel, there are several ways to produce it from refined or waste oil and grease [2]. They are; direct usage or blending, micro emulsifications, pyrolysis which is also known as thermal cracking, transesterification which is also known as alcoholysis. Of all these methods, the most common method used is transesterification [3]. This is because it produces and output high yield at low temperature and pressure and has short reaction time.

Waste cooking oil is the oil that is obtained from the fried food. When heated up to 180 °C in order to fry food, the chemical composition of cooking oil tends to change and thus the cooking oil is not advisable to be used over and over again because food will absorb over 5% of the used cooking oil and hence affect human health who consume the fried food [4,19]. The global consumption of vegetable oil is increasing every year thus increase the waste oil production and disposal [5, 19]. Waste cooking oil disposal is a problem because it can result in contamination and pollution of water and soil. Hence, it seems more environmental conscious and reserving that if we were to use the oil waste as a substitute to the fossil fuel.

There are numerous study and research made on engine testing and emission that require the input of fuel properties as the pre-requisite condition before applying any fuel in the engine. This is because properties of the fuels highly affect the performance of the engine. A study conducted by Liaquat *et al.,* [6] was emphasized on the performance of engine and emission nature of diesel engine by using coconut biodiesel blends. This study is one of the researches whereby the researchers pre-determined the critical fuel properties such as heating value and viscosity of the fuel blends because this particular research was resolving the engine performance with regards to the fuel properties of each blend intensity or percentage and the results of engine performance are to be compared with that of diesel fuel.

Aside from finding the fuel properties to perform engine testing, there is also a research that specify on the study of elemental properties of palm oil biodiesel blends. This study which is mentioned earlier was conducted by Pedro *et al.,* in 2007 [7]. Pedro *et al.,* used Kay's mixing rule to compare the key properties of biodiesel blends such as cetane number, viscosity and density with experimented results. Pedro *et al.,* presented graphs that are of linear relationships for all of the tested properties.

On top of that, another research is carried out on the estimation on the cold flow characteristics of biodiesel blends with diesel. The research was carried out by Donald *et al.,* in 2009 [8]. It was obtained that most of the thermal properties results as linear and curvilinear relationships.

In this study, the fuel properties that are viscosity, density, cloud point, pour point, flash point and heating value of diesel blends with respect to WCO and BD are to be determined. These are important fuel properties to run as fuel on diesel engine. This study is vital because fuel properties of biodiesel blends are prerequisite as input data for research regarding engine combustion diagnostically and in prediction [7].

2. Methodology

Sample preparation starts by collecting 4 litres of waste cooking oil (WCO) from any local restaurants and purchasing of 4 litres of pure biodiesel (BD) and 6 litres of diesel. The collected waste cooking oil is first filtered by using coffee cloth prior to filtering using 11 micron paper filter. Then the filtered oil is heated at temperature exceeding 100°C so that all the water content in the oil is gotten rid of. These processes are shown in Figure 1 and Figure 2. The oil is then ready to be blended with diesel and thus prepared to be tested for its properties.

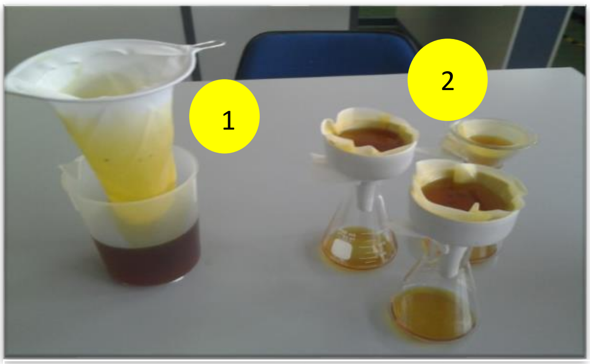

Fig. 1. WCO is first filtered using coffee cloth

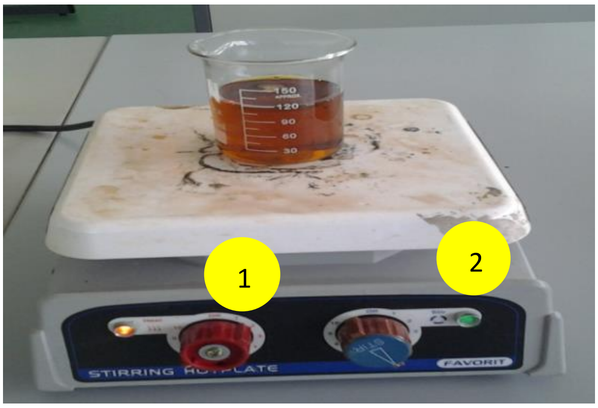

Fig. 2. Heating and stirring using a mechanical stirrer with heating mode (1) and stirring mode (2) turned on

2.1 Blending Preparation

Blending is done to obtain two set of blending sample; one sample set is for biodiesel blended with diesel and the other set is for waste cooking oil blended with diesel. The blending is done based on volume percentage. The blending is shown in Table 1 and Table 2.

Table 1
Biodiesel (BD) blending preparation

Denotation	Biodiesel Percentage of Volume (%)	Diesel Percentage of Volume (%)
B100	100	0
B80	80	20
B60	60	40
B40	40	60
B20	20	80
B10	10	90
B0	0	100

Table 2
Waste cooking oil blending (WCO) preparation

Denotation	WCO Percentage of Volume (%)	Diesel Percentage of Volume (%)
W100	100	0
W80	80	20
W60	60	40
W40	40	60
W20	20	80
W10	10	90
W0	0	100

2.2 Fuel Characterization

The equipment used to measure for the basic properties or fuel characteristics of each blend are summarized in Table 3.

Table 3
Equipment used for fuel characterization

Fuel characteristics	Equipment	Method
Heating value	IKA C200 Bomb Calorimeter	ASTM D240
Viscosity	Brookfield Viscometer	ASTM D445
Density	Hydrometer	ASTM D1298
Cloud point	Cloud point apparatus	ASTM D2500
Pour point	Pour point apparatus	ASTM D97
Flash point	SETA flash point tester	ASTM D93

3. Results
3.1 Viscosity

Viscosity is a very critical fuel property of any oil or fuel. This is because fuel with high viscosity can lead to poor atomization of fuel characteristics thus causing incomplete combustion and resulting in fuel injector blockage due to carbon deposited at the injector as well as resulting in cold start issues [9]. Therefore, fuel with high viscosity is not fit to be used and run in a diesel engine as the results of high viscosity fuels have immediate as well as long-term effect in damaging the engine [10]. Figure 3 shows the results of relationships between viscosity and the intensity of the blend in percentage.

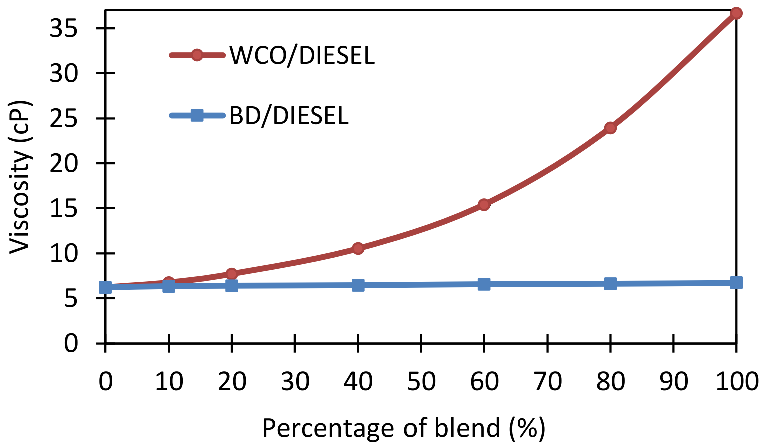

Fig. 3. Viscosity against percentage of blend

From Figure 3, it is indicated that the viscosity of both types of blends increases as the percentage of blend increases as they went from pure diesel to their pure forms of W100 and B100. Commercial diesel has the lowest viscosity of 6.2 cP whilst pure WCO, W100 is the most viscous fuel at viscosity of around 37 cP. It is also indicated that in the graph the pure biodiesel, B100 has slightly higher viscosity than diesel which is at around 6.7 cP. This is because palm oil is the origin for both WCO and BD. It must be well acknowledged that vegetable oil is more viscous than petroleum crude oil. This therefore explains the increasing trend line pattern for WCO/Diesel and BD/Diesel blends. For WCO/Diesel blends, the pattern for its trend line take up the polynomial second degree form whereas BD/Diesel blends has a linear trend line.

It is also observed that the viscosity of WCO/Diesel blends is relatively higher than that of the BD/Diesel blends as they are approaching their pure form as neat WCO, W100 and neat biodiesel, B100 respectively. This is due to the nature of the pure or neat WCO itself. Frying is one of the most well-known ways in food preparation. During frying, the oil is heated up to temperatures of 160 to 200 degree Celsius (°C) for a considerably continuous period of time. In addition, to economically use the cooking oil, the same cooking oil is used repeatedly and over and over again for long period of time until it can't be used anymore [4]. The presence of water and heat while the frying process on the other hand have increases the rate of hydrolysis of triglyceride and thus contribute to the adding up on the free fatty acid content within the edible cooking oil [11]. This therefore has degraded the oil with formation of many undesirable compounds such as oligomeric compounds including the unwanted increment in the free fatty acid content. The increase in free fatty acid content has led to the increase in the Conradson carbon residue (CCR) [4]. The cooking oil, being repeatedly used for a very long time thus can be concluded to have undergone many physical and chemical composition alterations thus contributing to the increase in the molecular mass of the oil [12]. The increase in molecular mass therefore is reflected on the increase of the viscosity as well as increase in the density of the waste cooking oil. This phenomenon therefore explains the considerably high viscosity of the WCO when it is compared to the BD. BD furthermore has undergone transesterification process that is proven to thoroughly decrease the viscosity of the neat palm oil or waste cooking oil because transesterification separate the glycerol from triglyceride and in this way making the molecule of BD lighter than that of palm oil before going through any chemical process such as transesterification or alcoholysis [9].

Additionally, it is also known that a diesel engine is able to run fuel with viscosity from the range of 3 to 8 mPa.s or cP. From Figure 3, it is observable that for WCO/Diesel blends, the maximum limit of blend that is allowable as engine fuel is at W20 which is fractioned as 20% WCO and 80% Diesel fuels. The viscosity at this point is around 7.7 cP thusly making any WCO/Diesel blends beyond W20 unsuitable as diesel engine fuel. In this study, the viscosity increment of W20 from pure diesel is by 24.0%. This means that the value of viscosity of W20 has deviated 24.0% from that of pure commercial diesel. Although W20 is acceptable to be used in a diesel engine, it is not comparable with the properties of B20 making W20 an inferior fuel. It is highly recommended for WCO to convert to biodiesel by undergoing any chemical process so that the critical fuel properties such as viscosity and density can be greatly improved. Study shows that the operation of compression-ignition (CI) with any oil or grease directly blended with petroleum diesel with intensity of oil of 10% to 20% is able to impair and shorten engine life span with maintenance issues such as carbon deposits and gelling of lube oil [13].

On the other hand, after chemical process such as transesterification, the oil will turn to pure biodiesel which is also known as B100. B100 is typically utilized as blend with commercial diesel because diesel has lower viscosity than B100. The event of blending will cause the fuel to run in diesel engine with benefits such as lower emission rate and the use of renewable source of energy to boost an engine [9]. In international level, such as in the United States, the government has already implemented the usage of B20 to run their diesel engine, turbines and boilers. This is due to the basis that B20 possess a favorable balance of engine performance, gas emission, cold weather workability and cost [13]. It is also well aware that fuel with higher intensity of biodiesel content or any fuel greater than B20 such as B50 or B100 may require engine modification and appropriate handling to make the fuel viable to run in the CI engines. In this study, the viscosity of B20 deviated from the commercial diesel by only 3.2% hence indicating that B20 is an internationally acceptable and ideal limit of fuel to run in CI engine due to its comparable value of critical property such as viscosity with the commercial diesel.

The trend lines yield the mathematical relationships or equations for both WCO/Diesel and BD/Diesel blends. The equations generated are VIS= $0.0035x^2 - 0.0612x + 6.8241$ with $R^2 = 0.9973$ and VIS = $0.0048x + 6.2646$ with $R^2 = 0.9630$ respectively where VIS is the viscosity of the fuel and x represents the percentage of the blend.

3.2 Density

Density, just like viscosity is a bulk and important fuel property of an oil if the oil is to become an engine fuel or playing roles in other applications such as to run turbines and boilers. Figure 4 shows the results of density of WCO/Diesel blends and BD/Diesel blends against the percentage of blend.

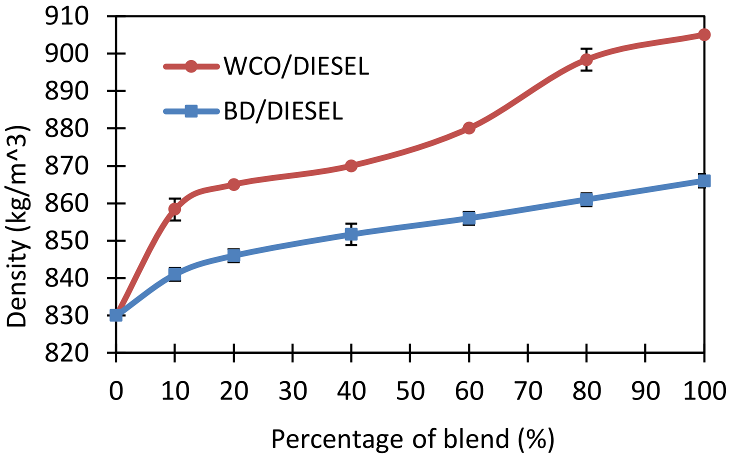

Fig. 4. Density against percentage of blend

From Figure 4, it is indicated that the density for both types of blend is rising as the intensity of the WCO and BD rises. Diesel has the lowest density at 830 kg/m^3 while pure WCO (W100) has the highest density at 905 kg/m^3. Besides that, it is also recognizable that the densities of WCO blends are again greater than that of the BD blends. This behavior is caused by the same explanation as the increment in viscosity of the fuel blends. The high molecular mass of WCO that does not go through alcoholysis or transesterification process had caused the WCO to have significantly higher density than BD for each intensity of blend ranging from 10% to 100% [12]. WCO carried more free fatty acids (FFA) that contain triglycerides which is heavier before it goes through transesterification that convert it to become the fatty acid methyl esters (FAME) that therefore has significantly lower density and other advantageous fuel properties.

Density is said to be a crucial fuel property because it also affects fuel atomization characteristics and also affects heating or calorific value of the fuel. Too high of a density can also lessen the life span of an engine and has immediate effect on the CI engine if fuel used is excessively viscous and dense [10].

The deviation of W20 from diesel is by the slight 4.2% whilst the deviation of B20 from diesel is by even slighter 1.9% making biodiesel blends a better choice than the WCO directly blend with commercial diesel.

The trend lines yielded appeared as polynomial second degree pattern for both WCO/Diesel blends and BD/Diesel blends. For respective blend, the mathematical relationships are DN = $-0.0033x^2 + 0.9687x + 839.84$ and DN = $-0.0024x^2 + 0.5538x + 833.29$ with the values of coefficient of determination $R^2 = 0.9260$ and $R^2 = 0.9669$ respectively where DN is the density of the fuel.

3.3 Heating Value

The heating value in this study is referred to the low heating value. By definition, heating value is the measurement of energy or heat released during the combustion of the fuel in the combustion chamber. Theoretically, it would be an ideal matter if the heating value of a fuel is high because the combustion will give off more energy to run the torque of an engine. Figure 5 shows the relationships between the heating values against the percentage of blend of both types of blends in this study.

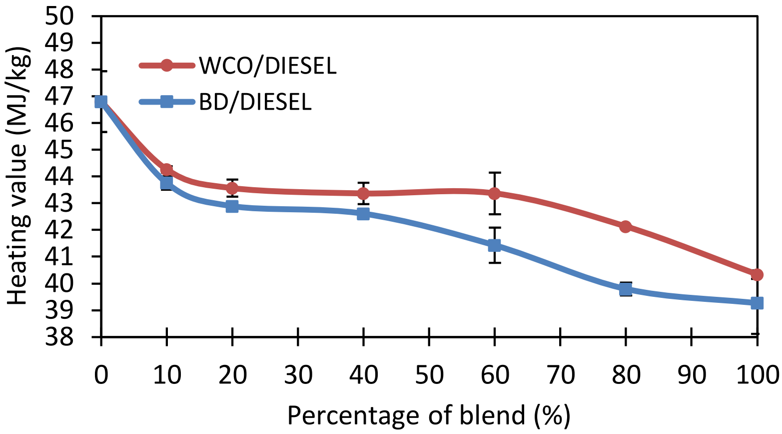

Fig. 5. Heating value against percentage of blend

From Figure 5, what can be observed is that the heating value for both types of blend decreases as the percentage or intensity of the blend increases. This phenomenon is happening due to the increase in density of the oils. Heat is an extensive property whereby it is highly dependent on the size of the matter. Study has shown that the relationship between higher heating value (HHV) and density is inversely proportional [14]. This means that as the density of the fuel increases, the heating value of the fuel will continue to decrease.

On top of that, it can also be seen that the heating value of WCO/Diesel blends is higher than that of the BD/Diesel blends. This is because after going through transesterification, the hydrogen to carbon bond ratio has been greatly reduced in order to convert the triglyceride of FFA into FAME or biodiesel [1]. Hence, all the blends mixed with BD and diesel has significantly lower heating value than WCO blends with diesel. The reduction of hydrogen to carbon ratio from a triglyceride mole into biodiesel mole is illustrated in Figure 6.

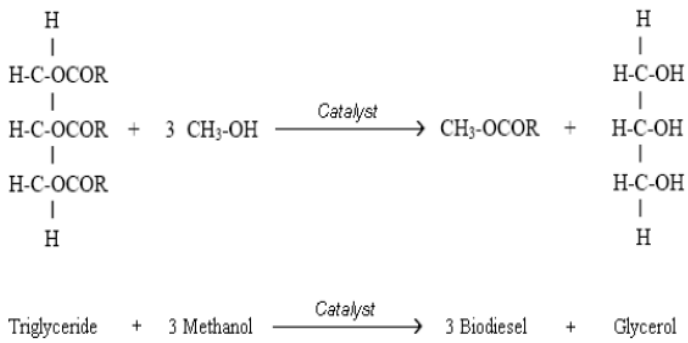

Fig. 6. Transesterification process reduces hydrogen to carbon ratio (Source: [15])

Although this may seem as a downside of BD blends over WCO blends, however, BD blends can still be used to run the compression ignition (CI) engines without compromising the engine's performance such as the brake thermal efficiency if the lower blend intensities are used as recommended such as B10 or B20. Besides that, in comparison to viscosity, heating value is a subordinate fuel property because viscosity is the ultimate determinant whether the engine life will be longer or not.

In addition, from the Figure 5, diesel has the highest heating value which is around 47 MJ/kg whereas B100 has the lowest heating value being measured as 39.2 MJ/kg. Pure WCO, W100 on the other hand has slightly higher heating value than B100 at 40.3 MJ/kg. W20 heating value has deviated in increasing pattern by 6.9% from the heating value of diesel while B20 increased 8.4% from the commercial diesel.

The trend lines for heating value are in polynomial third degree pattern for both WCO/Diesel blends and BD/Diesel blends. The mathematical relationships generated are $HV = -3E\text{-}05x^3 + 0.0043x^2 - 0.2122x + 46.464$ for WCO/Diesel blends and $HV = -2E\text{-}05x^3 + 0.0029x^2 - 0.199x + 46.23$ for BD/Diesel blends whereby HV is heating value with $R^2 = 0.9661$ and $R^2 = 0.9427$ respectively.

3.4 Flash Point

Flash point is a minor property that does not directly associated to the performance of an engine [10]. Flash point is the measure of volatility and flammability of a fuel being stored under ambient conditions. In ASTM standards, it is established that fuels with flash point lower than 130 °C is difficult to handle [16]. Hence, a high flash point fuel is desirable to ensure safe storage because of the reduced volatility nature. Figure 7 shows the results for the relationships between flash point and percentage of blend for the two types of blends used in this study.

The trend lines are in the form of polynomial second degree for both types of blends. The resulted mathematical relationships produced for WCO/Diesel blends is $FP = 0.0089x^2 - 0.1095x + 84.479$ with $R^2 = 0.9654$ and for BD/Diesel blends is $FP = 0.0083x^2 - 0.0348x + 86.563$ with $R^2 = 0.9566$ in which FP is flash point. Mathematically, W20 has increased 14.3% from the commercial diesel whereas B20 has increased 20.4% from the commercial diesel indicating that biodiesel blends have better stability and safety. High flash point is also beneficial in terms of fuel atomization and complete burning of fuel because the engine is going to have to operate at high compression ratio thus increases the air temperature inside the cylinder resulting in better combustion of fuel [1].

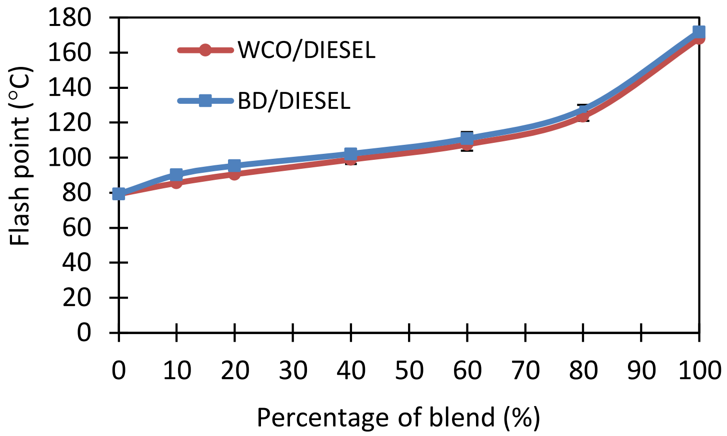

Fig. 7. Flash point against percentage of blend

From Figure 7, it is showing that the flash point increases as the blends went from W0 and B0 to W100 and B100 with respect to WCO/Diesel blends and BD/Diesel blends. From this graph, the minimum flash point is at W0 and B0 or simply diesel which is valued as 79°C. B100 on the other hand has the highest flash point thus making it the most stable and safe to handle fuel at 172°C. Pure WCO which is W100 has slightly lower flash point than B100 measured as 168°C.

Another observable matter from Figure 7 is that the flash points of BD/Diesel blends are slightly higher than that of the WCO/Diesel blends. The reason this occurrence takes place is because of higher degree of unsaturation [1]. Degree of unsaturation also affects cloud point and pour point which will be explained further under next subtopic.

3.5 Pour Point and Cloud Point

Pour point and cloud point are the indicator for cold flow operability of a certain fuel under cold climate circumstances [17]. High pour point and cloud point is challenging the operation of CI engine since gelling of oil can affect operability of the engine and reduces engine life. Figure 8 and Figure 9 shows the relationships between pour point and cloud point with the percentage of blend for WCO/Diesel blends and BD/Diesel blends.

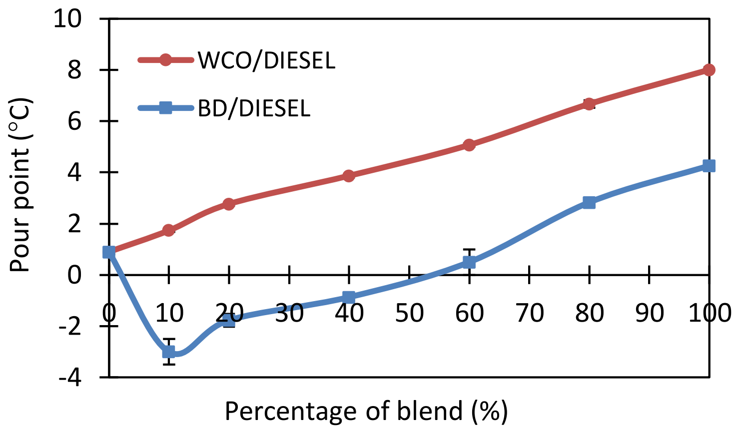

Fig. 8. Pour point against percentage of blend

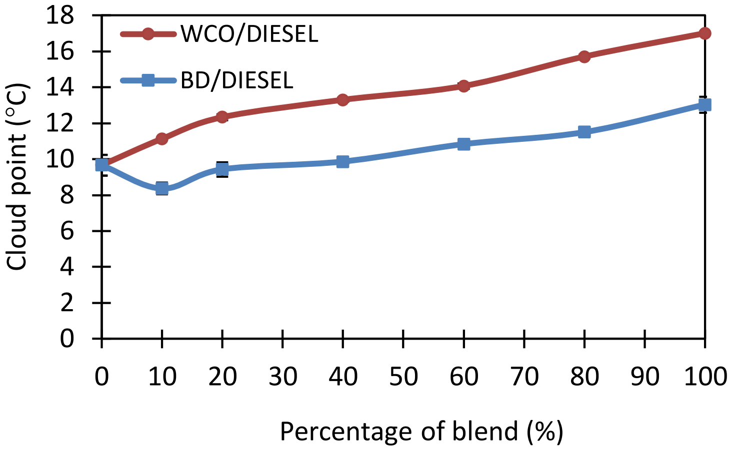

Fig. 9. Cloud point against percentage of blend

From Figure 8 and Figure 9, it is observable that the pour point and cloud point of both types of blends increase as the percentage of blend increases. This is because diesel has the lowest pour point and cloud point and in contrary, WCO and BD have higher pour point and cloud point. Thus, as the intensity of WCO and BD blend with diesel get higher, the pour point and cloud point are increasing along with the concentration of the WCO and BD which are palm oil origin fuels.

For pour point, line of WCO/Diesel blend is in linear form whereby the mathematical relationship generated is PP = 0.0693x + 1.0726 with R^2 = 0.9961. The pattern of BD/Diesel blend is a polynomial second degree curve with equation yielded as PP = $0.001x^2$ - 0.0472x - 0.769 and R^2 = 0.8063 where PP is pour point. For cloud point on the other hand, its WCO/Diesel blend also possess linear relationship with equation stated as CP = 0.0672x + 10.338 and R^2 = 0.9727 while its BD/Diesel blends having a polynomial second degree relation by having equation of CP = $0.0004x^2$ + 0.0013x + 9.1378 with R^2 = 0.9250 in which CP is cloud point.

The phenomenon occurring for both properties that can be seen is that, the pour point and cloud point of BD/Diesel blends are significantly lower than that of WCO/Diesel blends. There is even a sharp and sudden drop of temperature after diesel was blended with BD by making a low intensity fuel of B10. This drop occurred for both pour point and cloud point characteristics for BD/Diesel blend. This drop is due to the degree of unsaturation. Raw WCO is in actuality contains a highly saturated free fatty acid in its triglyceride molecule. By definition, saturated is meant by saturation with hydrogen atoms. The more saturated an oil is, the easier for it to convert into solid form even at considerably higher temperatures [18]. Moreover, palm oil is notoriously known as one of the most saturated oil in the market. Figure 10 shows the composition of fatty acid content in different oils and it is noted that palm oil falls to the second place after coconut oil for its high saturated fatty acid content. This therefore explains the reason why WCO/Diesel blends have higher cloud and pour point. BD is acknowledged to have undergone transesterification that separate the glycerol and free fatty acid from triglyceride by reacting the triglyceride with alcohol in the presence of an alkali catalyst. After this chemical process, there is an occurrence called degree of unsaturation whereby the saturated triglyceride become the less saturated fatty acid methyl ester (FAME) or simply known as biodiesel through the separation of glycerol and the free fatty acids. After certain degree of unsaturation, the cold flow characteristics of the biodiesel fuel is greatly improved and this therefore explain the sudden and sharp drop of temperature of pour point and cloud point after the diesel is being blended with BD. This transformation of degree of unsaturation can be seen through chemical composition of the transesterification process in Figure 11.

The cold flow indicator has improved after transesterification process was involved. Through the data obtained, it is clear that WCO blends are not suitable to be used in cold climate condition because the pour point is as high as 3°C even at lower intensity blend as W20. This is in contrary with the pour point for B20 which is as low as -2°C. Besides that, the gelling or crystal wax production or simply called the cloud point is also higher for W20 which is at 12.3°C while for B20 is around 9.4°C. Even for B20, the cloud point is considerably high and thus this is a limitation to use biodiesel during cold weather. Likewise, the cloud point of WCO blend which is higher thus making WCO blends even inferior to be used in cold climate challenging engine operation.

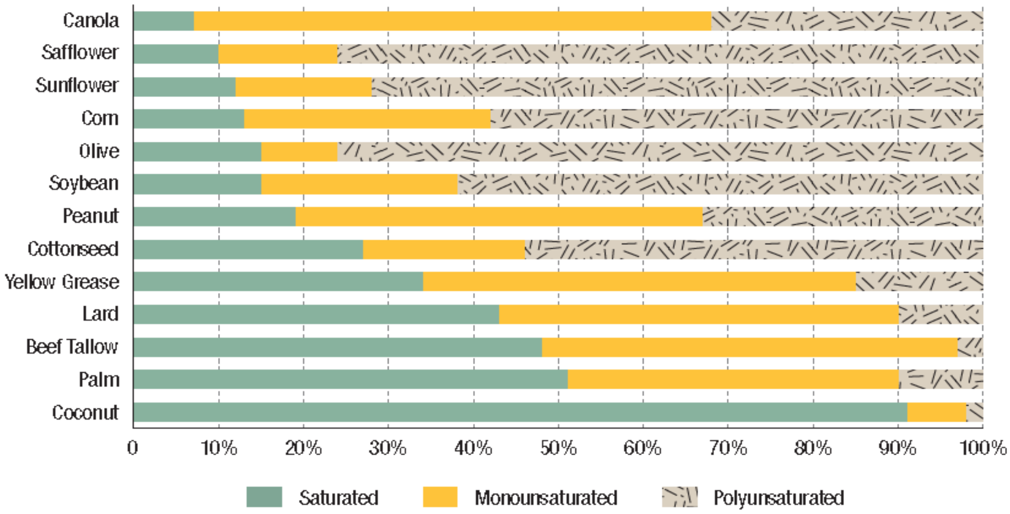

Fig. 10. Increasing saturated fatty acid content in assorted oils (Source: [13])

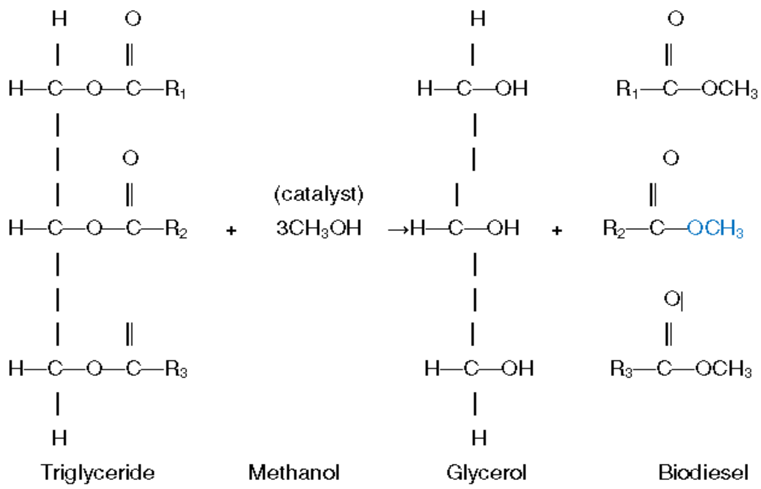

Fig. 11. Transesterification process causes degree of unsaturation (Source: [16])

4. Conclusions

As a conclusion, from the results obtained, BD blends can be concluded as a better fuel in comparison to the WCO blends. This is because transesterification or alcoholyis has brought about positive effects on the properties of the blends. The fuel properties of BD blends especially B20 is compatible to be used in a CI engine on a par with diesel fuel without the need to an engine modification or special handling of the fuel. Besides that, the objective of this study is achieved by the generation of the estimated mathematical relationships of the fuel properties with respect to the blend intensity. In summary, the mathematical relationships of the fuel properties for WCO/Diesel blends and BD/Diesel blends were determined.

In the future, it is highly recommended that the WCO collected to be undergoing chemical process such as transesterification to improve the fuel properties. In this study, directly blending the pre-treated WCO with diesel has made the resultant blends to be inferior fuels with the significantly high viscosity and density and poor cold flow operability. It is interesting to see how transesterification would modify the WCO into becoming a WCO biodiesel with greatly improved properties. By then, the properties are again to be compared with the neat palm oil biodiesel blends to check and observe for any significant change or positive altitude of the important properties as a fuel. On top of that, it is believed that the study of biodiesel fuels is incomplete without any engine testing. Hence, it is also recommended that by using the mathematical relationships or equations produced the fuel properties of any blend intensity can be determined without having the need to find for the fuel properties in the laboratory. Then, by using the values of fuel properties as prerequisite data, engine performance and emission test can be performed.

Acknowledgement
The authors would like to acknowledge the financial support that was received from Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka (UTeM) for the allocated fund to carry out this research. The author would also like to acknowledge all the technical support received from the laboratories of UTeM by granting the permission to use the available facilities with great assistants from the assistant engineers.

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