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Novelty of work: Development and characterization of non-oxidative biodiesels to improve engine performance and exhaust emissions

Evaluation of the characteristics of non-oxidative biodiesel- A FAME composition, thermogravimetric and IR analysis

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Abstract

This experiment evaluates the effect of non-oxidative biodiesels (low oxygen content biodiesels) characteristics and their engine performances. Biodiesel produce from different feedstocks typically contains 10 to 15% of oxygen by weight which enhance the combustion quality and reduce the emissions of hydrocarbons (HCs), Carbon monoxide (CO). However, it produces higher amount of oxides of nitrogen (NOx) due to increasing number of combustion products resulting higher cylinder temperature. In addition, lean air–fuel mixture can contribute to higher NO_x emissions because biodiesel is more oxygenated than diesel. In this study, biodiesels produced from different feedstocks by transesterification process were induced to reduce the oxygen content by using iron bar dipping in those biodiesels, which absorbs oxygen from

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biodiesels and get oxidized. Then, oil characteristics, such as, the percentage of saturated and unsaturated fatty acid of, thermal degradation, stability and existing functional groups by using Fatty acid methyl ester (FAME) composition analysis, thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Fourier transform infrared (FT-IR) spectroscopy analysis of neat biodiesel and non-oxidative biodiesel are analyzed. Here, the pongamia and moringa biodiesels were used to evaluate the experiment containing normal and reduced weight percentage of oxygen to improve the quality and stability of biodiesels to be used in the diesel engine which will also reduce the NOx emissions. Non-oxidative biodiesels had some positive effect on their properties which can further reduce the NO_x emissions. Here, Non-oxidative pongamia and moringa had quite similar characteristics and non-oxidative pongamia was observed to perform better according to its property in the reduction of NO_x and other emissions as well.

Keywords: Biodiesel, transesterification, non-oxidative, FAME, thermo gravimetric analysis, FT - IR analysis.

1.0 Introduction

Nowadays, biodiesel is one of the most suitable alternative energy provider for industrial, transportation and domestic consumption as being renewable, eco-friendly, readily available, biodegradable and non-toxic resource. Biodiesel can be used as pure or mixed with diesel by any volume percentage and also it is feasible to use in the diesel engine without any modification of the engine [1, 2]. Although, biodiesel accounts for emitted almost zero sulfur oxides, 14.2% HC, 26.8% PM and 9.8% CO_2 emissions by replacing the use of diesel fuel its negative impact on NO_x emissions arising several questions in case of environmental pollutions [3, 4]. Biodiesel is

typically produced by transesterification reaction in which triglycerides of vegetable oils or animal fats are reacted with short chain alcohol like methanol or ethanol to produce corresponding mono-alkyl esters and glycerin. So mainly biodiesel is a mixture of different fatty acid methyl esters (FAME) containing of long chain, high concentrated mono and poly unsaturated compounds [5, 6].

Typically, neat biodiesel consists of 11-15 wt% oxygen that is the main cause for the improvement of combustion efficiency of biodiesel. On the other hand, it degrades the biodiesel stability and also makes less efficient than fossil fuel and not to be used in the airplane. Moreover, it increases the emissions of NO_x although decreasing HC and CO emissions. These results in products of combustion is triggered by the higher oxygen content which raises the combustion chamber temperature improving combustion efficiency and consequently promoting NO_x formation [4, 7, 8]. In this study, the oxygen percentage in biodiesel is being decreased in an optimum amount which termed as a non-oxidative biodiesel with an aim to reduce NOx emissions. These reformed biodiesels were obtained from low temperature oxidation process in an iron-oxygen bath. The iron bar absorbed the oxygen molecule from biodiesels. Those biodiesels were characterized by FAME composition, TGA, DSC and FT-IR analysis.

Thermal degradation, FAME composition and IR characteristics of biodiesel are important quality assessment sources for biodiesel to be used in diesel engine commercially. Thermal characteristics give the information about thermal stability and volatility of biodiesel by measuring heat capacity, enthalpy, activation energy and melting point [2, 7]. Thermogravimetric analysis (TGA) is considered as thermoanalytical technique which measures the change in mass of a substance as a function of increasing temperature at a constant rate. The loss in mass of a substance with the increase in temperature may be caused by decomposition, oxidation or

vaporization. A derivative of the weight loss curve is normally used to get the decomposition or vaporization temperature for pure as well as mixed compounds. On the other hand, differential scanning calorimetry (DSC) is used together with TGA and also is a thermoanalytical technique. It typically measures the energy required for the temperature increase of the substance that studied. DSC curve provides important information about enthalpy of boiling, melting, oxidation and decomposition. An endothermic weight loss is accounted for endothermic decomposition or boiling and exothermic weight loss is attributed for exothermic oxidation or decomposition of the substance [9, 10]. Many studies used thermogravimetric analysis for the measurement of stability and production rate of biodiesels. Jain et al.[11] reported their study about the effect of antioxidants on the thermal degradation of *Jatropha curcas* biodiesel. By varying the concentration and type of antioxidants various thermodynamic properties of biodiesel such as activation energy (E_a), onset temperature (T_{on}) and offset temperature (T_{off}) were measured by TGA analysis. This study helped to improve the biodiesel thermal stability by selecting the suitable additives in engine fuel. On the other hand, Vega-Lizama et al. [1] conducted their research on the measurement of thermal degradation degree of soy biodiesel using the residual mass obtained from the decomposition curve. The obtained results showed that, TGA analysis is an efficient method to find the oxidation degree of biodiesel without knowing the biodiesel oxidation process. Moreover, Niu et al. [2] studied the thermal degradation of different biodiesels produced from different feedstocks through transesterification process by TGA analysis. Also, the combustion characteristics of palm and rapeseed biodiesels by thermogravimetric analysis in the furnace of thermogravimetry - differential scanning calorimetry (TGA- DSC) thermal analyzer instead of diesel engine was studied by Yuan et al. [7]. This study was focused on

comparing the suitability of non-oxidative biodiesels with neat biodiesels and diesel which will affect the engine performance and exhaust emissions characteristics.

2.0 Materials and methods

2.1 Materials

Crude moringa and pongamia oil were collected from India. The characteristics of those crude oils are listed in **table 3**. The diesel fuel (B0) was purchased from PETRONAS. Other materials, reagents, and chemicals, such as methanol, H_2SO_4, KOH, and Na_2SO_4, were obtained from LGC Scientific Sdn. Bhd. (Malaysia).

2.2 Production of pongamia and moringa biodiesels

The production of pongamia and moringa biodiesels from their corresponding crude oils was performed in the energy laboratory of the University of Malaya. A 1L batch reactor equipped with flux condenser, magnetic stirrer, thermometer, and sampling outlet were used to produce biodiesels. Crude moringa oil was transesterified to produce biodiesel from it as the acid value was less than 4 mg KOH/g. On the other hand, for pongmia biodiesel production, to reduce the high acid value of feedstocks, a two-step process, involving esterification and transesterification was performed. Firstly, moringa oil was reacted with 25% (v/v oil) of methanol (6:1molar ratio) and 1% (w/w oil) of potassium hydroxide (KOH) and maintained at 60°C and 600 rpm for 2 h. After the reaction, the mixture was deposited in a separation funnel for 12 h to separate glycerol from the produced biodiesel. The lower layer containing glycerol and impurities was drained. In the post-treatment process, the methyl ester formed from the previous process was washed with hot distilled water at 60° C to remove glycerol and impurities. The upper layer was poured into a control rotary evaporator (IKA) to remove water and excess methanol from methyl ester,

whereas the lower layer was drained. Methyl ester was dried using Na_2SO_4. The produced biodiesel was filtered using a qualitative filter paper to obtain the final product. For, pongamia oil, in the esterification process, the molar ratio of methanol was maintained at 12:1 (50% v/v oil) and 1%(v/v oil) of sulfuric acid (H_2SO_4) were added to the pre-heated oils at 60 °C and 600 rpm for 3 h in a glass reactor to refine the crude oils. After reaction completion, the product was transferred to a separation funnel, in which the esterified oil (lower layer) was separated from the upper layer. The upper layer included excess alcohol, sulfuric acid, and impurities. The lower layer was then loaded into a control rotary evaporator (IKA) and heated at 60 °C under vacuum conditions for 1 h to remove methanol and water from the esterified oil. Then, during transesterification, the esterified oils were reacted with 25% (v/v oil) of methanol and 1% (m/m oil) of potassium hydroxide (KOH) and maintained at 60°C and 600 rpm for 2 h. After reaction completion, the produced biodiesels were deposited in a separation funnel for 12 h to separate glycerol from the biodiesels. The upper layer was washed three times with hot distilled water. The formed methyl ester was poured into a control rotary evaporator (IKA) to remove water and excess methanol and then dried using Na_2SO_4.The lower layer containing impurities and glycerol was drained. The produced methyl ester was filtered with qualitative filter paper to obtain the final products as biodiesel.

2.3 Oxygen reducing process from produced biodiesels

The oxygen reducing process was conducted by using a commercial grade iron bar of length 3 cm, width 1.5 cm and thickness 0.3 cm, which was dipped in the produced biodiesel. The iron bar was dipped in 10-20 ml biodiesels at 60°C and 100 rpm after cleaning. All the biodiesels with iron bars were kept in airtight glass bottle at room temperature for 6 weeks. All the iron bars were weighted before and after the test period balanced by Scaltec SBA 31 (0.0001g resolution). There was a change of weight of iron bars which was observed 1.04% and 0.7% for pongamia and moringa biodiesels respectively. The iron bars were get oxidized by reacting with oxygen from biodiesels, which was the main cause for reduced oxygen weight percentage in non-oxidative biodiesels than neat biodiesels.

2.4 Iron oxidation and elemental composition

The oxidation of iron bars due to dipping in biodiesels was observed using SEM (Scanning electron microscope) model Hitachi TM3030 at 150x magnification with acceleration voltage of the microscope of 5 KV while operating. Elemental composition of normal and oxidized iron bars has been analyzed by Bruker Quantax 70 EDX (energy dispersive system) at 150x magnification attached with the microscope. Each bars was scanned at three different spots and their average result is reported in this article.

2.5 Fatty acid methyl ester (FAME) composition

The fatty acid methyl ester composition of neat and non-oxidative pongamia and moringa biodiesels were measured by using gas chromatography (GC) analysis in an Agilent 7890A model equipped with a flame ionization detector with HP- INNOWax column (30 m × 0.25 mm, 0.25 μm of thickness). The flow rate of carrier gas Helium was 3.5mL/min. The oven temperature was held at 50°C for 5 min initially and then programmed to increase at a rate of 20 °C/min to 210°C and held for 18 min. Then another increase was made to 230°C at a rate of 20 °C/min which was held for 13 min. Both the injector and detector temperature was maintained at 250°C. A sample was injected at a spilt ratio of 50:1 of 0.3μL volume.

2.6 Property analysis of neat and non-oxidative biodiesels

Biodiesels can be characterized by several important physicochemical properties that determine the quality and suitability of those biodiesels in order to be used in the unmodified diesel engine as a blend with diesel or in a pure form. In this study, some key characterization properties of neat and non-oxidative coconut, pongamia and moringa biodiesels are measured and compared which include kinematic viscosity, density, calorific value, cetane number, oxidation stability and flash point. These physicochemical properties were measured according to the international standard specifications of ASTMD6751 or EN14214, then compared between neat and non-oxidative biodiesels and also with conventional diesel.

2.7 Thermogravimetric (TGA) analysis

The TGA analysis test of neat, non-oxidative biodiesels and diesel was performed by using TGA Q500 V20.13 Build 39 thermal analyzer at a constant heating rate of 50 °C/min under nitrogen

atmosphere at a flow rate of 40 ml/min. About 10-20 mg of samples were used in a 40μL platinum pan at temperature interval from 4.0°C- 950°C.

2.8 Differential scanning calorimetry (DSC) analysis

The DSC analysis test for neat, non-oxidative biodiesels and diesel was performed in a instrument named DSC Q200 V24.11 Build 124 DSC analytical module in standard cell under inert (nitrogen) atmosphere with gas flow rate of 50 ml/min and at a 10°C/min heating rate to 130 °C to heat the samples. DSC cell was loaded with one sample and one reference pans. About 10 mg of sample was put in sealed in an aluminum pan and one identical empty pan was set as a reference to perform the test. For heating scans, samples were cooled rapidly and held isothermally for 2 min at -60°C and then heated to 130°C and then the samples were held isothermally for 2 min at 130°C, then cooled to -80°C for cooling scans.

2.9 Fourier transform infrared (FT-IR) spectroscopy analysis

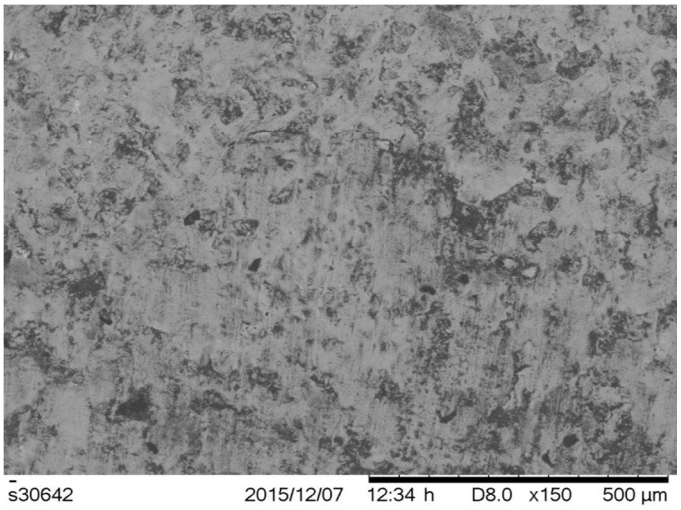
The FT-IR spectroscopy analysis of neat, non-oxidative biodiesels and diesel was done in a Perkin Elmer biodiesel FAME analyzer connected with an MIR TGS detector. The range of spectrum was 4000-450 cm^{-1} and the resolution and scans were 4 cm^{-1} and 16 scans, respectively. This spectrum was processed by e-spectrum software.

3.0 Results and discussions

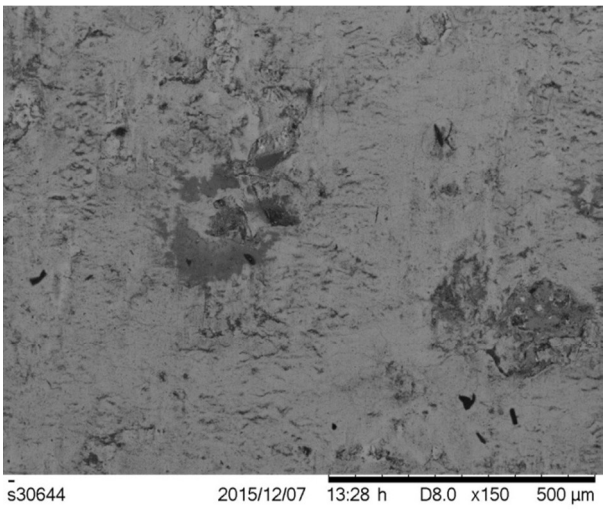
3.1 Oxidation of iron bars to reduce the oxygen content of biodiesels

Figure 1 (a), **(b)** and **(c)** presents the SEM images of normal, oxidized iron bars from pongamia and moringa biodiesel, respectively. From the SEM images we can observe the change in the iron bars from normal to oxidized mode due to reacting with oxygen in biodiesels, which in turns confirmed that the iron bars were oxidized. Moreover, it can be comprehended from the image

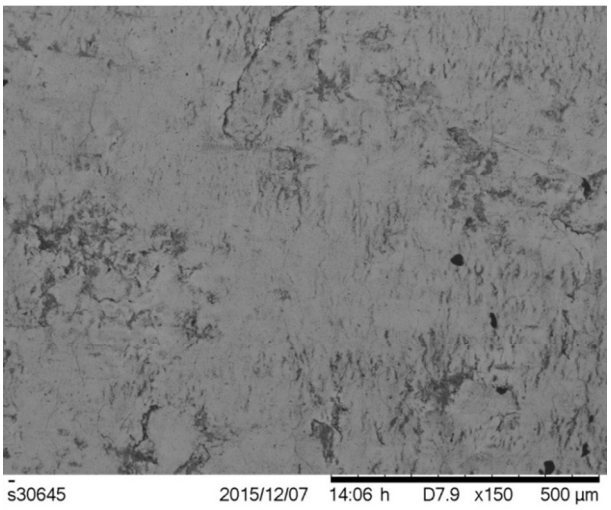
that, the iron bar from pongamia biodiesel was oxidized higher than iron bar from moringa biodiesel. As a result, there was a higher reduction of oxygen content from pongamia biodiesel than moringa. As biodiesels were kept in an airtight opaque bottle and they were examined before and after the oxygen reduction process.



(a)



(b)

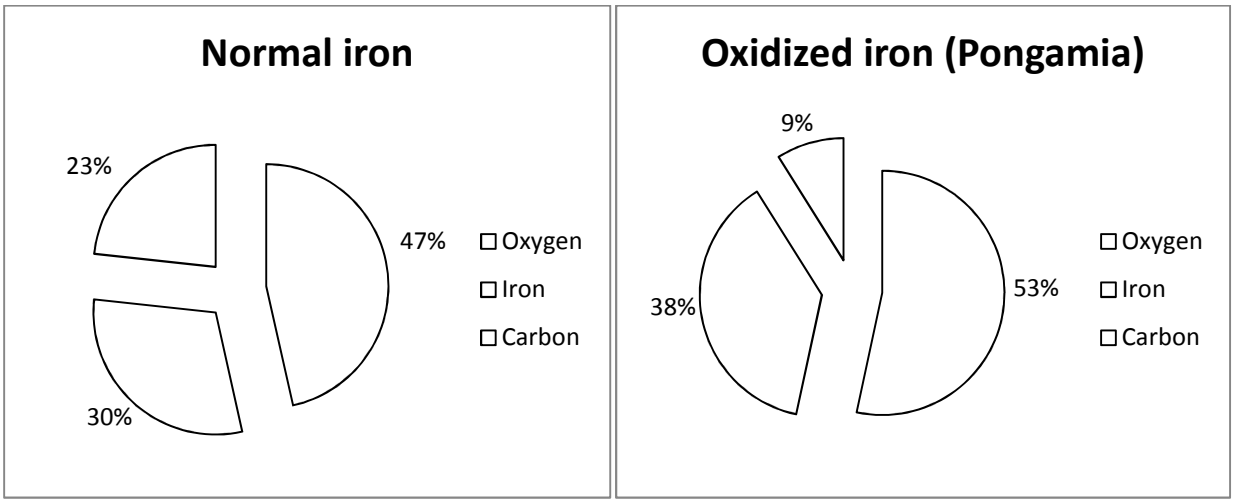


(c)

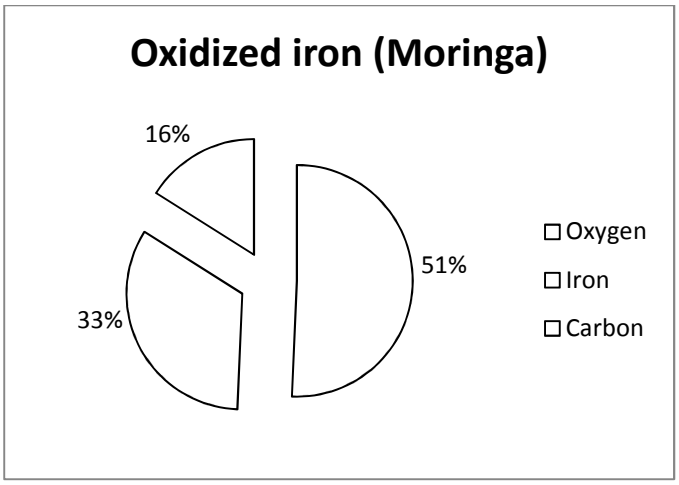
Fig 1: SEM images of (a) Normal iron (b) Oxidized iron (Pongamia) and (c) Oxidized iron (Moringa)

3.1.1 Elemental composition analysis of normal and oxidized iron bars

The elemental composition of normal and oxidized iron bars was analyzed to see the main components of those bars before and after the oxidation process. Results were obtained from three different spots and the atomic percentage of elements were presented in **figure 2**. The elements presented in the bars were oxygen, iron and carbon. From the **figure 2 (a)**, **(b)** and **(c)** it can be seen that the atomic percentage of oxygen of normal and oxidized iron bars were different and the iron bar from pongamia biodiesel had higher oxygen molecule than the iron bar from moringa biodiesel. However, the elemental composition also confirmed the oxidation of iron bars due to reacting with oxygen from the biodiesels as the oxygen percentage increases from normal to oxidized mode and therefore, higher oxygen reduction from pongamia biodiesel.



(a) **(b)**



206

207 **(c)**

208 **Fig 2: Elemental composition of (a) Normal iron (b) Oxidized iron (Pongamia) and (c)**

209 **Oxidized iron (Moringa)**

3.2 FAME composition of neat and non-oxidative biodiesels

In **Table 1**, the FAME composition of neat and non-oxidative pongamia and moringa biodiesels are presented. The saturated and unsaturated fatty acid composition of both the neat and non-oxidative biodiesels are compared to find the most suitable one for better performance.

Table 1: Fatty acid composition of neat and non-oxidative pongamia and moringa biodiesels

				Neat biodiesels		Non-oxidative biodiesels	
FAME	**Structure**	**Molecular weight**	**Formula**	**Pongamia (wt%)**	**Moringa (wt%)**	**Pongamia (wt%)**	**Moringa (wt%)**
Methyl hexanoate	6:0	130.18	$CH_3(CH_2)_4COOCH_3$	-	< 0.1	< 0.1	< 0.1
Methyl octanoate	8:0	158.24	$CH_3(CH_2)_6COOCH_3$	< 0.1	< 0.1	< 0.1	< 0.1
Methyl decanoate	10:0	186.29	$CH_3(CH_2)_8COOCH_3$	< 0.1	< 0.1	< 0.1	< 0.1
Methyl laurate	12:0	214.34	$CH_3(CH_2)_{10}COOCH_3$	< 0.1	< 0.1	0.1	< 0.1
Methyl myristate	14:0	242.39	$CH_3(CH_2)_{12}COOCH_3$	< 0.1	< 0.1	0.1	0.1
Methyl palmitate	16:0	270.45	$CH_3(CH_2)_{14}COOCH_3$	9.7	10.8	10.2	10.9
Methyl palmitoleate	16:1	268.43	$CH_3(CH_2)_5CH=CH(CH_2)_7COOCH_3$	< 0.1	0.1	< 0.1	0.2
Methyl heptadecanoate	17:0	284.48	$CH_3(CH_2)_{15}COOCH_3$	-	-	0.1	0.1
methyl (Z)-heptadec-10-enoate	17:1	282.46	$CH_3(CH_2)_5CH=CH(CH_2)_8COOCH_3$	-	-	< 0.1	0.1
Methyl stearate	18:0	298.50	$CH_3(CH_2)_{16}COOCH_3$	6.8	4.4	6.9	4.0
Methyl Oleate	18:1	296.49	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	50.9	25.2	50.8	32.1
Methyl Linoleate	18:2	294.47	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOCH_3$	18.2	52.1	17.0	44.1
Methyl Linolenate	18:3	292.46	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOCH_3$	4.0	6.0	3.6	4.6
Methyl archidate	20:0	326.56	$CH_3(CH_2)_{18}COOCH_3$	1.6	0.4	1.7	0.4
Methyl eiosenoate	20:1	324.54	$CH_3(CH_2)_7CH=CH(CH_2)_9COOCH_3$	1.2	0.3	1.3	0.2
Methyl Behenate	22:0	354.61	$CH_3(CH_2)_{20}COOH$	5.6	0.4	5.6	0.4
Methyl erucate	22:1	352.59	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	-	0.2	-	-
Methyl Lignocerate	24:0	382.66	$CH_3(CH_2)_{22}COOH$	1.6	0.1	1.6	0.2
Other				0.4	-	1.0	2.6
			Saturation	25.3	16.1	26.3	16.1

Mono-unsaturated	52.1	25.8	52.1	32.6
Poly-unsaturated	22.2	58.1	20.6	48.7
Total	99.6	100	99	97.4

The monounsaturated fatty acid was same for both neat and non-oxidative pongamia biodiesel, whereas it was increased for moringa biodiesel from neat to non-oxidative mode. These were consisted of mainly oleic acid C 18:1 (50.9%) and (50.8%) for neat and non-oxidative, and eicosenoic acid C 20:1 (1.2%) and (1.3%) for neat and non-oxidative pongamia biodiesel respectively. Meanwhile, for moringa biodiesel it was consisted of oleic acid C 18:1 and eicosenoic acid C 20:1 as (25.2% and 32.1%) and (0.3% and 0.2%) for neat and non-oxidative mode respectively. Other unsaturation percentage was completed by polyunsaturated fatty acid which was due to the presence of linoleic C 18:2 and linolenic acid C 18:3. For both pongamia and moringa biodiesel the percentage of linoleic (18.2% to 17.0% and 52.1% to 44.1%) and linolenic (4.0% to 3.6% and 6.0% to 4.6%) acid were decreased from neat to non-oxidative mode respectively, which resulted the total decreased in polyunsaturation of both biodiesels from neat to non-oxidative mode. High monounsaturated fatty acid resulted in high oxidation stability of pongamia biodiesel which was also confirmed from the test. Moreover, low amount of polyunsaturated fatty acid develops higher cetane number and also produces lower emissions of NO_x [12-15]. On the other hand, the saturated fatty acid composition was same for moringa but increases for pongamia biodiesel from neat to non-oxidative mode. The highest saturated fatty acid was palmitic C 16:0 (9.7% to 10.2% and 10.8% to 10.9%), followed by stearic C 18:0 (6.8% to 6.9% and 4.4% to 4.0%), behenic C 22:0 (5.6% to 5.6% and 0.4% to 0.4%) and arachidic C 20:0 (1.6% to 1.7% and 0.4% to 0.4%) for pongamia and moringa biodiesel from neat to non-oxidative mode, respectively. High saturated fatty acids contained biodiesels have low quality cold flow properties and also they have high melting points [12, 14]. In this study, both the biodiesels had low amount of saturated fatty acids and high amount of monounsaturated fatty

237 acid with a higher value in pongamia biodiesel for both neat and non-oxidative mode. These
238 results are comparable with the previous literatures [16-22].

239 **3.3 Elemental composition of neat and non-oxidative biodiesels**

240 **Table 2** presents the elemental composition of neat and non-oxidative pongamia and moringa
241 biodiesels. Generally, biodiesel contains carbon, hydrogen and oxygen content whereas diesel
242 contains only carbon and hydrogen. Although high oxygen content in biodiesel helps to reduce
243 CO and HC emissions by complete combustion process that influences the oxidation of unburned
244 hydrocarbons, which in turns increase the NO_x emissions by raising the combustion chamber
245 temperature. On the other hand, for reducing the NO_x emissions from produced biodiesels non-
246 oxidative pongamia and moringa biodiesels contain optimum amount of oxygen that helps to
247 reduce the CO and HC emissions as well as decreases the NO_x emissions unlike the typical
248 biodiesels. From the table, it can be seen that, neat pongamia biodiesel contained higher oxygen
249 and hydrogen content whereas had lower carbon content than moringa biodiesel. So, pongamia
250 biodiesel had more complete combustion characteristics which also increase the NO_x emissions
251 higher. The reduction of oxygen weight percentage was observed 1.9% and 1.4% for pongamia
252 and moringa biodiesels respectively. Moreover, the carbon percentage increases for both
253 biodiesels from neat to non-oxidative mode, which can be from the iron bar that had lower
254 carbon percentage from normal to oxidized mode. From the table, it can be concluded that, non-
255 oxidative moringa had the lowest oxygen content hence more suitable for NO_x reduction,
256 although the reduction percentage was higher for pongamia biodiesel.

257

258

Table 2: Elemental composition of neat and non-oxidative pongamia and moringa biodiesels

		Neat biodiesels		Non-oxidative biodiesels		
Wt%	**Test Method**	**pongamia**	**moringa**	**pongamia**	**moringa**	**Diesel**
Carbon (C)	ASTM D5291	74.0	75.8	76.1	77.1	85.2
Hydrogen (H)	ASTM D5291	12.4	12.3	12.2	12.4	14.8
Oxygen (O)	ASTM D5291	13.6	11.9	11.7	10.5	0
C/H	-	5.97	6.16	6.24	6.22	5.76
Empirical formula	-	$C_{6.17}H_{12.3}O_{0.85}$	$C_{6.32}H_{12.2}O_{0.74}$	$C_{6.34}H_{12.1}O_{0.73}$	$C_{6.43}H_{12.3}O_{0.66}$	$C_{7.1}H_{14.68}$

3.4 Characterization of neat and non-oxidative biodiesels

The major physicochemical properties of neat and non-oxidative pongamia and moringa biodiesels are listed in **Table 3** to compare with no. 2 diesel (B0). All the properties were compared with the ASTM D6751 standards. Cetane number was determined three times using fatty acid methyl ester composition with several empirical equations [23-26] presented below:

$$CN = 46.3 + (5458/SV) - (0.225* IV) \quad (1)$$

$$SV = \sum (560* A_i)/M_{wi} \quad (2)$$

$$IV = \sum (254*A_i*D)/M_{wi} \quad (3)$$

where A_i is the weight percentage of each fatty acid component, D is the number of double bonds in each fatty acid, M_{wi} is the molecular mass of each fatty acid component SV is the saponification value and IV is the iodine value.

273 **Table 3: Physicochemical properties of crude oil, neat and non-oxidative pongamia and moringa biodiesels**

				ASTM D6751 B100		Crude oil		Neat biodiesels		Non-oxidative biodiesels		ASTM D975 Diesel	
Property	**Units**	**Equipment**	**Accuracy**	**Test Method**	**Limits [b]**	**Pongamia**	**Moringa**	**Pongamia**	**Moringa**	**Pongamia**	**Moringa**	**Limits [c]**	**Results**
Kinematic viscosity at 40°C	mm^2/s	SVM 3000	0.1%	ASTM D445	1.9-6	44.17	33.26	5.13	4.43	6.50	4.33	1.3-4.1	3.85
Density at 15°C	Kg/m^3	SVM 3000	±0.1 kg/m^3	ASTM D1298	860-894	941.2	921.3	894.7	883.2	909.5	885.2	850	839.1
Oxidation stability	h	873 Rancimat	±0.01 h	EN ISO 14112	3 h min[a]	13.47	6.27	6.70	4.99	11.98	0.88	-	19.89
Calorific value	MJ/kg	C2000 basic calorimeter	±0.001 MJ/kg	ASTM D240	-	38.85	39.60	38.19	39.97	39.45	39.90	42-46	45.67
Cetane number	-			ASTM D613	47 min	-	-	56.13	45.97	56.60	49.28	40-55	48

274 [a] Limit according to EN-14214

275 [b] Ref. [27, 28]

276 [c] Ref. [27]

277 **3.4.1 Kinematic viscosity**

278 In table 3, there is fluctuation in the change of the property for neat and non-oxidative biodiesels. The kinematic viscosity decreases
279 for moringa biodiesel from neat to non-oxidative, but increases for pongamia biodiesel. However, both the biodiesels had higher
280 viscosity than diesel for both neat and non-oxidative mode. Moreover, in case of crude oil, pongamia had higher viscosity than
281 moringa. As, viscosity influences the fuel injection system specially the spray atomization, penetration of the injected jet, air-fuel
282 mixture combustion quality at low temperatures, it is very important for combustion quality. Biodiesels have higher viscosity than

283 diesel fuel because of the presence of electronegative oxygen which makes the biodiesels more polar than diesel [28-30]. Hence, the
284 reduction of oxygen from biodiesels can improve the viscosity.

285 **3.4.2 Density**

286 The changes in density are almost similar to the changes in kinematic viscosity except in the case of moringa biodiesel, as shown in
287 table 3. The density increases for pongamia and moringa biodiesels from neat to non-oxidative mode. However, all the neat and non-
288 oxidative biodiesels had a higher density than diesel, among them moringa biodiesel had lower density range for both neat and non-
289 oxidative mode. Crude pongamia oil had higher density than moringa similar as the neat and non-oxidative biodiesels. Density is an
290 important parameter for fuel property as it affects the fuel atomization and combustion as well as Other engine properties are also
291 related to fuel density such as heating value, cetane number and viscosity. The density of biodiesel is normally higher than diesel as
292 the density of biodiesel depends on its fatty acid composition, molar mass, water content and purity [28, 29].

3.4.3 Oxidation stability

The oxidation stability increases for pongamia biodiesel from neat to non-oxidative mode, whereas decreases for moringa biodiesel from neat to non-oxidative mode which was under the minimum requirement. This decrease indicates the lower oxidation stability of moringa biodiesel from neat to non-oxidative mode. However, diesel had the highest oxidation stability among all crude oils, neat and non-oxidative biodiesels. Meanwhile, non-oxidative pongamia biodiesel had higher oxidation stability after diesel among all other neat and non-oxidative biodiesels due to high monounsaturated fatty acid. oxidation stability affects biodiesel quality by oxidizing it during storage for distribution or in the fuel system. Biodiesels are fatty acid methyl ester which oxidize automatically to form aldehydes, ketons and resins and makes the fuel useless to run the engine. The oxidization rate of biodiesel depends on temperature, fatty acid composition, reaction catalyst, radiation intensity, light etc. and it can be delayed by adding different antioxidants [28, 29].

3.4.4 Calorific value

It can be inferred from the table 3 that, for moringa biodiesel the calorific value decreases from neat to non-oxidative mode but increases for pongamia biodiesel. However, among all the biodiesels moringa had the highest calorific value for both neat and non-oxidative mode. Meanwhile, all the biodiesels and crude oils had lower calorific value than diesel. Biodiesels have lower heating value than diesel fuel because of the deviation in the hydrogen and carbon content and presence of high oxygen molecule that decreases the heating value about 10-13 percent in biodiesel than diesel. Heating value of biodiesel increases with its number of carbon atoms and decreases with its number of double bonds [28, 29]. So, it can be shown that, in pongamia

biodiesel the calorific value increases with increasing carbon molecules and decreasing oxygen molecules.

3.4.5 Cetane number

The cetane number for all biodiesels was increased from neat to non-oxidative mode, as seen in table 3. However, Pongamia biodiesel had higher cetane number than moringa for both neat and non-oxidative mode. Moreover, all the biodiesels had higher cetane number than diesel except neat moringa and also the non-oxidative moringa had almost similar value with diesel. Cetane number is defined as the dimensionless measure of the ignition quality of diesel fuel during combustion of a compression ignition engine. It describes the fuel quality based on the ease of self-ignition of the particular fuel. Ignition delay (ID) period of diesel fuel is also indicated by it during the ignition period of injected diesel fuel in combustion chamber. The higher ignition time lag indicates the lower cetane number and vice versa. The range of cetane number in ASTM D6751 standards is based on the two experimental measured fuels named hexadecane ($C_{16}H_{34}$) with cetane number 100 and 2,2,4,4,6,8,8- heptamethylnonane with cetane number 15. The first one is easily ignited fuel and the other one is highly resistive to ignite. Typically, biodiesels have higher cetane number than diesel fuel. 41-56 is the usual range of cetane number for no. 2 diesel and it should not be higher than 65 [28, 29]. So in that case, moringa biodiesel had the more suitable cetane number but as indicated earlier that lower polyunsaturated fatty acid indicates high cetane number and thus a low level of NO_x emissions, so non-oxidative pongamia can perform better than moringa biodiesel. Moreover, all the neat and non-oxidative pongamia and moringa biodiesels satisfied the requirements according, which ensures the suitability of use of those biodiesels in the diesel engine without any modification by blending with diesel or in a pure form.

By analyzing all the properties, it can be observed that all the neat and non-oxidative pongamia and moringa biodiesels satisfied the requirements according to the ASTM D6751 standards, which ensure the suitability of use of those biodiesels in diesel engine without any modification by blending with diesel or in a pure form.

3.5 Thermogravimetric analysis of neat and non-oxidative biodiesels

Thermogravimetric analysis of neat, non-oxidative biodiesels and diesel were conducted to understand the decomposition, thermal degradation behavior and volatility of those biodiesels.

In **Figure 3**, the TGA curves of neat, non-oxidative pongamia, moringa biodiesels and diesel were compared. In this figure 3, all the curves had the similar trend. Firstly, the TGA curves achieve ascending trend due to buoyancy and molecular adsorption effect but not in a distinct way and all of the neat and non-oxidative biodiesels and diesel were decomposed in only one step which was clearly observed [2]. The decomposition temperature decreases from neat to non-oxidative biodiesels. Neat pongamia and moringa biodiesels had almost similar thermal stability range. Pongamia and moringa biodiesels were thermally stable up to 170.16 °C and 172.20 °C respectively. However, non-oxidative pongamia and moringa biodiesels were thermally stable up to 158.28°C and 171.78°C, respectively. On the other hand, diesel was thermally stable up to 129.04°C. Hence, moringa biodiesel is thermally more stable than pongamia biodiesel and diesel at both neat and non-oxidative mode. Then, with the increasing temperature the TGA curves were descending due to volatilization of weak chemical bonds and small molecules. Around 99% of weight loss took place at the temperature ranges from 95 °C to 279 °C, 107 ° C to 317 ° C and 61 °C to 302 °C for neat pongamia, moringa biodiesels and diesel, respectively. On the other hand, for non-oxidative biodiesels the 99% weight loss range increases than the neat biodiesels. Then, the final thermal degradation was observed with the 0.09%, 0.006% and 0.02024% carbon

residue at the end of decomposition for neat pongamia, moringa biodiesels and diesel, respectively. However, in case of non-oxidative biodiesels there were negative percentage of carbon residue observed at the end of the decomposition [2, 31, 32].

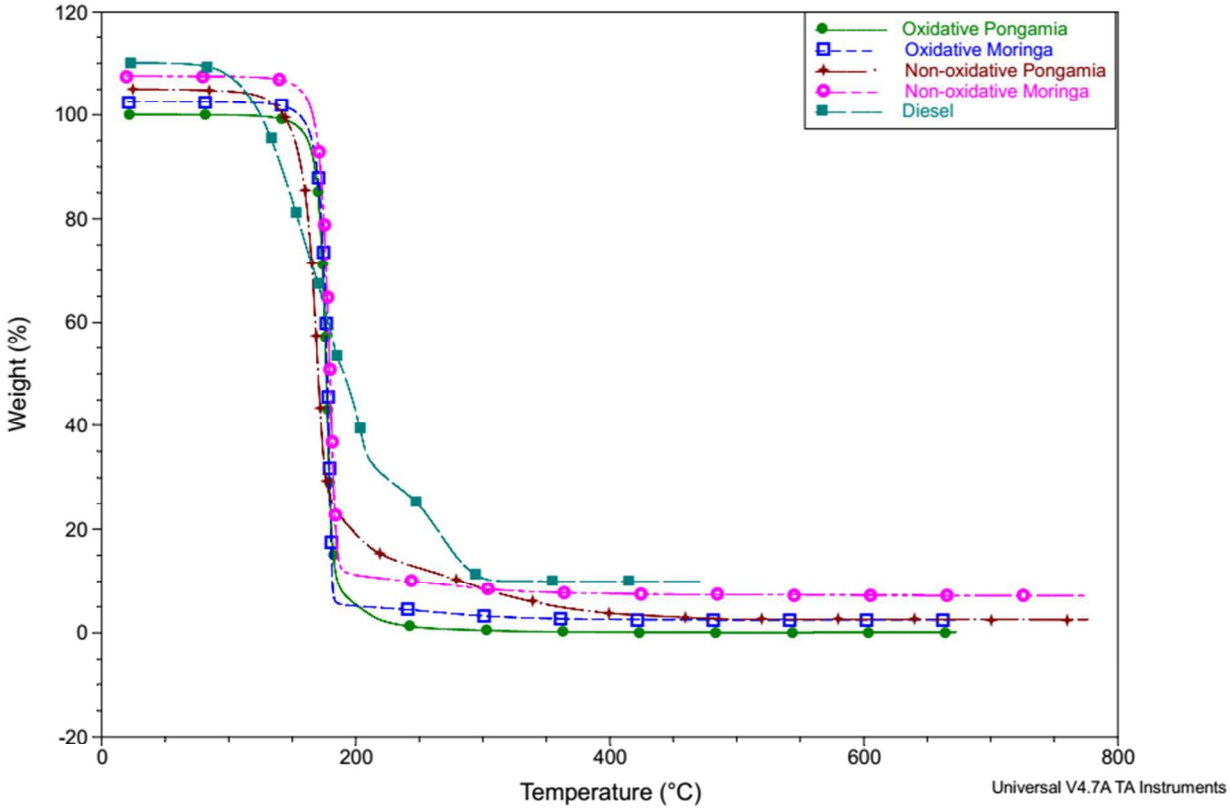
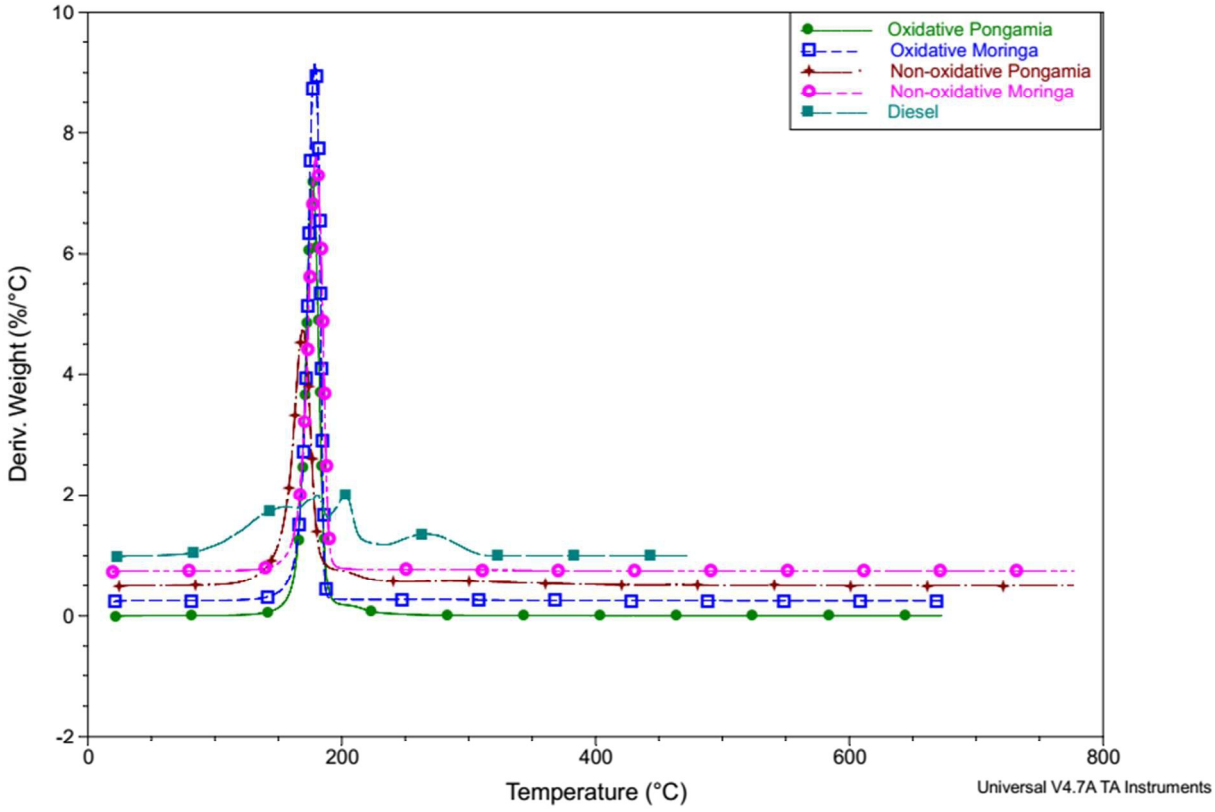


Fig 3: TGA curves of neat, non-oxidative pongamia, moringa biodiesels and diesel at 50 °C/min heating rate

In **Figure 4**, the derivative of thermogravimetric curves (DTG) are also presented. This curves showed the temperature at its peak point where the maximum rate of change of thermal decomposition (dm/dT_{max}) took place for all of the neat and non-oxidative biodiesels and diesel. From the figure, it can be seen that, the peaks of the DTG curves occurred at 177 °C, 179 °C and 203 °C for neat pongmia, moringa biodiesels and diesel, respectively. For non-oxidative moringa

372 biodiesel the peak was increased but it decreased for pongamia biodiesel. So, moringa biodiesel
373 had the highest temperature for the maximum rate of change of thermal decomposition
374 (dm/dT_{max}) for both neat and non-oxidative mode, but lower than that of diesel [10, 33].



375

376 **Fig 4: DTG curves of neat, non-oxidative pongamia, moringa biodiesels and diesel at 50**
377 **°C/min heating rate**

378 From the two figures it can be concluded that, almost all the biodiesels and diesel had the similar
379 TGA and DTG curves and thermal characteristics with slight variations. In **Table 4**, all the
380 results are summarized.

381

Table 4: Thermal characteristics (TGA) of neat and non-oxidative pongamia, moringa biodiesels and diesel

Parameters	Neat biodiesels		Non-oxidative biodiesels		Diesel
	Pongamia	Moringa	Pongamia	Moringa	
Product weight (mg)	18.07	19.72	14.04	20.56	19.89
Decomposition temperature (°C)	170.16	172.20	158.28	171.78	129.04
Volatility (%)	Not found	Not found	Not found	Not found	Not found
1st weight loss (%mg/mg)	99.3	99.4	101.8	99.67	99.5
1st weight loss temperature range (° C)	95 - 279	107 - 317	57 - 444	95 - 353	61 - 302
Lost weight at 1st weight loss (mg)	17.95	19.60	14.29	20.49	19.79
Residue (%mg/mg)	0.08	0.006	-2.48	-0.3379	0.02024
Weight at residue (mg)	0.0156	0.0013	-0.3481	-0.06946	0.004
Peak temperature (°C)	177	179	169	180	203

3.6 DSC analysis of neat and non-oxidative biodiesels

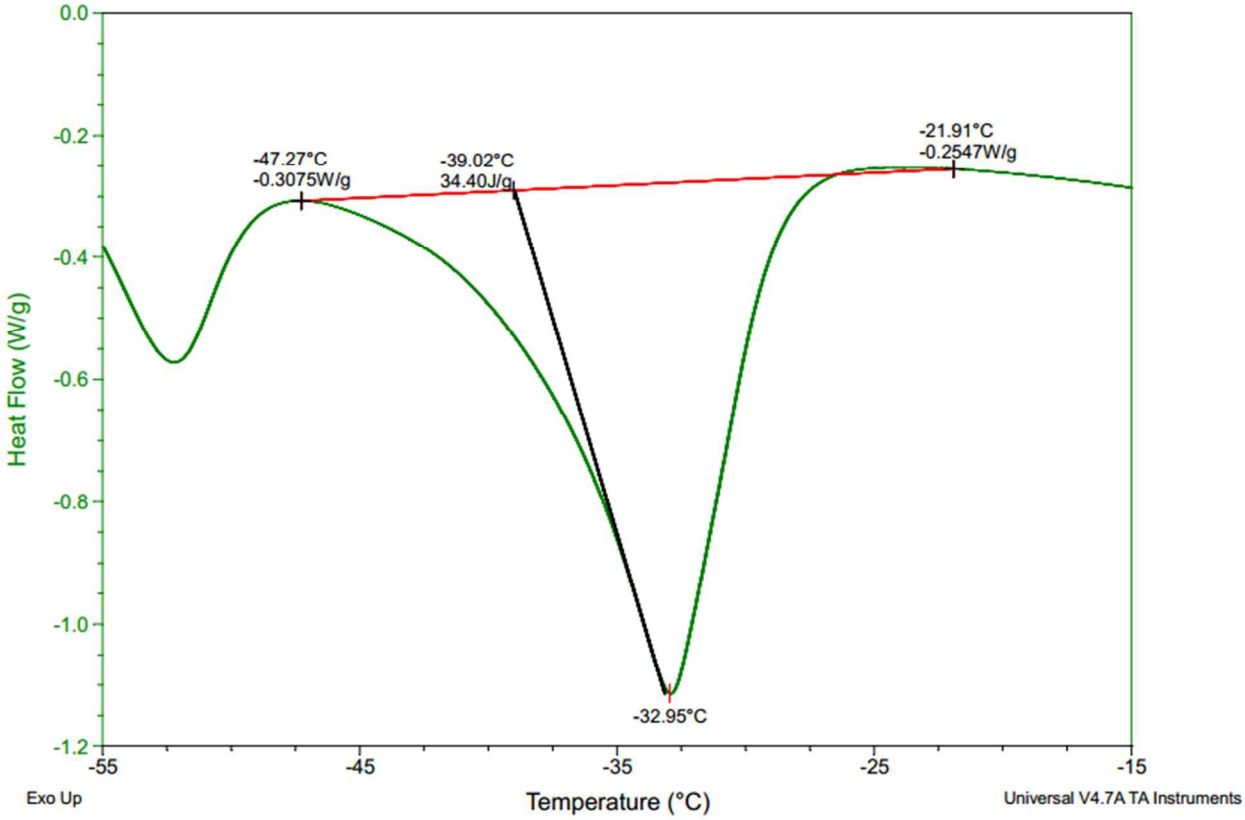
Differential scanning calorimetry (DSC) is one of the measurement methods for determining the thermal stability of biodiesels. It determines the differential heat flow of biodiesel samples either endothermic or exothermic in respect with a reference as a function of temperature. In other words, DSC measures the energy absorbed or released by a sample as it is heated or cooled [34]. In the DSC curves, heat flow (W/g) was plotted against temperature (°C). In the curves, there were variations in transitions and in the inert nitrogen atmosphere the transitions was endothermic which means to be cracked the molecules of the samples were taking heat from surrounding. The melting point and the corresponding enthalpy for those temperatures can be determined from the heating curves and from the cooling curves crystallization point and corresponding enthalpy can be obtained. There was no glass transition found for all of the biodiesel samples [35-39].

In **Figure 5 (a) and (b)**, DSC curves of neat pongamia biodiesel for heating and cooling are shown respectively. It represents all the parameters that are important to analysis the curves. The curves showed that, there was no glass transition phase only melting and freezing phases were visible. So, it was clear from the curves that, in heating curve only endothermic and in cooling curve only exothermic reactions occurred. Moreover, the enthalpy change for melting and freezing were also presented in the curves including the reaction temperature range and heat flow range.

In **Figure 6and 7,** the DSC curves for heating and cooling are presented for neat, non-oxidative pongamia, moringa biodiesels and diesel to compare their changes. For diesel and both neat and non-oxidative biodiesels only cracking reactions occurred and there is no distillation region for both diesel and neat, non-oxidative biodiesels as per the figure. From the heating curves, the melting point of both neat and non-oxidative pongamia were higher than both neat and non-oxidative moringa biodiesels but lower than that of diesel. However, the melting point decreases for moringa biodiesel from neat to non-oxidative mode but increases for pongamia biodiesel. On the other hand, the enthalpy of melting decreases for all of the biodiesels from neat to non-oxidative mode. It was the highest for both neat and non-oxidative moringa biodiesels and the lowest for diesel.

On the other hand, from the cooling curves, it is clearly comprehended that, diesel had the highest and moringa had the lowest crystallization temperature for both neat and non-oxidative mode, among all the biodiesels. However, the crystallization temperature decreases from neat to non-oxidative mode for both pongamia and moringa biodiesels. Meanwhile, for the enthalpy of crystallization it was highest for moringa biodiesel for both neat and non-oxidative mode and

418 lowest for diesel among all other biodiesels. Moreover, the enthalpy of crystallization decreases
419 for all of the biodiesels from neat to non-oxidative mode.



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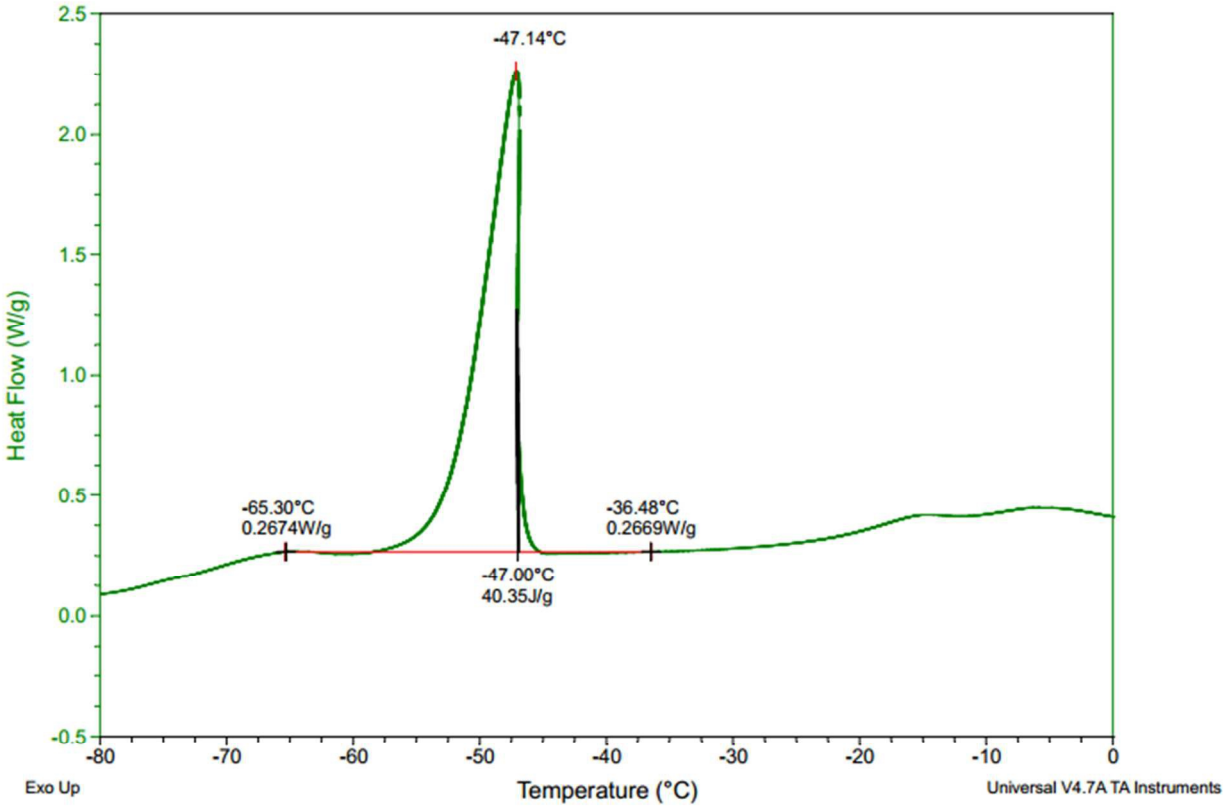
421 **(a)**



422

423 **(b)**

424 **Fig 5: DSC curves analysis of pongamia biodiesel at 10 °C/min heating rate for (a) heating**

425 **scans (b) cooling scans**

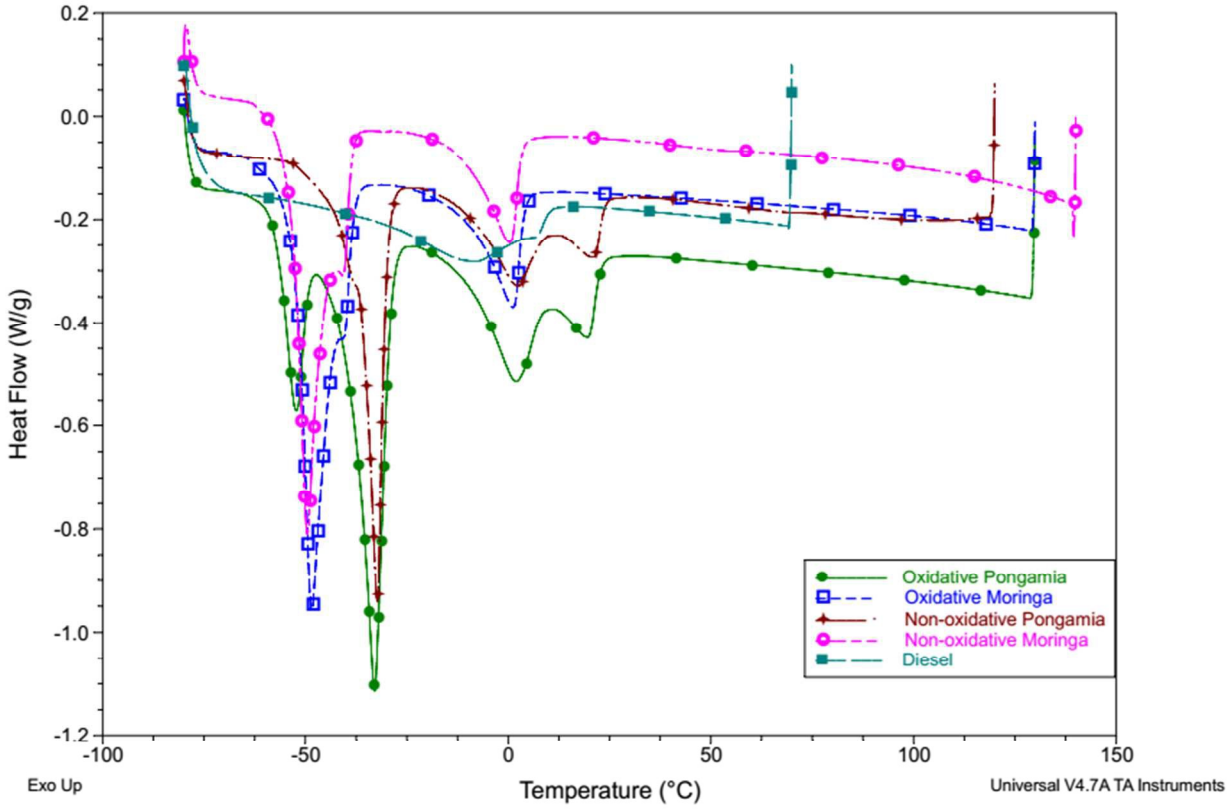


Fig 6: DSC heating curves of neat, non-oxidative pongamia, moringa biodiesels and diesel at 10 °C/min

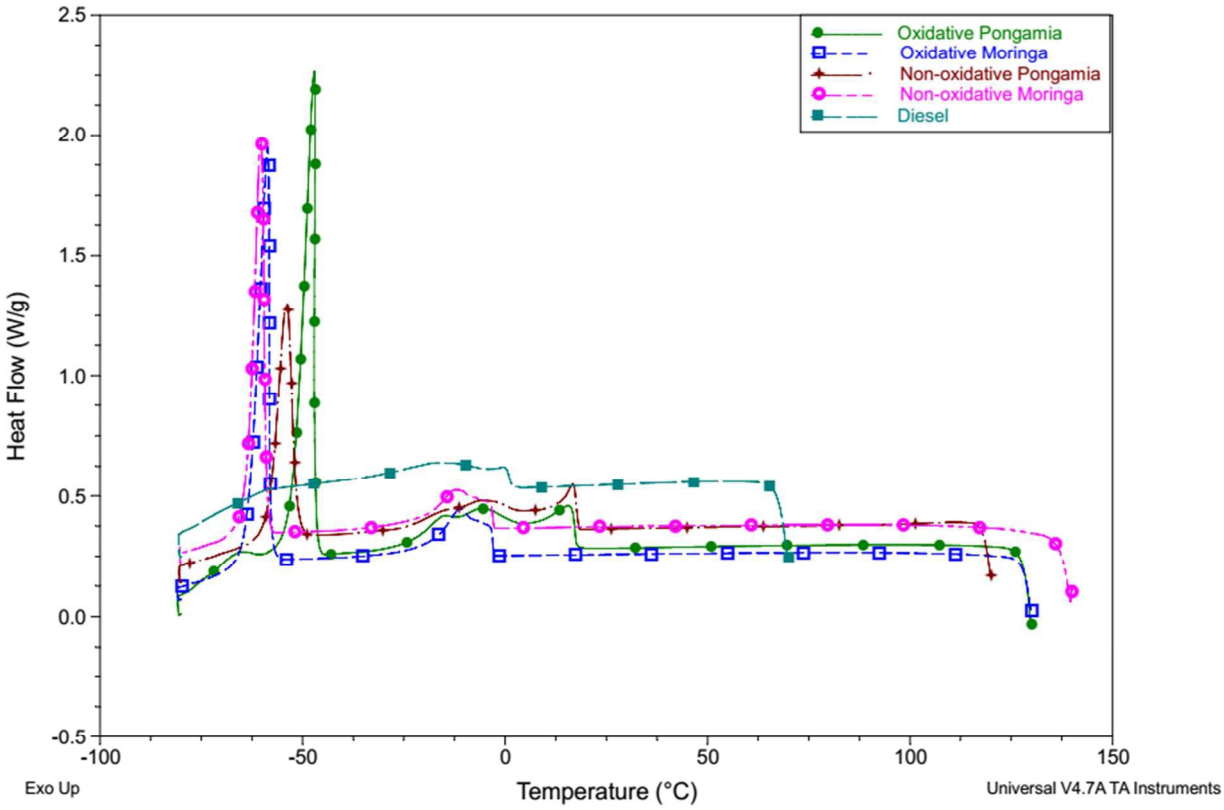


Fig 7: DSC cooling curves of neat, non-oxidative pongamia, moringa biodiesels and diesel at 10 °C/min

In **Table 5**, all the results for heating and cooling curves of DSC for diesel and neat, non-oxidative pongamia and moringa biodiesels are summarized to be clearly understand the comparison among them.

Table 5: Thermal characteristics (DSC) of neat and non-oxidative pongamia, moringa biodiesels and diesel

Parameter	Neat biodiesels		Non-oxidative biodiesels		Diesel
	Pongamia	Moringa	Pongamia	Moringa	
Product mass (mg)	17.7	14	11.2	5.8	15.8
Melting temperature (T_m) (°C)	-32.95	-48.49	-32.31	-49.52	-8.36
Onset temperature for melting (°C)	-39.02	-52.59	-36.84	-53.62	-39.03
Enthalpy of melting (ΔH) (J/g)	34.40	43.58	29.16	41.53	22.82
Temperature range of melting (°C)	-47.27 ~ -22.91	-70.81 ~ -33.34	-54.78 ~ -20.24	-70.90 ~ -25.62	-57.89 ~ -19.60
Heat flow range for melting (W/g)	-0.31 ~ -0.25	-0.09 ~ -0.16	-0.14 ~ -0.19	-0.04 ~ -0.11	-0.26 ~ 0.28
Crystallization temperature (T_c) (°C)	-47.14	-58.65	-53.97	-60.32	-16.49
Onset temperature for crystallization (°C)	-47.00	-58.24	-51.43	-59.02	1.67
Enthalpy of crystallization (ΔH) (J/g)	40.35	40.81	28.68	36.73	21.04
Temperature range of crystallization (°C)	-65.30 ~ -36.48	-74.33 ~ -46.69	-70.46 ~ -42.03	-73.02 ~ -48.12	-58.33 ~ 12.70
Heat flow range for crystallization (W/g)	0.2674 ~ 0.2669	0.09 ~ 0.18	0.13 ~ 0.22	0.11 ~ 0.16	0.28 ~ 0.29

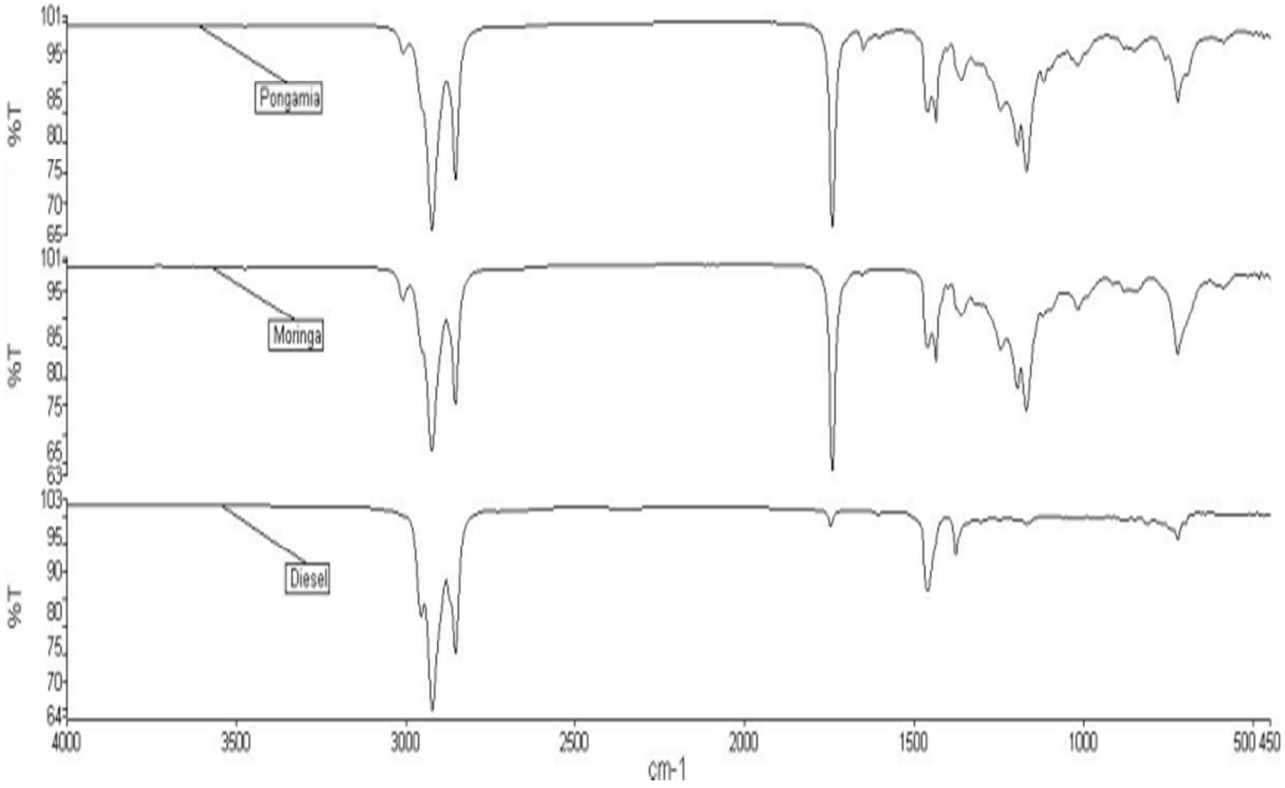
3.7 Fourier transform infrared spectroscopy (FT-IR) analysis of neat and non-oxidative biodiesels

In this study, the FT-IR characteristics of all neat and non-oxidative biodiesels are presented to compare with diesel fuel and also to confirm that the functional groups presented in non-oxidative biodiesels were similar to neat biodiesels and diesel. This proofs the suitability of those biodiesels in the diesel engine without any modification.

In **figure 8** and **9** the IR spectrum of neat and non-oxidative pongamia and moringa biodiesels are shown in comparison to diesel fuel. **Table 6** summarized all the frequency range, functional groups, absorbance peaks and percent transmittance (%T) for all neat and non-oxidative biodiesels along with diesel fuel. There is slight difference in the functional group presents between neat and non-oxidative biodiesels. All the neat and non-oxidative biodiesels contained esters and the absence of any broad peaks of O-H stretching vibration of carboxylic acids in the

455 region of 2500–3300 cm^{-1}indicates the absence of moisture in those biodiesels and diesel.
456 Moreover, the %T decreases from neat to non-oxidative mode for all biodiesels [19, 31, 40].

457



458

459 **Fig 8: FT-IR spectrum of neat pongamia and moringa biodiesels compared with diesel**

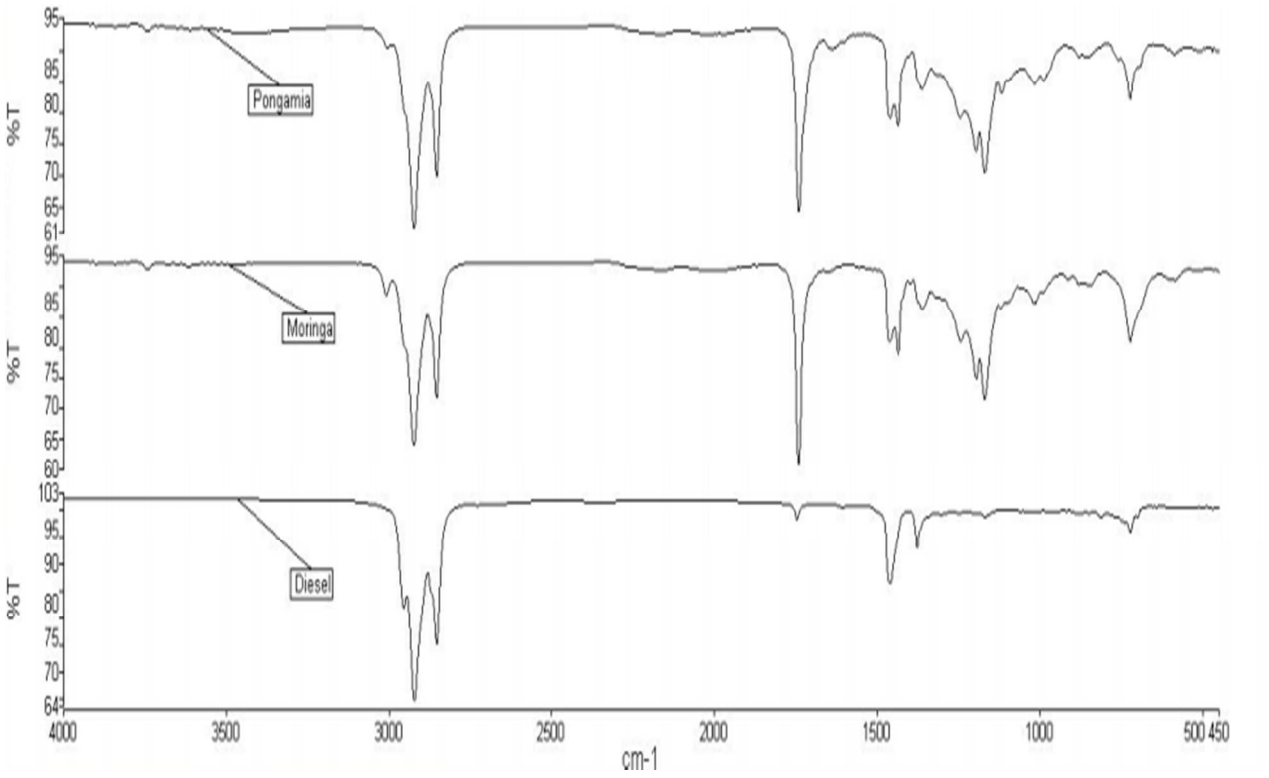


Fig 9: FT-IR spectrum of non-oxidative pongamia and moringa biodiesels compared with diesel

468 **Table 6: IR characteristics region for neat, non-oxidative biodiesels with diesel fuel**

			Neat biodiesels		Non-oxidative biodiesels		
Frequency range (cm^{-1})	**Bond type**	**Functional group**	**Pongamia**	**Moringa**	**Pongamia**	**Moringa**	**Diesel**
2850-3000	C-H stretching	Alkanes	Present (2922.97 cm^{-1}, 65.92 %T) (2853.55 cm^{-1}, 74.08 %T)	Present (2923.49 cm^{-1}, 67.48 %T) (2853.98 cm^{-1}, 75.26 %T)	Present (2923.07 cm^{-1}, 61.90 %T) (2853.62 cm^{-1}, 69.8 %T)	Present (2923.56 cm^{-1}, 64.06 %T) (2854.07 cm^{-1}, 71.82 %T)	Present (2954.89 cm^{-1}, 81.75 %T) (2922.9 cm^{-1}, 64.65 %T) (2853.41 cm^{-1}, 75.18 %T)
1735-1750	C=O stretching	Esters	Present (1741.66 cm^{-1}, 66.58 %T)	Present (1741.53 cm^{-1}, 63.84 %T)	Present (1740.96 cm^{-1}, 64.33 %T)	Present (1741.66 cm^{-1}, 61.03 %T)	Absent
1350-1480	-C-H bending	Alkanes	Present (1462.97 cm^{-1}, 85.31 %T) (1435.92 cm^{-1}, 83.55 %T)	Present (1461.95 cm^{-1}, 85.47 %T) (1435.71 cm^{-1}, 83.09 %T)	Present (1436.12 cm^{-1}, 77.95 %T)	Present (1435.64 cm^{-1}, 79.04 %T)	Present (1462.24 cm^{-1}, 92.94 %T) (1377.22 cm^{-1}, 88.7 %T)
1000-1300	C-O stretching	Esters	Present (1195.72 cm^{-1}, 79.93 %T) (1168.30 cm^{-1}, 75.44 %T)	Present (1244.40 cm^{-1}, 84.92 %T) (1195.63 cm^{-1}, 78.25 %T) (1169.46 cm^{-1}, 74.28 %T) (1120.07 cm^{-1}, 90.71 %T)	Present (1169.09 cm^{-1}, 70.48 %T)	Present (1169.62 cm^{-1}, 71.69 %T)	Absent
700-725	C-H rock	Alkanes	Absent	Present 722.52 cm^{-1}, 84.14 %T)	Present (722.82 cm^{-1}, 82.33 %T)	Present (722.64 cm^{-1}, 81.10 %T)	Present 722.04 cm^{-1}, 95.87 %T)
2500-3300	O-H stretching	Carboxylic acids	Absent	Absent	Absent	Absent	Absent

All the non-oxidative biodiesels satisfied the minimum requirements and had some improvements in their properties with very few exceptions, to be used as an alternative fuel mixed with diesel instead of neat biodiesels. This new form of biodiesels will affect the performance of engine by reducing the NO_x emissions as well as maintain the other performance and exhaust emissions similar to neat biodiesels. However, the non-oxidative biodiesels is an alternative fuel source of the future for commercial use in large scale.

4. Conclusions

In this study, non-oxidative biodiesels were characterized by fuel physicochemical properties, FAME composition, thermogravimetric and IR analysis to compare with neat biodiesels and diesel fuel and find the suitability of those biodiesels to be used in the diesel engine according to stability and quality remarked by that analysis. By considering and optimizing all the properties, it can be said that non-oxidative pongmia has the higher suitability to be used in diesel engine although it has higher viscosity and density than its neat biodiesel but had an improvement on oxidation stability and calorific value. Further research can be done on the improvement of those properties. The findings of this study are summarized here-

- The oxidation of iron bars was higher for pongamia biodiesel than moringa biodiesel.
- The oxygen reduction percentage was higher for pongamia than moringa biodiesel.
- The kinematic viscosity of moringa biodiesel was decreased due to reduction of oxygen content but it increases for pongamia biodiesel. Density increases for both pongamia and moringa biodiesels for the reduction of oxygen content.
- Non-oxidative pongamia had the highest oxidation stability after diesel among other biodiesels.
- Pongamia biodiesel had increased calorific value due to the reduction of oxygen.

- Non-oxidative pongamia had the highest cetane number among other neat and non-oxidative biodiesels and diesel. Lower polyunsaturated fatty acid indicates high cetane number and thus low level of NO_x emissions. Hence, non-oxidative pongamia can reduce more NO_x compared to moringa biodiesel.
- TGA and DSC analysis confirmed the thermal, oxidation and storage stability for both the non-oxidative biodiesels compared with neat biodiesels and diesel. For all biodiesels and diesel, no volatile characteristics were found.
- FT-IR analysis confirmed the suitability of all non-oxidative biodiesels to be used with diesel fuel replacing the neat biodiesels by defining the esters content and transmittance rate of those biodiesels.

5. Acknowledgement

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