Production and Analysis the Properties of Mahua Methyl Ester

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Abstract— Chemically, the methyl ester is mono-alkyl esters of long-chain fatty acids derived from raw vegetable oils. Transesterification is a chemical process between triglycerides of vegetable oil and alcohol (i.e. methanol or ethanol) in the presence of a catalyst to obtain methyl or ethyl ester and glycerol as by-product. In this work, the extraction process adopted to obtain biodiesel from mahua seed oil and analyse the properties of mahua methyl ester (MME). For transesterification process, ethanol and KOH catalysts were used. After extraction of MME, analyse the thermo-physical properties and compared with diesel fuel. Also analyse the Fourier Transform Infrared (FTIR) spectroscopy, Gas Chromatography (GC) and Thermo-Gravimetric Analysis (TGA) were conducted.

I. INTRODUCTION

One of the principal elements to affect the world economy and global politics is the sustainability of petroleum resources, which is a significant source of global energy resource. The world energy demand is increasing faster due to too much use of fuels [1]. The increase of demand forecast forces the researchers to develop the new technology in the field of automobile industry. Diesel engines have high thermal efficiency, high fuel economy, high durability and reliability which have resulted in them becoming the preferred engines in all heavy and many light duty vehicles [2-3]. The high thermal efficiency results from the high power output with lower fuel consumption due to a high compression ratio. However, diesel engines emit lower levels of emissions such as CO and HC when compared with gasoline engines [4]. The most challenging task in diesel emissions controls is the combination of smoke and NO_x emissions. Much research has been done on biodiesel as an alternative renewable fuel since both fuels have similar characteristics to diesel fuel. Biodiesel has special advantages in terms of higher cetane number, lower sulphur, and lower aromatic hydrocarbons. The biodiesel fuel is easy to combine with fossil diesel and can be used in diesel engines without requiring any engine modification [5-9].

Owing to depletion of fossil fuel and increasing environmental anxiety, alternative energy source like biodiesel has been developed. The history of biodiesel is as long as that of the diesel engine itself and the use of vegetable oils were investigated as early as the period when the diesel engine was developed [10]. From the early 1920s, several vegetable oils were investigated, including palm oil, mahua oil, cottonseed oil and castor oil. These early studies showed adequate performance of vegetable oil as fuel for diesel engines [11]. In spite of their performance in diesel engines, vegetable oils produce engine problems when used as fuel in diesel engines. The important drawback of vegetable oils is their high viscosity which produces choking and glazing formation on the injectors that consequence in poor atomization and leads to difficulties such as engine deposits [12-13]. Potential solutions to reduce the viscosity of vegetable oil include transesterification, thermal and catalytic cracking [14].

Therefore, much research has been done on biodiesel as an alternative renewable fuel since both fuels have characteristics similar to diesel fuel. Biodiesel has special advantages in terms of higher cetane number, lower sulphur and lower aromatic hydrocarbons [15-17]. The biodiesel fuel is easy to combine with fossil diesel and can be used in diesel engines without requiring any engine modification. In general, engines fuelled with biodiesel emit a lower level of emissions like HC, CO and smoke, except NO_x, when compared with fossil diesel fuel. In some biodiesel cases, the diesel engine emits high amount of smoke and particulates.

II.   TRANSESTERIFICATION

In the transesterification of vegetable oil mechanism, the carbonyl carbon ion (ester: -RCOOR[1])

undergoes nucleophilic attack by the incoming electrophile of alcohol (alkoxide: -R[2]O-). These combinations give tetrahedral intermediate, which on further proceeding gives (RCOOR[2]). The relative energies of the reactant and product determine the distribution of the intermediate equilibrium species. The mechanism of transesterification is shown in Figure 1. The presence of strong acids influences the reaction by donating a proton to the carbonyl group, making it a strong electrophile while bases present in the reaction removes a proton from the alcohol, making it a strong nucleophile. These formed ions have very much affinity towards each other and thus combine with each other and forms biodiesel and glycerin. The glycerin formed can be removed by water washing to obtain pure biodiesel.
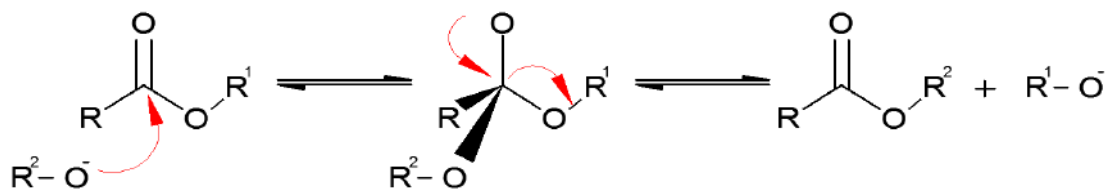

Fig.1 The mechanism of transesterification process

There are many accepted technologies that have been used for the production of biodiesel fuel. Vegetable oils are appropriate to be customized in order to reduce their densities and viscosities, so that the product obtained has appropriate properties to be used as fuels for diesel engine. Transesterification is the process of using an alcohol in the presence of a catalyst such as potassium hydroxide or sodium hydroxide, to break the molecule of the raw vegetable oil into ethyl or methyl esters, with glycerin as a by-product. Vegetable oils with huge amount of FFA are difficult to pass through the transesterification process because it will produce soap formation in the presence of the alkali catalyst. The FFA additionally prevents the separation of methyl ester from glycerol. The di-glycerides are the intermediates in this chemical process. The glycerol layer settles at the base of the container.

In this work, the potassium hydroxide is used as a catalyst and is dissolved into methanol in a reactor. Then, the catalyst/methanol mixture is mixed with the raw mahua

vegetable oil. The final mixture is stirred vigorously for one hour at 60˚C in ambient pressure. It produces two different liquid phases, methyl ester and crude glycerin. Crude glycerin is the heavier liquid and will accumulate at the bottom later after some hours. Phase separation completed within 2-3 hours of settling. Complete settling of methyl ester can take 8-10 hours. Washing the methyl ester is a two-step process. A water wash solution at the rate of 26% by volume of vegetable oil and 1 g of tannic acid/litre of water is added to the methyl ester and stirred. This process is continued until the methyl ester becomes clear. Prepared methyl esters were then blended with neat diesel in different concentrations for making methyl ester blends to be used in the common rail diesel engine for conducting engine tests. The physical and chemical properties of methyl esters and their blends were determined by using ASTM standard methods shown in Table 1. With the intention to measure the properties of the mahua methyl ester and its blend (MME20), the test methods used are as follows.

Table 1 Properties of biodiesel and biodiesel blend samples

Description	Viscosity @40ºC (cSt)	Density @ 15°C (kg/m³)	Flash point (°C)	Calorific value, (kJ/kg)	Cetane number
Diesel fuel	3	815	56	42,000	47
Biodiesel standards(ASTM)	1.9-6	850-900	>130	≥36000	47 to 65
Mahua methyl ester (MME)	4.9	869.8	136	39,950	58

III. FOURIER TRANSFORM INFRARED ANALYSIS

Fourier transform infrared (FTIR) spectroscopy spectra were recorded using a FTIR – Shimadzu 8400 spectrophotometer in the wave range of 4000-500 cm^{-1} with a resolution of 2 cm^{-1}. The mahua biodiesel and its blend were analysed using FTIR spectrophotometry. Figures 2 and 3 represent the spectrographic image of diesel and MME, respectively. From the spectrum, it is clear that the band located at approximately 2900-3000 cm^{-1} is attributed to the C-H stretching of the double bonds of the C-H group which frame the olefins; the bands located at 2918 to 2854 cm^{-1} are related to C-H vibrations of the methylene groups and to extending and reduction vibrations of the methyl group. Figure 4.3 indicate how water vapour absorbs IR between 4000 cm-1 and 3500 cm^{-1} and between 2000 cm^{-1} and 1200 cm^{-1}. The peaks for water vapour coincide with other peaks, such as -OH and -NH group peaks between 4000 cm^{-1} and 3500 cm^{-1} or C=O and -CH$_2$- group peaks between 2000 cm^{-1} and 1200 cm^{-1}. The vapour peaks can affect when analysing infrared spectrum. From the spectrum, it is clear that the water vapour is present in the methyl ester. The extreme peak located at 1740 cm^{-1} relates to the carbonyl radical and is characteristic of esters. The bands located at 1454-1457 cm^{-1} correspond to the irregular stretching of the C-H bond and the irregular bending of the functional group. There is a customary of bands between 1000 and 1300 cm^{-1} that are connected to irregular vibrations of the C-C(=O)-O and O-C-C bonds; the high intensity bands found between 1150 and 1170 cm^{-1} are attributed to the stretching of the methyl group O-CH$_3$ and to the axially irregular deformation of the C-C=O bonds. The bands between 1100 and 1170 cm^{-1}are related to the vibrations of the C-CH$_2$-O group, the uneven stretching of C-O-C and C-C bond stretching. The high-intensity peak located at 721 cm^{-1} corresponds to bends out of the plane of the C-O group and the one located at 1158 cm^{-1} is attributed to the regular angular deformation of the C-H bond of olefins.

From spectrum in Figure 4.3, there are two bands that correspond to the methyl and methylene groups in the area between 2920 and 2870 cm^{-1}; the first peak is recognized as the stretching vibrations of the terminal CH$_2$ group in the olefins. The second peak corresponds to the stretching vibration and contraction of the C-H and CH$_2$ bonds of the methylene and methyl groups. These bands show similarity between diesel fuel and methyl esters. The most pertinent folding vibrations of the methyl groups are consistent with the phase folding deformation (between 1350 and1400 cm^{-1} bands) and the beyond degenerate phase folding deformation (between 1450 and1470 cm^{-1} bands). The folding ascends from twisting and matching that are seen at low frequencies. The methylene group offers scissors vibrations at 1457 cm^{-1}. Based on the above discussion, it is clear that both diesel and MME20 are saturated hydrocarbons and the presence of hydrocarbon group C-H indicates that it has a potential as a fuel for diesel engine. The range frequencies, bond type and associated families are given in Tables 2.
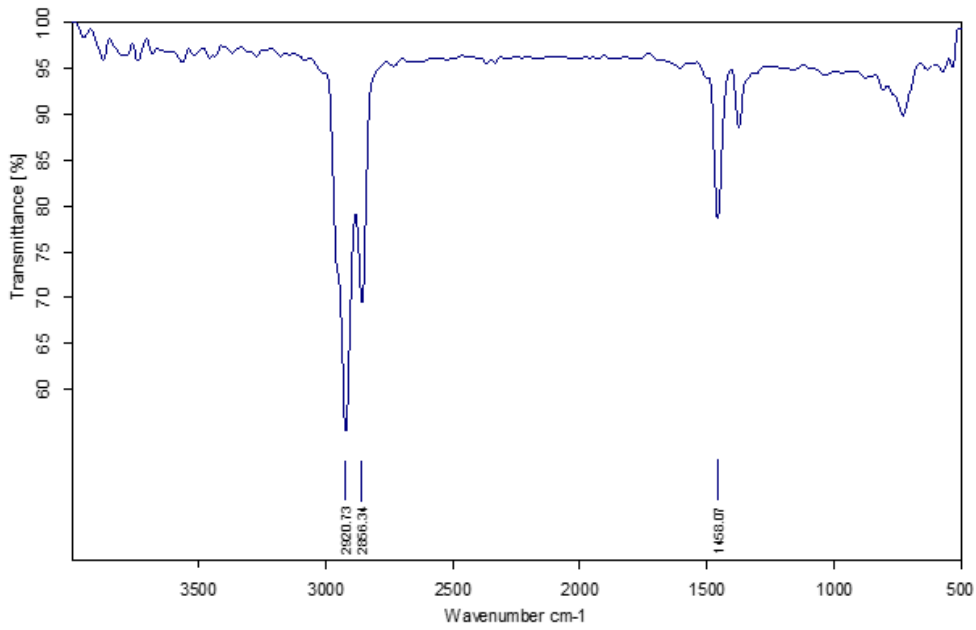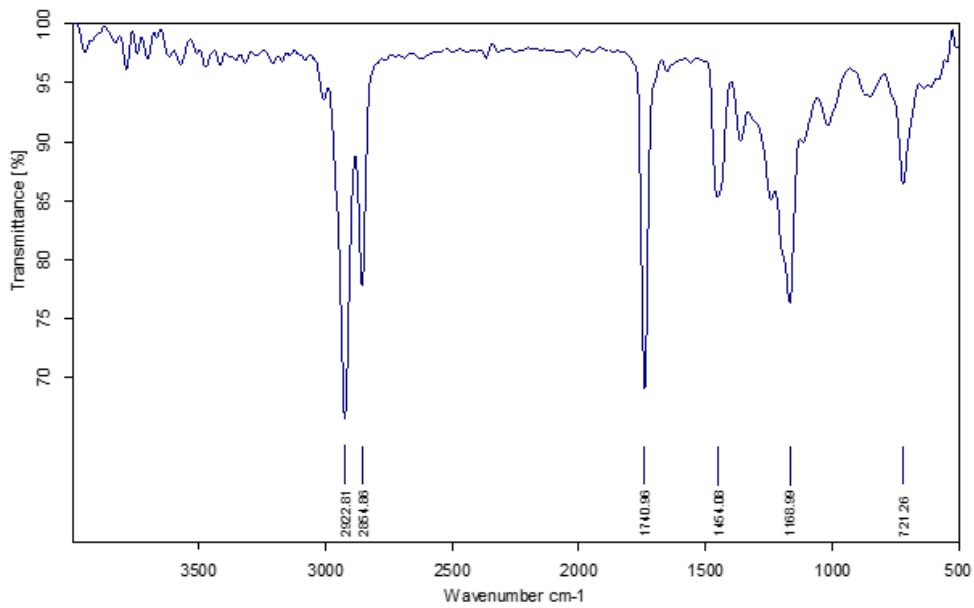
Fig.2 FTIR spectrum of diesel fuel

Fig.3 FTIR spectrum of mahua methyl ester (MME) fuel

Table 2 FTIR analysis of diesel and MME

Diesel fuel			Mahua methyl ester (MME)		
Frequency range (cm^{-1})	Bond	Family	Frequency range (cm^{-1})	Bond	Family
2899 – 2920	C-H stretching	Alkanes	2864-2922	C-H stretching	Alkanes
1458.07	C-H bending	Alkanes	1740	C=O stretching	Aldehydes/ketones
1382	C-X	Fluoride	1454	C-H Bending	Alkanes
716	=C-H bending	Alkanes	721	C-H out-of-plane bending	Alkanes

IV. GC-MS ANALYSIS

Fatty acid methyl esters composition was determined by gas chromatography. From Figure 4, we can see that there are five major peaks indicate the various important methyl esters present in the biodiesel. The first peak in the GC spectrum indicates the methyl hexadecanoate and methyl 14-methyl pentadecanoate in the second peak. Methyl *cis*, *cis*-9,12-octadecadienoate and methyl *cis*, *cis*-10,13-octadecadienoate are indicated in the third peak of the chromatogram while the fourth peak was methyl *cis*-9-octadecenoate.The fifth peak was recognized as methyl octadecanoate and methyl 16-methyl-

heptadecanoate. All the five components separated by GC are probably methyl palmitoleate, methyl linoleate, methyl palmitate, methyl stearate and methyl oleate. This means that the major fatty acids present in the mahuamethyl ester are palmitic acid, palmitoleic acid, oleic acid, linoleic acid and stearic acid. The individual esters were determined from the retention time, noted above the peak of each compounds, with the standard database. Deeper scrutiny of their structure reveals that both are unsaturated hydrocarbon, perhaps with longer hydrocarbon chain length and inherent oxygen in their structure, in the likes of other contemporary biodiesel.
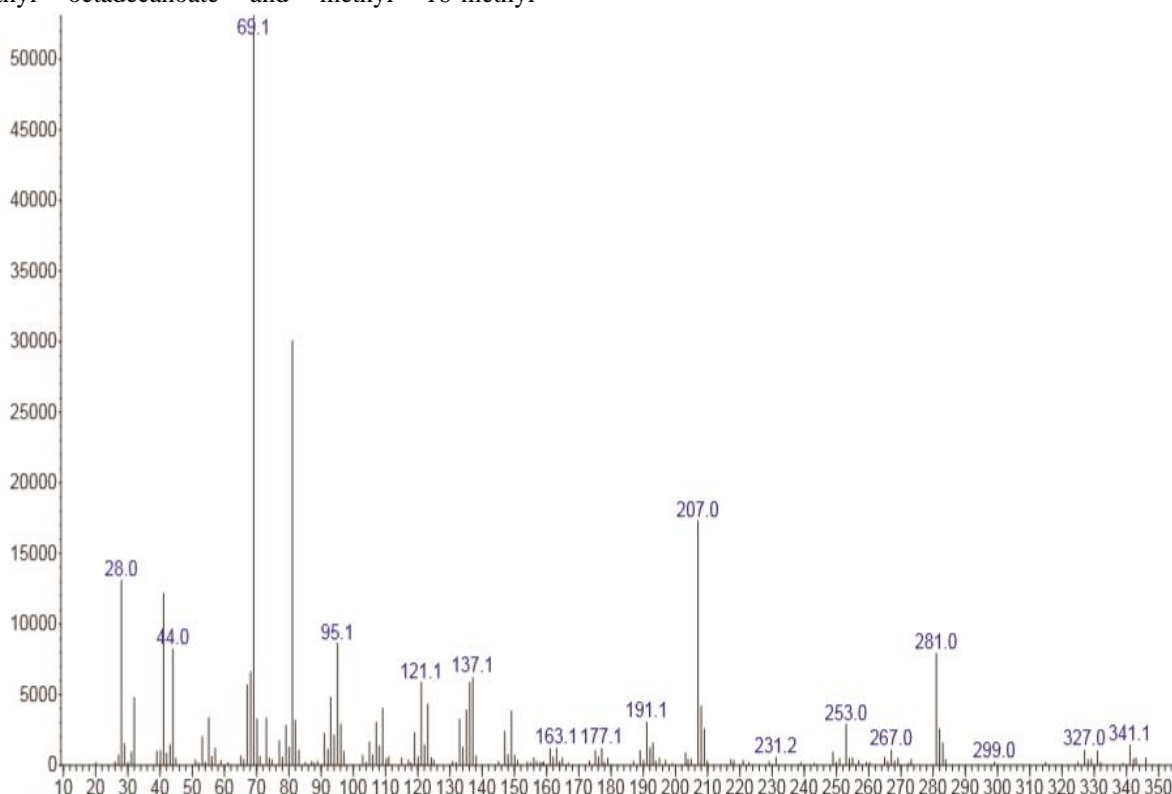

Fig.4 GC-MS of mahua methyl ester (MME)

V. THERMO-GRAVIMETRIC ANALYSIS (TGA)

The TG curve of mahua methyl ester is shown in Figure 5. It is evident that the phase change of mahua methyl ester mainly occurs in the temperature range 200°C-300°C. A huge mass change occurs in this temperature range which will help during the combustion. The DTG curve from first peak temperature (182.7°C) to

second peak temperature (287.5°C) confirms that the percentage of mass transfer per minute is considerably high. In general, fast thermal degradation characteristics can be helpful for thermo-chemical conversion process. The DSC curve also shown in Figure 6 indicates the heat absorption (endothermic) from 299 to 345ºC with the area of 95.3J/kg for the mass change after mass change of 75%.
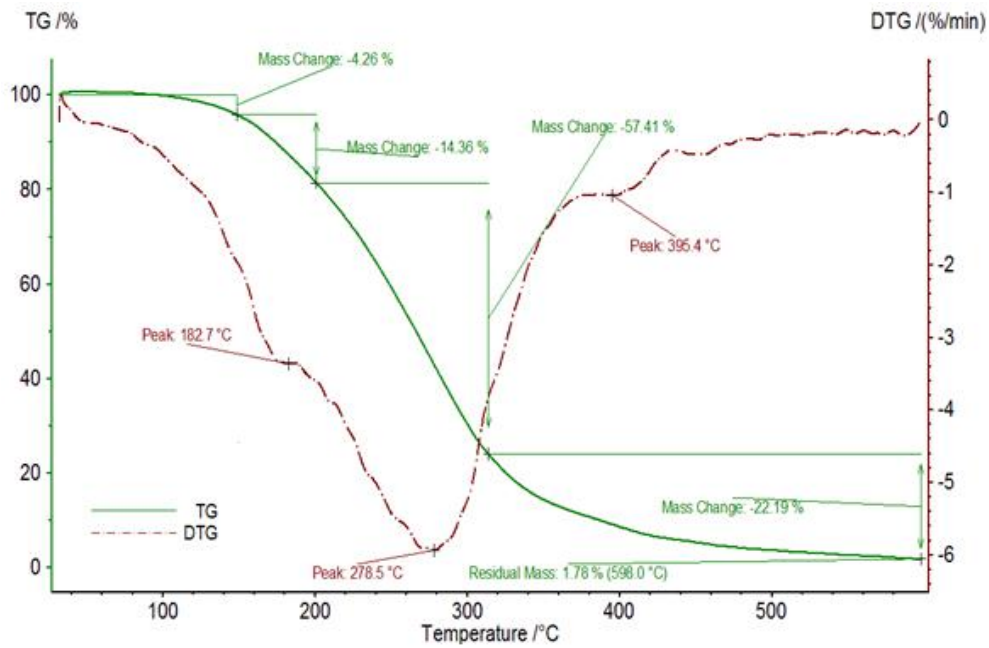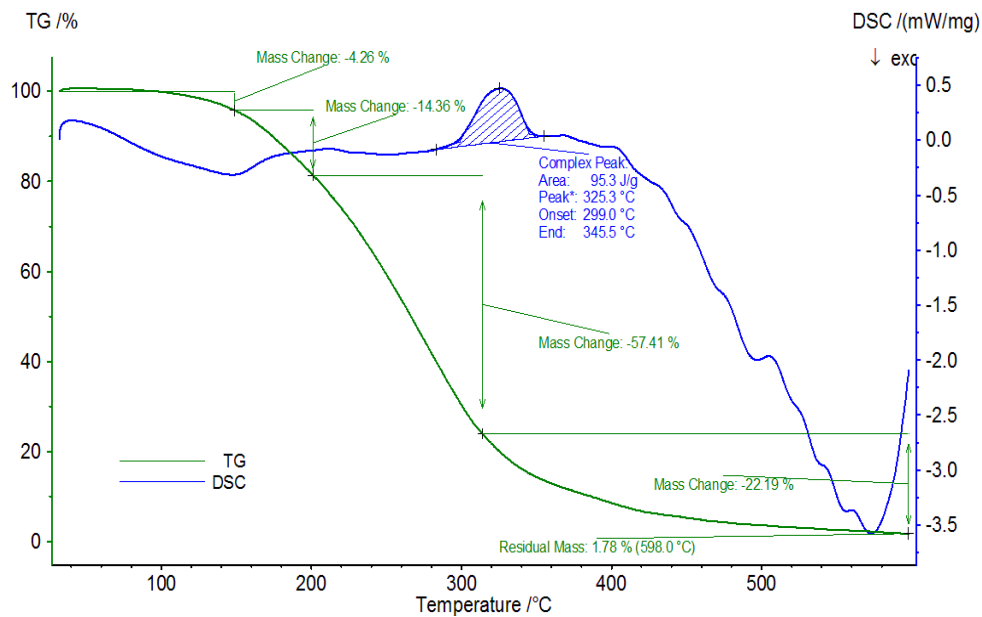
Fig.5 TG and DTG image of MME

Fig.6 TG and DSC image of MME

VI. CONCLUSION

In this investigation, Mahua methyl ester (MME) derived through catalytic transesterification using KOH as catalyst. The viscosity of the MME was slightly higher than that of diesel. The calorific value of MME was closer to the diesel and cetane index was slightly higher. The MME was expensive than diesel. From the results obtained, it is clear that the mahua biodiesel can use in diesel engine directly or blended with diesel. With the latest hikes in petroleum prices and worries regarding fuel availability, there is revitalized interest in biodiesel for Diesel engines.

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