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Use of Fourier Transformation Infrared (FTIR) Spectroscopy for Analysis of Functional Groups in Peanut Oil Biodiesel and Its Blends

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Authors' contributions

This work was carried out in collaboration between both authors. Author AYO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript and managed literature searches. Author EIB managed the analyses of the study and literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: The paper studied how fourier transformation infra-red (FTIR) spectroscopy can be used to monitor homogenous alkali catalyzed alcoholysis of peanut oil and methanol to produce biodiesel. The spectrum generated was used to identify the functional groups in the fuel sample for qualitative analysis and associated type of vibrations. Analyses on biodiesel blends with fossil diesel were also carried out with FTIR spectroscopy.
Place and Duration of Study: Department of Mechanical Engineering, Federal University of Technology, Akure, Ondo State, Nigeria, between December 2014 and March 2015.
Methodology: Biodiesel was produced by transesterifying peanut oil with methanol in the presence of sodium hydroxide as catalyst. Molar ratio of 6:1 (methanol to oil) was followed to shift the reaction to product side for more yield of fatty acid methyl esters (FAME) and the use of catalyst enabled the reaction to proceed faster. The oil and biodiesel were characterized following ASTM standards. The biodiesel obtained was separated from glycerol, washed with distilled water

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and dried. Biodiesel blends with fossil diesel from 10% v/v to 90% v/v in a step of 10% were produced. Samples of biodiesel and biodiesel blends were scan within mid-infrared region of 4000 cm^{-1} – 400 cm^{-1} with fourier transform infrared spectrometer by agilent technologies. The spectra obtained were interpreted and analyzed with the aid of structure correlation chart. A visual basic computer program was developed based on the data analyzed and experience gained.

Results: The results revealed that the biodiesel contained fatty acid methyl esters (FAME). The FTIR spectrum for the biodiesel revealed the functional groups with characteristics bands, C=O, $-(CH_2)_n-$, C-O, C=C and C-H in the spectrum. The absorbance intensity (peak), at a region where strong absorption of FAME occurred in each blend spectrum increases with biodiesel concentration when verified with Beer's law and the R^2 value of 0.992 was obtained to show good fitting. Changes of transmittance with concentration and absorbance of blend spectra explored showed that transmittance decreases with both concentrations and absorbance and the R^2 values of 0.991 and 0.997 were obtained respectively.

Conclusion: Catalyzed complete transesterification was performed on the peanut oil and methanol. The biodiesel produced contained an ester functional group and showed that it can be used as a substitute for fossil diesel in diesel engines. The biodiesel is miscible with fossil diesel and blending of any biodiesel concentration can be obtained. The computer program developed can help to identify the functional groups of similar fuels and associated type of vibrations at a given wavenumber within mid-infrared region.

Keywords: Peanut oil; alcoholysis; transesterification; biodiesel; fatty acid methyl esters (FAME); FTIR spectroscopy.

1. INTRODUCTION

The increasing importance of sustainability in energy production worldwide has led to a recent global effort in the reduction of dependence on fossil fuels and to harness the use of fuels derived from renewable biological sources such as biodiesel produced from plant based crops and animals. There are so many alternative forms of energy and most of them are only capable of generating thermal and electrical energy, whereas more than 40% of the world energy demand is in liquid form [1]. Therefore, the use of biomass as a new source of alternative liquid fuel has attracted a lot of attention lately. One of the options of utilizing biomass as liquid fuel is the use of vegetable oils in diesel engines, however vegetable oils cannot be directly used in these engines due to their high viscosities and in order to utilize vegetable oils successfully in diesel engines, their viscosities must be lowered [1,2].

Among the various methods used for the viscosities reduction in vegetable oils, transesterification and blending are the most common and easiest methods [3]. Transesterification reaction involves chemical reaction between vegetable oil or animal fats (triglyceride) and alcohol with or without catalyst. Transesterification can improve the properties such as cetane number, viscosity, and oxidative stability to the limit required for a standard diesel engine operation [4]. Vegetable oils include soybean oil, rapeseed oil, canola oil, peanut oil, palm oil, recycled frying oil, sunflower oil. Catalyst enables the reaction to proceed faster to yield mono alkyl esters and there are two forms of catalytic process namely; homogenous and heterogeneous. Homogeneous transesterification method has been long regarded as the use of mainly alkalies and acids for the transesterification reaction while heterogeneous transesterification can be described as the use of solid catalysts like WZA (tungsten zirconia – alumina), SZA (sulfated zirconia – alumina) and STO (sulfated tin oxide) for the reaction [2]. Many conventional industrial process favors homogeneous base catalyst such as alkaline hydroxides (NaOH and KOH) due to higher reaction rate and requirement of lower reaction temperature (between 25℃ and 70℃) and pressure (atmospheric) as compared to acid-catalyzed reaction [5]. Homogeneous transesterification is the easiest method to produce biodiesel and the product of transesterification reaction gives biodiesel which consists of fatty acid alkyl esters compounds and by-product called glycerol. The general chemical equation for the transesterification reaction is shown in Fig. 1.

Blending can be produced by mixing of the pure biodiesel, known as B100 with ordinary petroleum diesel in particular percentage concentration. In simple form, Bx refers to the

biodiesel blend with x% being the percentage of biodiesel present in the content on volume basis and, 100 – x% means the percentage of ordinary diesel present). Depending upon the relative amount of fatty acid methyl ester (FAME) compounds present, biodiesel has been shown to have many desirable fuel properties such as being cleaner burning than fossil fuel, contain lower sulfur content, and help in the reduction in engine wear [6]. Biodiesel being an emerging renewable fuel has been proved to be environmental friendly, biodegradable and less toxic, its combustion products have reduced level of particulates of carbon oxides, sulphur oxides and nitrogen oxides. It is capable of substituting fossil diesel; it is receiving much attention in the world as a means of preventing global environmental problems caused by the use of fossil diesel. Also, due to the concerns over the availability of recoverable fossil fuel reserves, attention has been shifted to the biodiesel production as an alternative to diesel. The finished biodiesel can be used in the compression ignition engine after quality control and without any modification in the engine [2,4,7,8]. Several researchers have worked in various capacities on FTIR spectroscopy analysis of different vegetable oils. Alexsandr, 2014 [6] applied FTIR spectroscopy analysis to verify the FAME contents of biodiesel blends. FAME concentrations were found using the regression analysis with correlation coefficient of $\geq$0.999. Precision in terms of percent relative standard deviation and accuracy in terms of percent relative error were also estimated in his study. Meanwhile, the study carried out research on commercially available biodiesel which its feedstock was unknown, the analysis of the pure biodiesel from which the blends were produced could not be found, and the biodiesel yield from the feedstock used in his study was unknown. Another major contribution was from Ndana et al. [9]. They used FTIR spectroscopy to evaluate the possible functional groups in each biodiesel produced from the oils of three seeds; *Ricinus communis, Hevea brasiliensis and Jatropha curcas*. The responses of their functional groups were characterized in terms of stretching and bending. The problem with their study was the inadequate information about the type stretching or bending that existed within the functional groups.

The concerns over the scarcity of petroleum and availability of their reserves as well as awareness on their negative global environmental effects like CO_2, SO_2 and other particulate emissions led to the recent efforts to facilitate and utilize alternative non-petroleum based fuels and one of such fuels is the biodiesel for diesel engines. Problem mostly arise on the choice of feedstock selection for biodiesel production which depends on factors like; availability, country's geographical, climatic and economy conditions, abundance and how it is able to displace fossil diesel.

Peanut is a potential oil crop for biodiesel production because it contains high amount of oil when compared to other feeds tocks for biodiesel production. Its oil has about 40%-50% of mass of dried nuts when compared to other feeds tocks [10]. Its abundance and low cost in Nigeria can necessitate its usage for biodiesel production. It is affordable in the market and cheap when compared with other feeds tocks.

Many methods exist for determining the quality of finished biodiesel. The use of gas chromatography (GC) takes more time in sample preparation which involves derivatization of samples before the GC scan. Near Magnetic Resonance (NMR) and Mass Spectroscopy (MS) are another powerful tools used by researchers in sample analysis. NMR and MS are advanced technologies that are too costly, their analysis results require further studying by experts to enable for right interpretations before it can be guaranteed for quality control of biodiesel and its blends [11]. The use of Optical spectroscopy in sample examinations has limitations on the amount of functional groups in can detect for qualitative analysis, this makes the method less efficient in sample analysis. Most compounds, especially organic molecules are found to respond more to infra-red region of electromagnetic radiation through vibrations. When molecules absorb infrared radiation, the atoms or group of atoms in them vibrate at their chemical bonds, they can stretch, contract or bend. Each type of vibration occurs at unique frequency called wavenumber. This is why infrared spectroscopy is a type of vibrational spectroscopy which quickly collect more information about sample analysis when compared to other spectroscopy methods. Even in terms of sample preparation, it is efficient because it does not involve rigorous sample preparations when compared to other spectroscopy methods. The dispersive type of infrared instruments have some shortcomings in sample analysis. These instruments separated individual frequency of energy emitted from infrared source through the use of grating while

detector only measures the amount of energy at each frequency which passed through the sample. There is always the need for measuring all infrared frequencies simultaneously rather than individual as in dispersive method for sample analysis, the use of FTIR can overcome this limitation through the use of optical device called interferometer that provides a unique type of signal which has all infrared frequencies encoded into it. FTIR Spectroscopy is a powerful scientific tool which have an incorporated computer system and which can be used for analyzing the biodiesel and biodiesel blends. The infrared spectrum produced represents the fingerprints of the sample with absorption peaks which correspond to the frequency of vibration between the bonds of the atoms making up the biodiesel. Since each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in positive identification (Qualitative Analysis) of every different kind of material, in addition, the size of the peaks in the spectrum is a direct indication of material present leading to the quantitative analysis [12]. In FTIR spectroscopy, analysts require the plot of intensities at each individual frequency in order to quick sample identification. The measured signal is further processed by decoding the individual frequency which is accomplished through a mathematical technique called fourier transformation, this transformation is performed by the incorporated computer system of the FTIR spectrometer unit/device which lastly presents the user the spectra result.

The objectives of this research is to study product (peanut oil biodiesel) of catalyzed transesterication (alcoholysis) process of peanut oil and methanol through the use FTIR spectroscopy and analyze the functional groups and associated vibrations for qualitative analysis. FTIR spectroscopy was used to monitor the completeness of transesterification reaction in the biodiesel. This study is expected to reveal important fatty acid methyl esters, characteristics functional groups and associated type of vibrations for the quality control of peanut oil biodiesel and as part of its tendency to replace fossil diesel in diesel engines without major modifications and as alternative diesel fuel in Nigeria. The study also covers analysis of the biodiesel blends (with common fossil diesel in Nigeria) with FTIR spectrometer in the region where strong absorption of fatty acid methyl esters exist for quantitative analysis.

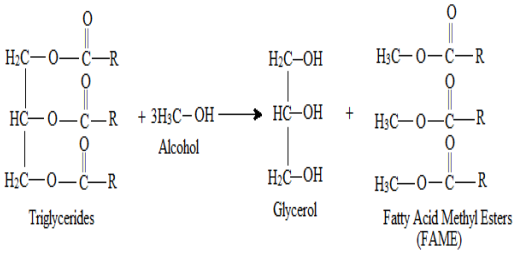

Fig. 1. Transesterification reaction of triglycerides and alcohol [6]

2. MATERIALS AND METHODS

2.1 Materials

Refined food grade peanut oil was used for the biodiesel production. The oil was obtained at Tapa local market, Central Mosque area, Ado Ekiti. The chemicals used in this present study are analytical grade, they include: Sodium hydroxide, Methanol, sodium thiosulphate, carbon tetrachloride solution, wij's solution (Iodine monochloride), potassium iodide solution, phenolphthalein, indicators, powdered iodide, potassium hydroxide solution, sodium hydroxide (NaOH). These chemicals were obtained at Pascal Delson Scientific Limited, Akure. The equipment used are: Separating funnel, thermometer, mechanical stirrer and reaction vessel, sample bottles, syringes, hollow needles, burette, pipette, beakers, conical flask and measuring cylinders. All these were also bought at Pascal Delson. The analytic apparatus used was fourier transformation infra-red spectrometer (FTIR), Agilent Technologies with model 4100 Excoscan. All experiments were carried out in Central Research Laboratory, Federal University of Technology, Akure, Nigeria.

2.2 Methodology

2.2.1 Biodiesel production procedures

Sodium methoxide (Mixture of methanol and NaOH) was first prepared by adding 2% weight of oil of NaOH to 175 ml of methanol and stirred at 300 rpm until it dissolved completely for about two minutes in the reaction vessel. Prior to this, 700 ml of oil had been preheated to a temperature range of 60℃ and was poured gently into the glass bottle reactor containing Sodium methoxide. The mixture was stirred at 500 rpm for 2 hours at ambient pressure. The mixture was then poured into the separating funnel and stored for 24 hours for the mixture to separate into two liquid phases, the denser

phase (higher density), glycerol which was the reaction by product moved to the lower part of the separating funnel and methyl esters (biodiesel) at the top. The biodiesel was separated by running the glycerol off into another beaker via the base with the help of stopcock. To obtain pure biodiesel, excess alcohol and catalyst were removed by washing with warm distilled water by stirring gently for about 2-3 minutes. The top layer was drained off and the biodiesel was dehydrated with anhydrous sodium sulfate. The clear biodiesel mixture was finally obtained which consist of fatty acid methyl esters (FAME).

2.2.2 Biodiesel yield (Y %)

Biodiesel yield was calculated from biodiesel and oil weights using the equation 1.

$$Y\,\% = \frac{\text{weight of biodiesel produced (g)}}{\text{weight of oil peanut oil used (g)}} \times 100 \quad (1)\ [13]$$

2.2.3 Blends production

Ten biodiesel blend samples were prepared from the raw biodiesel produced. The raw biodiesel is called B100. The blends are: B10, B20, B30, B40, B50, B60, B70, B80, B90 and B95. They are produced by mixing uniformly ordinary fossil diesel with preheated (40℃) pure biodiesel on percentage by volume. Measuring cylinder (calibrated in ml) was used to measure the volume of each constituent into 60ml capacity bottle followed by shaken the bottle for 5 minutes to allow for the uniform mixing. The volume of each blend prepared was 60 ml.

2.2.4 Samples collection method

Each sample was collected into 10 ml sample bottle using 10ml capacity syringe. In this study, one pure biodiesel sample and ten biodiesel blend samples were prepared for the FTIR test.

2.2.5 Peanut oil and biodiesel properties

The Physiochemical properties of the oil and peanut oil properties were determined according these ASTM methods: acid value (ASTM D664); cetane index (ASTM D976); saponification value of the oil (ASTM D5558); flash point (ASTM D92); kinematic viscosity (ASTM D445); pour point (ASTM D97) cloud point (ASTM D2500); specific gravity (ASTM D4052) [14].

2.2.6 Fourier transform infrared analysis

The mid – infrared spectra of biodiesel and biodiesel blend samples were obtained in a fourier transform spectrometer by agilent technologies, FTIR 4100 excoscan at The Federal University of Technology, Akure, Ondo State, Nigeria. The supporting software was microlab software and the FTIR spectrometer employed diamond attenuated total reflectance (ATR) sample interface system. No sample cell was needed and the method of sample introduction was by simple intake on the diamond interface. Each spectrum was taken within few seconds at the resolution of 4 cm^{-1}, in the region of 4000 cm^{-1} – 400 cm^{-1} and not more than 0.5 ml per sample. Cleaning was done with tri-solvent mixture of acetone – toluene – methanol, this was employed to clean the sample crystal before background collection. The scan results were obtained on the incorporated computer system as spectra.

2.3 Data Interpretation

2.3.1 Analysis of the Biodiesel spectrum

The peaks of biodiesel spectrum were identified and interpreted. This led to the identification of functional groups in the molecules of the biodiesel with the aid of structure correlation chart.

2.3.2 Analysis of the biodiesel blends

The spectra of the biodiesel blends obtained were interpreted. The absorbance and transmittance peak heights of each of the biodiesel blend sample were taken at the region of 1741 cm^{-1} – 1750 cm^{-1} where strong absorption of fatty acid methyl esters exist. The datas obtained were used for the calibration plot between absorbance and concentration according to beer's law. Plots between transmittance, absorbance and concentrations of biodiesel sample were also obtained respectively to determine their relationships.

3. RESULTS AND DISCUSSION

3.1 Biodiesel Yield (Y %)

The biodiesel yield was calculated from the equation 1:

$$Y\,\% = \frac{W_{biodiesel}}{W_{oil}} \times 100$$

$$Y\,\% = \frac{616.75\text{g}}{635.50\text{g}}$$

$$Y = 97.05\%$$

3.2 The Properties of the Oil and Biodiesel

The Table 1 shows the properties of the peanut oil and biodiesel produced by transesterification. The Cetane index relates to the readiness of the fuel to self-ignite when exposed to the high temperatures and pressure in the diesel engine combustion chamber. The cetane number affects a number of engine performance parameters such as combustion, stability, drivability, white smoke, noise and emission of CO. The number is also indicative of the relative fuel stability and guarantees good control of the combustion, increasing performance and improving cold starts. The value obtained in this study was above ASTM acceptable minimum standard, this indicates ignition delay and better ignition properties [15-17].

Kinematic viscosity of the biodiesel produced was obtained to be 5.32 mm^2/ s and for oil was 36.84 mm^2/s. The value obtained for peanut methyl ester falls within the range of 1.9-6.0 mm^2/s as recommended by ASTM DS 6751. However, the value obtained shows that the transesterification reaction has successfully reduced the viscosity of oil from 36.84 mm^2/s to 5.32 mm^2/s and as such increases its tendency to flow.

Since kinematic viscosity described the resistance of a fluid to flow under gravity and it is important in determining optimum handling, storage, and operational conditions. High viscosity can cause fuel flow problems and lead to stall out or fuel pump failure [5].

A higher value of flash point decreases the risk of fire. It is described as a tendency of a sample of fuel to form a flammable mixture with air [16]. The value of flash point measured in this study was 173 for biodiesel and 273 for oil. The value obtained is found to be greater than the value specified by ASTM D6751. The value for biodiesel shows that it is not flammable.

Cloud point is a fuel property that is particularly important for the low temperature operability of biodiesel fuel. Initially, cooling temperatures cause the formation of solid wax crystal nuclei that are small in scale and invisible to the human eye [16]. The temperature at which crystal accumulation is extensive enough to prevent free pouring of fluid is called its pour point. The values of cloud and Pour points of peanut methyl ester produced in the present work can influence the cold weather applications.

Pour and cloud point depressors can be used to reduce problem associated with cold weather applications of the biodiesel fuel. According to ASTM standard D6751, no value is given for cloud and pour point and the value obtained in this work is according to [16].

Table 1. Properties of peanut oil and biodiesel

Properties	Experimental values		Standard value		Test method	
	Peanut oil	Biodiesel	AOCS 1998 for oil	ASTM D6751 for biodiesel	Oil	Biodiesel
Specific gravity at 20℃	0.912	0.89	0.890 – 0.915	0.87 – 0.90	ASTM D4052	
Cloud point (℃)	12.8	5.0	-	-	ASTM D2500	
Pour point (℃)	-6.2	-1.11	-	-	ASTM D97	
Kinematic Viscosity ($mm^2\,sec^{-1}$) (25℃)	36.84	5.32	32 – 38	1.9 – 6.0	ASTM D445	
Flash point (℃)	272	173	-	130 min	ASTM D92	
Saponification value (mg KOH/g oil)	189.24	-	187 – 196	-	ASTM D5558	-
Free fatty acid (%)	0.312		<1%			
Iodine value (g/100 g)	87.24		85 – 90			
Peroxide value (meq/kg)	0.66	-	0.059 – 22.25	-	-	-
Acid value (mgKOH/g)	2.390	0.45	2.174 – 2.610	0.8 max	ASTM D664	
Cetane index	41.8	54.0	-	47 min	ASTM D976	
Colour	Yellow	Light Yellow	Yellow	-	-	-

The acid value of the produced biodiesel and peanut oil are as shown in the Table 1. The acid number correlates to the fuel's long-term stability and corrosiveness, the smaller the acid value, the higher the quality of the fuel. The acid value of the biodiesel produced is lower than recommended standard value ASTM D 6751.

The saponification value is a measure of the tendency of oil to form soap during transesterification reaction. It is defined as the number in milligram (mg) of KOH required to saponified 1 g of the sample [18]. The saponification value obtained for the sample of refined peanut oil is lower compared to 188-195 recommended by AOCS standard (1998). The high saponification values indicate the presence of high percentage of fatty acids which might lead to soap formation and hence low biodiesel yield.

The peroxide value and specific gravity obtained for the oil were also found to be between AOCS, 1998 standard.

The acid number correlates to the fuel's long-term stability and corrosiveness, the smaller the acid value, the higher the quality of the fuel. The acid value of the biodiesel produced was lower than recommended standard value ASTM D 6751.

Free Fatty Acid (FFA) value of the oil sample used in this research was 0.312%, and was found to fall within the AOCS standard having oil maximum free fatty acid content <1% [19]. Different literatures also revealed that for groundnut oil to be fit for biodiesel production its free fatty acid content should be <2%, this is to enable efficient conversion of the oil into biodiesel [18].

3.3 FTIR Spectra Interpretations

The biodiesel spectrum is shown in Fig. 2 and the lists of functional groups identified were shown in Table 2.

3.3.1 Interpretation of functional groups in the biodiesel produced

Table 2 shows peaks identified from the spectrum of biodiesel in Fig. 2. The region 678.55 cm^{-1} – 960 cm^{-1} indicate the presence of =C-H functional groups. They possess bending type of vibrations appearing at low energy and frequency region in the spectrum and they are all double bounded. They are attributed to olefinic (alkenes) functional groups in the biodiesel and they are unsaturated. They are part of fatty acid methyl esters with unsaturated bond in the biodiesel, such as methyl oleate and methyl linoleate [13,20].

The specific peak at 721.4 cm^{-1} which was overlapped by =C-H groups, has the rocking mode of vibrations. This group indicate methylene functional group in the biodiesel ($-(CH_2)_n-$). The rocking mode of vibration further help to know more about the basin structure of FAME component in the biodiesel and it is an indication that the biodiesel consists of long-chain aliphatic structure [13].

The characteristics peaks found in the region 1030.98 - 1240.08 cm^{-1} indicate stretching vibrations of C-O and C-O-C. They can also indicate the bending vibration of $O-CH_3$ in the spectrum [9,13,21,22].

The band region of 1377.23 – 1465.03cm^{-1} can be ascribed to the bending vibration of C-H methyl groups in the fuel, while the band at 1602.94 cm^{-1} is ascribed to C=C bending vibrations in the biodiesel [10,23].

The characteristics peak at wavenumber 1745.89 cm^{-1} which is strongest in the spectrum is attributed to C=O groups with the stretching mode of vibration. These groups indicate the presence of carbonyl functional groups in the biodiesel. The groups indicate the conversion of triglycerides in the oil to methyl esters [9,13,20, 23].

The peaks at 2850.41 cm^{-1} and 2924.32 cm^{-1} indicate symmetric and asymmetric stretching vibrations of C-H alkane groups respectively. They could be methyl (CH_3) or methylene groups in the esters chains of the biodiesel and they require high energy to cause stretching vibrations within their bond when compared to the ordinary C-H bending vibrations of alkene groups detected at low energy and frequency region [10, 20].

The peak at 3007.06 cm^{-1} is attributed to the stretching vibration of =C-H alkene groups. They are detected above wavenumber 3000 cm^{-1} in the spectrum compared to corresponding alkane C-H stretching groups detected below 3000 cm^{-1}. The peak at 3500 cm^{-1} with stretching mode of

vibration is ascribed to the presence of O-H groups. They are single bounded and at high energy region in the spectrum [10,20,24-26].

3.3.2 Analysis of the biodiesel blends

The peaks inspected for the blends show variations at 1745.83 cm^{-1} (C=O stretching), 1030.98 cm^{-1}, 1117.54 cm^{-1}, and 1170.23 cm^{-1} (C – O alkoxyl stretching), they are visible in these blends but their intensities vary according to the concentration of the biodiesel. These peaks increase with the concentration of biodiesel present in each of the blend and this shows that the fatty acid methyl esters (FAME) is an indication of the amount of the biodiesel present in each of the biodiesel blend with petroleum diesel since FAME exhibits its appearance at 1745.83 cm^{-1} and 1170.23 cm^{-1} - 1030.98 cm^{-1} [6]. Methyl esters also show their absorptions characteristics in the peak around 1820 – 1680 cm^{-1} which is typical for carbonyl absorption and this range is not observed in the convectional diesel fuel [7].

Also discovered are variations in the intensities within the region of 678.55 – 721.41 cm^{-1} (=C – H bending; cis - disubstituted alkenes and aromatic). Their intensities were also found to increase with biodiesel concentration in each of the spectrum obtained. The intensities of peaks at 2850.41 cm^{-1}, 2924.32 cm^{-1} and 3007.06 cm^{-1} (C – H alky and alkenes stretching) are found to remain unchanged in each of the blend sample which is an indication that both petroleum diesel and biodiesel contain these functional groups appearing within the frequency range [6].

The blending of biodiesel with fossil diesel can help to reduce cold flow problems associated with methyl esters (B100) which is as a result of their feedstock. Also, it helps to reduce the effects of degradation and breaking down of certain parts made of elastomers (gaskets, hoses, seals, and o-rings) in diesel engine. Blending was also discovered to further decrease the bound and free glycerol left after transesterification reaction which can settle in the storage tank to form very viscous mixture and which can affect fuel flow and may cause blockage of filter and consequently restrict fuel flow. Such fuels are prone to coking and may thus cause the formation of deposits on injector nozzle, piston and valves that can affect fuel economy [4].

The values measured from the blend spectra at the region where strong fatty methyl esters (FAME) occur in the biodiesel blends are shown in Table 3. Peak height values of absorbance (A) from the blend spectra were used to fit straight line relationship between absorbance (A) and concentrations (C) and R2 value of 0.992

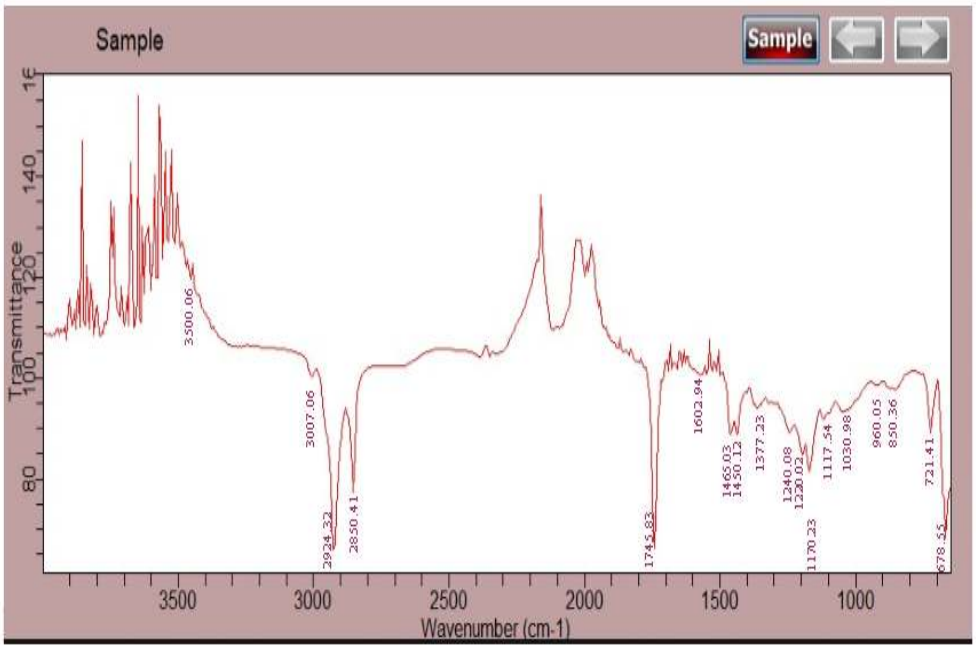

Fig. 2. FTIR spectrum of biodiesel

Table 2. Functional group frequencies of peanut oil biodiesel identified

Wave number (cm^{-1})	Types of vibration	Functional groups	References
3500	Stretching	O – H (alcohols)	[9,20,23,24]
3007.00	Asymmetrical stretching	=C-H (alkenes)	
2924.32	Asymmetrical stretching	C-H (alkanes)	
2850.41	Symmetrical stretching	C-H (methylene)	
1745.83	Stretching	C=O (ester carbonyl functional group in FAME)	[10,13,20]
1602.94	Bending	C =C	[10,23]
1377.23-1465.03	Bending and rocking	C – H (methyl or $–CH_3$)	
1030.98 - 1240.08	Stretching	C-O alkoxy esters, ethers and C-O-C	[9,20-25]
960.00	Out of plane bending	=C-H (trans-disubstituted alkene)	[9,10,20,23,27]
850.36	Out of plane bending	=C-H alkenes	
721.41	Bending of alkenes and overlapping of rocking vibration of methylene	=C-H and $–(CH_2)_n$ methylene groups (cis disubstituted alkenes and aromatic)	
678.55	Out of plane bending	=C-H cis-disubstituted alkene and aromatics	

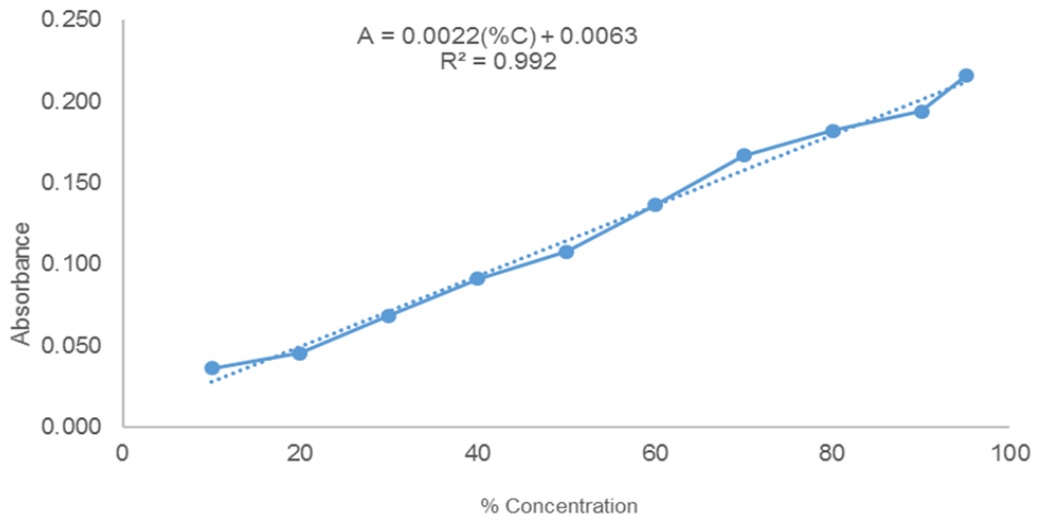

Fig. 3. Graphical curve fitting between absorbance and % concentrations of biodiesel blends

was obtained. Microsoft excel was used for the calibration plots and was in line with beer's law (A = KC) and good fit was obtained. Plots between transmittance (T) against concentrations and absorbance were also made and the R2 value of 0.991 and 0.997 were obtained respectively. These plots are shown in Figs. 3- 5.

3.4 Computer Program Development

The results of the data interpreted in this research were used to develop a computer program application, functional group identifier that run on visual basic. Proper syntaxes were collected with the help of literatures [28,29]. The graphics user interface of the application is as shown Fig. 7.

The program is compatible with window 7 and 8 computers with Microsoft.NET Framework installed on them.

The program has input where the user can enter the wave number; menu which comprises of check, exit and reset buttons respectively; and 7 checkboxes, when checked can be used to quickly preview general table of infrared (IR) absorptions, IR flowcharts of functional groups, alkenes region functional groups, carbonyl

regions, general chart of functional groups, spectrum of peanut oil biodiesel and blends interface. The input of the program has the limit range of wave number (400 cm^{-1} – 4000 cm^{-1}) it can assess, it only works within mid-infrared range of wave number and any number entered which is out of this range will bring out message indicating out of range. This program can be used to predict by displaying possible functional groups of any wave number within mid-infrared region and associated type of vibrations. After the result is displayed, the reset button, which appears after is result is displayed, can be pressed to return the program to the default settings. Apart from entering the number, any of the 7 checkbox can be checked to preview any general chart. The reset button always return the program to the default.

This program can help in monitoring the quality of biodiesel through functional groups correlation with the inputted wave number within the mid infrared region. It is easy and quick since the user needs to enter the wave number and see the displayed result. Fig. 6 shows the flowchart of the program developed while Fig. 7 is the graphics user interface.

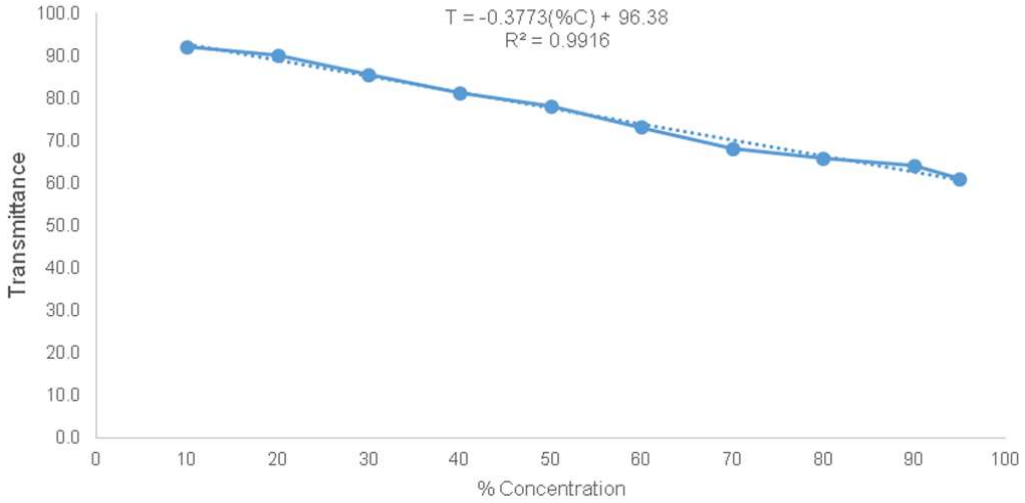

Fig. 4. Graphical curve fitting between transmittance and % concentrations of biodiesel blends

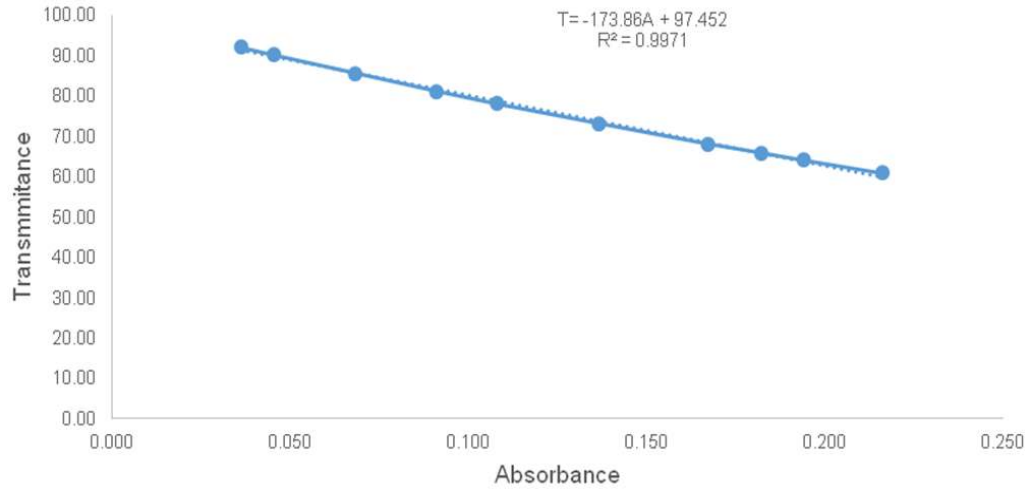

Fig. 5. Graphical curve fitting between transmittance and absorbance of biodiesel blends

Table 3. Results of absorbance and transmittance peaks measured from different biodiesel blend spectra

Blend	Concentration (%C)	Absorbance (A)	Transmittance
B10	10	0.0362	92.02
B20	20	0.0455	90.01
B30	30	0.0683	85.45
B40	40	0.0910	81.10
B50	50	0.1080	77.98
B60	60	0.1365	73.03
B70	70	0.1670	67.98
B80	80	0.1820	65.77
B90	90	0.1940	64.02
B95	95	0.2160	60.81

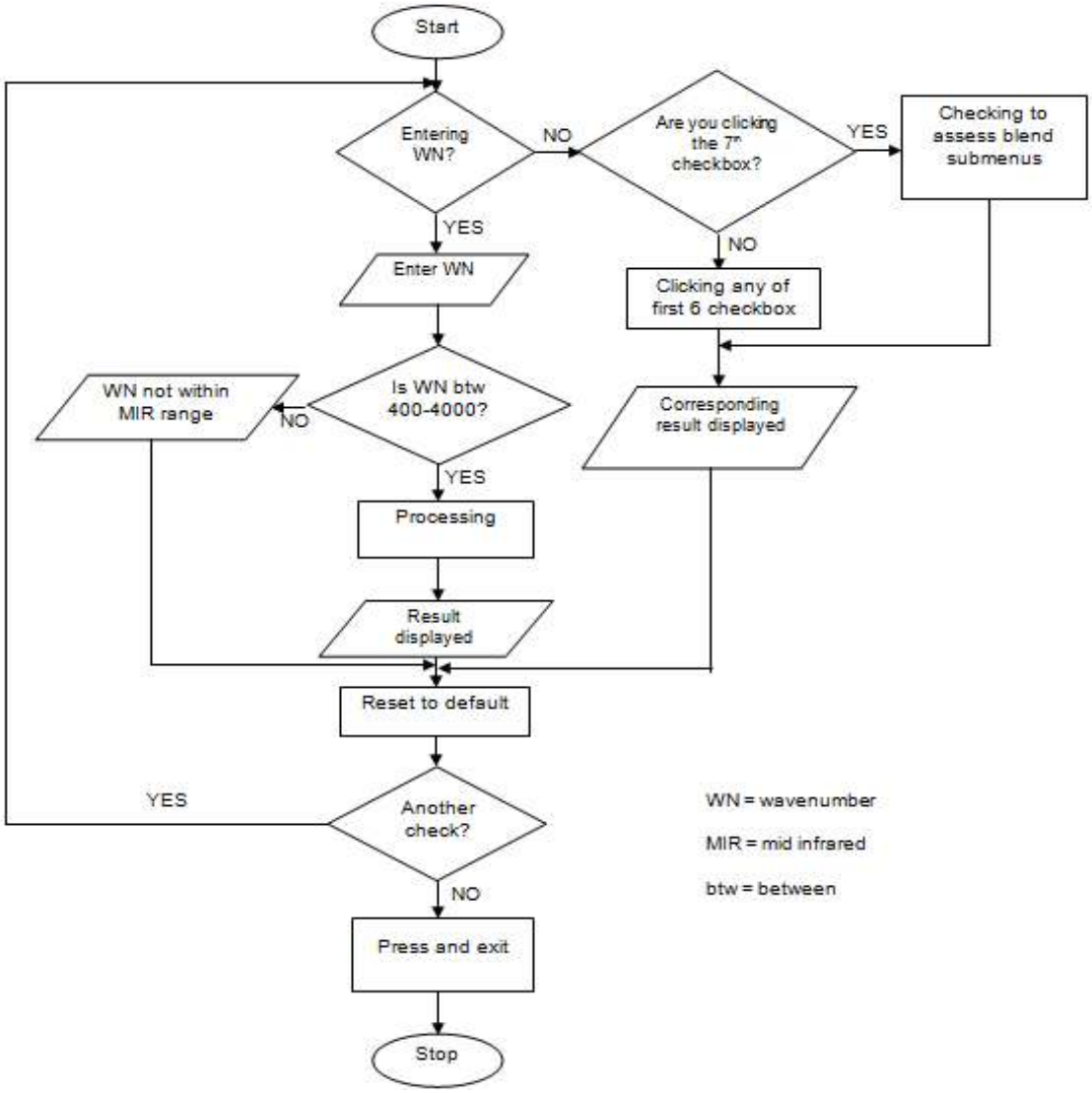

Fig. 6. Flowchart of the program

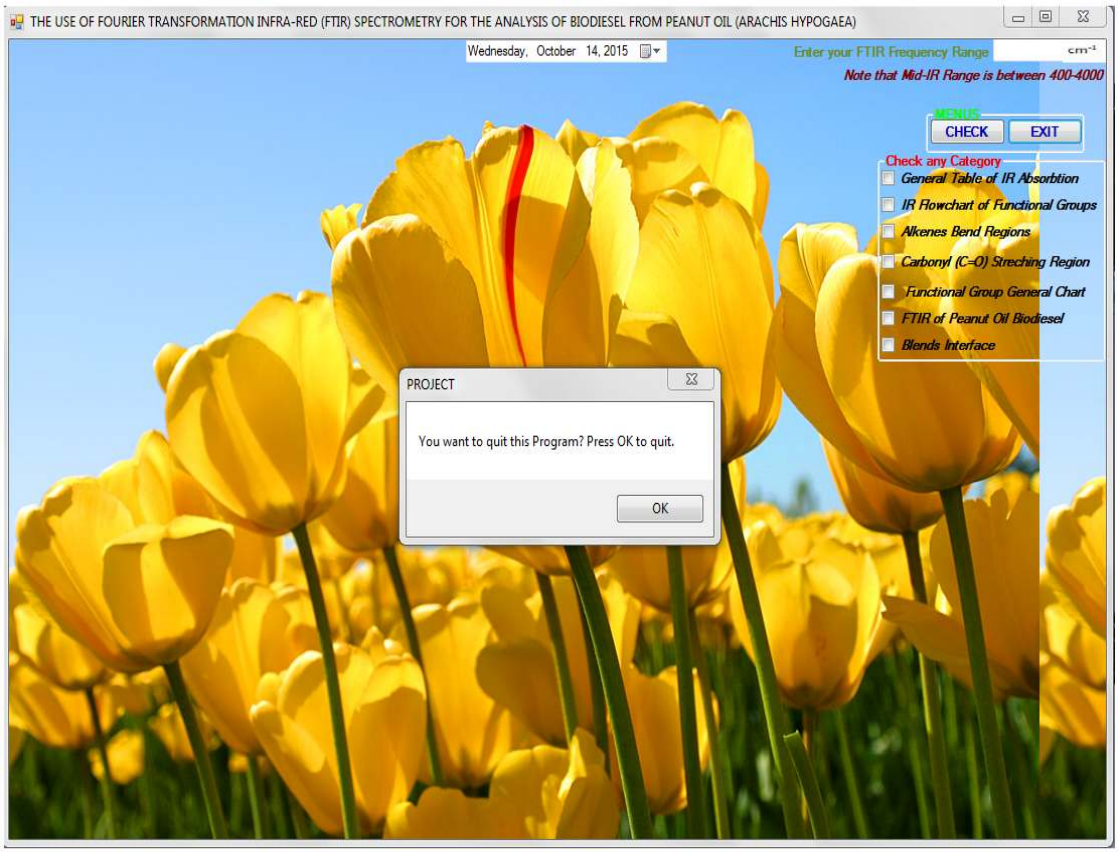

Fig. 7. Graphics user interface of the program

4. CONCLUSIONS

The increasing importance on the use of quality biodiesel in automobiles and electricity generating plants calls a rapid and dependable analysis, so as to reveal some properties and functional groups that are not traceable by manual analysis. However with modern instrumentation such as the FTIR spectrometry as an emerging technique for analysis of biodiesel even at low concentrations, it can be used for detecting the functional groups and indicate the amount of fatty acid methyl esters in biodiesel blends. It is very good tool for both quantitative and qualitative analysis and it indicates biodiesel reactivity and stability. The analyses of the functional groups in the biodiesel produced from peanut oil and its blends were carried out in this study. In the biodiesel, all absorptions corresponding to C – O and C=O stretches in the regions 745.83 cm^{-1} and 1030 – 1240cm^{-1} respectively reveal that the biodiesel produced contains the ester functional groups desired in any biodiesel type. The characteristics peaks in the biodiesel sample observed showed the range of the functional groups which indicate the presence of alkyl, methyl, methylene, alcohol, ester and carbonyl functional groups.

The results for the biodiesel blends show that the intensities of the stretches at 1745.84 cm^{-1} increase with the concentration of the biodiesel in the blend. The significant of this is that fatty acid methyl esters (FAME) present in any blend is an indication of the amount of biodiesel in it. This trend can be seen in the Fig. 3. It is also discovered that Transmittance of the blends decrease with increase in % concentration (Fig. 4) and also with absorbance (Fig. 5), this indicates that the amount of the infrared radiation passing through any sample decreases with increase in absorbance and concentrations (FAME). The Beer's Law regression analysis obtained showed high degree of correlations for fitting of datas in Table 3 as shown by coefficient of determinations (R^2) of values 0.992; 0.9916; 0.9971 for Absorbance against concentration, transmittance against concentration, and transmittance against absorbance calibration plots respectively using Microsoft excel, 2013.

The computer program developed in the course this study can be used to predict the range of functional groups when the user enters any wave numbers within the mid infrared region (4000–400 cm^{-1}) and the functional group result is displaced as output.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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