



Fourier Transform Infrared Spectroscopic Analysis of Rubber Seed Oil and Its Biodiesel

¹Otu, F.I., ¹Bello, E.I., ¹Ogedengbe, T.I., ²Lajide, L.

1.Department Of Mechanical Engineering, Federal University Of Technology, Akure, Ondo State, Nigeria

2.Department Of Chemistry, Federal University Of Technology, Akure, Ondo State, Nigeria.

A B S T R A C T

Keywords:

Fourier transform infrared spectroscopy, rubber seed oil, biodiesel.

The characteristics of the molecular vibrations of rubber seed oil and its biodiesel were determined using Fourier transformation infrared spectroscopy. Rubber seed oil was extracted from rubber seeds using soxhlet extractor. The rubber seed oil was then used to produce biodiesel through transesterification of the triglycerides in the vegetable oil using methanol and sodium hydroxide catalyst. The two samples were subjected to FTIR spectroscopic test and the obtained FTIR spectra were interpreted and analyzed with the aid of infrared interpretation rules and correlation charts. The functional group and molecular vibration of the rubber seed oil and rubber seed oil biodiesel were also determined using the FTIR spectroscopy. The biodiesel functional groups and molecular vibration were then compared to the benchmark diesel as a control. The major functional groups identified in the FTIR spectra are C=O, (CH₂)_n, C-O, C=C, C-H and O-CH₃. The produced and characterized biodiesel contained the fatty acid methyl esters. The rubber seed oil biodiesel consists mainly of alkyl esters. Inferring from the results obtained, it can be said that FTIR spectroscopy can successfully be used to quantitatively analyze the contents of rubber seed oil and its derived biodiesel. The biodiesel produced can used as fuel for diesel engines.

1. Introduction

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Spectroscopic data is often represented by a spectrum, a plot of the response of interest such as radiation intensity as a function of wavelength (Crouch and Skoong, 2007). Fourier Transform Infrared (FTIR) spectroscopy is the process whereby infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted through the sample. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint, no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several purposes such as the analysis of biodiesel to determine the group frequency, type of molecular vibration,

functional group and fatty acid methyl ester constituents. Biodiesel has attracted considerable interest in recent years due to its merits. The increasing consumption and depletion of fossil fuels, environmental pollution and climate change as a result of the use of fossil –based fuels. Some of the merits of biodiesel are: low sulphur content, renewable, biodegradable, non –toxic, high cetane number, less emission of exhaust gases and particulate pollutants. Vegetable oils are typically analyzed by determining certain components such as fatty acid and triglyceride compositions rather than analysis of oils as a whole, therefore fourier transform infrared spectroscopy is developed in order to overcome this problem. Fourier transform infrared spectroscopy is a fast and non –destructive technique, sensitive and simple in sample preparation (Rohman et al., 2011). It has been widely used for analysis of vegetable oils, fats, diesel, biodiesel and biodiesel

Correspondence: Otu, F. I. '
E-mail: Otufrancis42@yahoo.com.)

blends due to its capability to serve as “fingerprint technique”. Fourier Transform Infrared (FTIR) spectrometry is particularly well –suited to the measurement of several important fuel parameters, such as the rapid determination of critical impurities at sub percent levels in biodiesel. The concentration of biodiesel in diesel fuel – whether it is a desired blend component or a contaminant can be accurately quantified by fourier transform infrared spectroscopy at concentrations as low as tens of part per million (ppm). Furthermore, the specific biological origin of biodiesel affects its properties, and fourier transform infrared spectroscopic analysis allows discrimination between biodiesel samples from various feedstocks such as palm, soyabean, rapeseed, sheabutter and rubber seed oil (Perston, 2015). The rubber seeds are produced by the rubber tree (*hevea brasiliensis*) which belongs to the family *Eupharbiaceae*. The rubber tree is a native of the tropical rain forest and it grows in hot, humid climate. Rubber seed is a waste product obtained from rubber plantation. Rubber seed oil is extracted from the seeds of rubber trees. Each tree produces about 1.3 kg of seeds twice a year. A rubber plantation is estimated to be able to produce about 800 – 2000 kg rubber seeds per hectare per annum. (Yousif *et al.*, 2013).

Fatima Bezerra de Lira *et al.*, (2010) obtained near infrared (12,000 – 4000 cm^{-1}) and mid infrared (4000 – 400 cm^{-1}) spectra region of blends prepared from soyabean, castor, sunflower, cottonseed and canola methyl esters as well as diesel samples using fourier transform infrared spectrometer. Rohman *et al.* (2011) acquired the spectra analysis of cod liver oil in binary mixture with corn oil using fourier transform infrared spectroscopy combined with multivariate calibration. The presence and the nature of functional groups and molecular vibrations provide important information such as the purity and stability of the biodiesel fuel. Hence, this paper presents the fourier infrared spectroscopic analysis of rubber seed oil and its biodiesel.

2. Materials and method

2.1 Materials

The rubber seeds were obtained from Amoya rubber plantation at Otuo in Edo State, Nigeria. The n-hexane, methanol, sodium hydroxide and hydrochloric acid used where of analytical grade and procured from Pascal Scientific Instruments Laboratory, Akure, Nigeria.

2.2 Method

The rubber seeds were dried, sorted and milled to granulated particles of average size of 2 mm. The oil was extracted with the aid of a soxhlet extractor using normal hexane as solvent. The oil was poured in air – tight bottle and stored in a refrigerator to prevent oxidation. the transesterification process which led to the production of biodiesel was done using sodium hydroxide as

catalyst and methanol as reagent. 0.1wt% of catalyst was used at a molar ratio of 4:1 and reaction temperature of 60°C. The catalyst and methanol were first mixed before they were added to the oil in the processor and stirred at 400 rpm for 2 hours. The mixture was allowed to settle for 8 hours to ensure complete separation of biodiesel and glycerol. Finally, the biodiesel was washed with deionized water and dried. The oil and biodiesel were characterized according to the American Society for Testing and Materials (ASTM D6751) and European Union Norm (EN 14214) protocols for biodiesel.

The nature of chemical bonds and functional groups in the oil and biodiesel were evaluated by Fourier Transformation Infrared (FTIR) spectroscopy using a Bruker spectrometer. It was scanned 64 times with a spectral resolution of 4 cm^{-1} within the range 4000 cm^{-1} to 400 cm^{-1} .

3. Results and Discussion

3.1 Characterization of Rubber Seed Oil and its Biodiesel

The physical and chemical properties of the rubber seed oil and its biodiesel were determined following ASTM D6751 and EN 14214 standard testing procedures as shown in Table 1. The fatty acid compositions of triglycerides differ in relation to the chain length, degree of unsaturation and the presence of other functional groups. The fatty acid compositions are affected by factors such as climatic conditions, soil type, plant health, and plant maturity upon harvest (Jahirul *et al.*, 2013). Through transesterification reaction the vegetable oil is combined with alcohol to form fatty acid methyl esters also known as biodiesel. The properties of the rubber seed oil and its methyl ester are shown in Table 1.

Table 1: Properties of Rubber Seed Oil (RSO) and Its Methyl Ester (B100 RSOB) to ASTM D 6751-02 and EN 14214.

S/n	Property	Units	RSO	B100 RSOB	Limits	
					EN D 6751	EN 14214
1	Density at 15°C	kg/m^3	910.5	877.3	860-900	860-900
2	Refractive index at 25°C		1.468	1.343		
3	Kinematic viscosity at 40°C	mm^2/s	74.31	5.77	1.9-6.0	3.5-5.0
4	Dynamic viscosity at 40°C	mNs/m^2	67.72	5.07		
5	Lower heating value	MJ/kg	37.10	37.15		
6	Higher heating value	MJ/kg	40.20	40.30		
7	Flash point	°C	165	141	130min	120min
8	Cloud point	°C	25	9	Report	
9	Pour point	°C	18	7	0	
10	Cold filter plug point	°C	22	8	-5	

3.2 Fourier Transform Infrared Spectroscopic Analysis of Rubber Seed Oil and Its Biodiesel

The Fourier transform infrared spectra in the mid- infrared region (4000 – 400 cm^{-1}) was used for the analysis and identification of the functional

groups and molecular vibrations of the rubber seed oil and its biodiesel samples.

3.2.1 Rubber Seed Oil (RSO)

The spectrum for the oil is shown in Figure 1 and Table 2 shows the results of the functional group analysis and the molecular variations of the rubber seed oil as interpreted from the rubber seed oil spectrum

Figure 1: The spectrum for rubber seed oil.

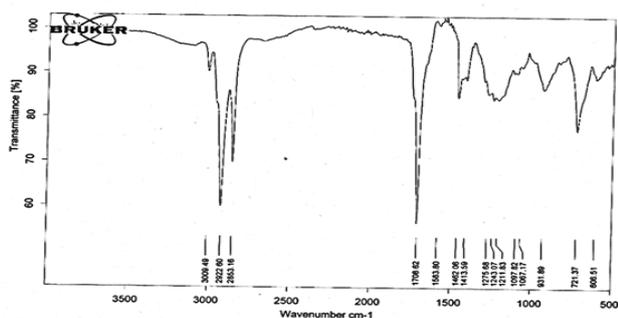


Table 2: The spectrum results of functional group analysis and type of molecular vibration of the rubber seed oil.

Group Frequency (cm^{-1})	Type of Vibration	Intensity	Functional Group	Origin	References
3009.49	Asymmetrical stretching	Strong	Trans = C - H alkene	C - H	Coates (2000)
2922.60	Asymmetrical stretching	Strong	>CH ₂ Methylene (alkane/alkyl group)	C - H	
2853.16	Symmetrical stretching	Strong.	>CH ₂ Methylene (alkane)	C - H	Gullein et al. (1999)
1708.62	Stretching	Medium to weak	C = O dimerized carboxylic acid group	C = O	
1583.80	Stretching	Medium	Aromatic ring (O - CH ₃)	C=C-C	Coates (2000);
1462.06	Asymmetrical bending	Medium to weak	Methyl C - H alkane group	C=C-C	
1413.59	In - plane bending	Strong	Vinyl C - H or cis = C - H (alkene)	C - H	Lerma - Gracia et al. (2010)
1275.68	Stretching	Strong	C - O alkoxyl ester (alcohol, aromatic ether, aryl - O, or ester group)	C - O	
1243.07	Stretching	Strong	C - O alkoxy ester, ether, C = C, or C - O - C	C - O	Pinetel (2016)
1211.83	Stretching	Strong	C - O alkoxy ester	C - O	
1097.82	Stretching	Strong	C - O alkoxyl ester, ether, C = C or C - O - C	C - O	
1067.17	Stretching	Strong	C - O alkoxyl ester	C - O	
931.89	Bending	Strong	= C - H trans disubstituted alkene and aromatic	C - H	Oyerinde and Bello (2016)
721.37	Bending	Medium	= C - H cis - disubstituted alkene or C - H aromatic	C - H	
606.51	Bending	Medium	= C - H cis - disubstituted alkene	C - H	

The major functional groups identified here are the frequency of 3009.49 cm^{-1} which indicates the presence of the unsaturated olefinic double bond group with a medium intensity (Zhang, 2012). This was closely followed by the saturated aliphatic groups of 2922.60 cm^{-1} with its asymmetrical stretching and strong intensity as well as 2853.16 cm^{-1} with its associated symmetrical stretching and strong intensity (Coates, 2000). The double bonded dimerized carboxylic acid group of wavenumber 1708.62 cm^{-1} was also present. It has C=O stretching vibration with a strong intensity. A carboxylic acid salt (COO⁻) of frequency 1583.80 cm^{-1} with a COO⁻ stretching vibration was also present. The CH asymmetrical bending vibration of 1462.06 cm^{-1} can be ascribed to -CH₃ methyl of the alkane group. The frequency of 1413.59 cm^{-1} corresponded with the in-plane bending of the vinyl C - H or cis = C - H bond of the olefinic group (Coates, 2000 and Zhang, 2012) and it is associated with a strong intensity. The frequency stretch of 1275.68 cm^{-1} to 1067.17 cm^{-1} was assigned to the C - O ester carbonyl group with its characteristic strong intensity and stretching vibration. The frequency range of $931.89 - 606.51 \text{ cm}^{-1}$ was ascribed to the = C - H trans or cis - disubstituted alkene group. Thus, it can be said that the functional groups present here are CH₂ and CH₃ of the saturated aliphatic compounds, the C = O of the dimerized carboxylic acid group, the C - O ester carbonyl group and the trans or cis - disubstituted alkene group (Gullein et al., 1997; Zhang, 2012; Oyerinde and Bello, 2016).

3.2.2 The Biodiesel (B100)

The spectrum for the biodiesel is shown in Figure 2 and Table 3 shows the results of functional group and type of vibration in the biodiesel as interpreted from the biodiesel spectrum and infrared radiation charts

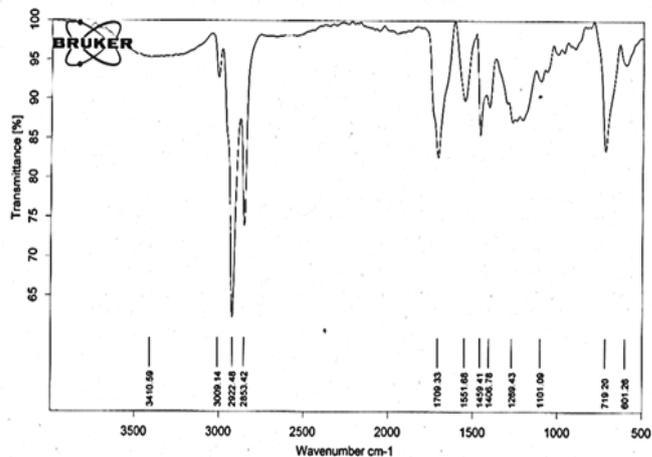


Figure 2: FTIR spectrum for pure biodiesel (B100)

Group Frequency (cm ⁻¹)	Type of Vibration	Intensity	Functional Group	Origin	References
3410.59	Stretching	Medium	Normal polymeric OH stretch	C – H	Coates (2000); Knothe (2001);
3009.14	Asymmetrical stretching	Medium	Trans or cis = C – H alkene	C – H	Bradley (2015)
2922.48	Asymmetrical stretching	Strong	– CH ₂ alkene	C – H	Oyerinde and Bello (2016)
2853.42	Symmetrical stretching	Strong	– CH ₂ methylene (alkane)	C ≡ C	Knothe (2001)
1749.33	Stretching	Strong	C = O ester carbonyl in triglycerides and FAME	C=C-C	
1551.68	Stretching	Medium to weak	Aromatic ring (O – CH ₃)	C – H	Pikolov (2014)
1459.41	Asymmetrical bending	Medium	Methyl CH or – CH ₃ (alkane)	C – H	Coates (2000); Knothe (2001);
1406.78	In – plane bending	Strong	Vinyl C – H (alkene)	C – H	Bradley (2015)
1269.43	Stretching	Strong	Trans – disubstituted alkene	C–O–C	
1101.09	Stretching	Strong	Vinylidene C – H (alkene)	C–O–C	Perston (2015)
719.20	Bending	Medium	= C – H olefinic (alkene) group	C–O–C	
601.26	Out – of – plane bending	Medium	=C – H cis-disubstituted alkene and aromatic	C – H	Oyerinde and Bello (2016)

The pure biodiesel (B100) contains the frequency of 3410.59 cm⁻¹ with OH stretching vibration ascribed to the normal polymeric OH alcohol group with its medium intensity (Coates, 2000 and Knothe, 2001). The wavenumber of 3009.14 cm⁻¹ with its CH asymmetrical stretching vibration and medium intensity was assigned to the trans = C – H alkene group while the saturated aliphatic hydrocarbon functional group of 2922.48 cm⁻¹ with its CH asymmetrical stretching vibration and strong intensity along with 2853.42 cm⁻¹ frequency band with its CH symmetrical stretching vibration and strong intensity represented the >CH₂ and CH methylene of the alkane group respectively. The most prominent functional group is the C = O ester carbonyl with its frequency of 1749.33 cm⁻¹, C = O stretching vibration and strong intensity. This is the distinctive feature of biodiesel which distinguishes it from conventional diesel. The major limitation is that this C = O ester carbonyl group is also present in vegetable oils because of its linkage with the triglycerides in the fatty acids in raw oil. Hence, it is difficult to differentiate between diesel – vegetable oil blend and diesel – biodiesel blend (Knothe, 2001 and Bradley, 2015). The stretching frequency of 1551.68 cm⁻¹ with a variable intensity was assigned to

the carboxylic acid (Coates, 2000 and Knothe, 2001). The frequency of 1459.41 cm⁻¹ with CH asymmetrical bending vibration and medium intensity represented the CH₂ and CH₃ methyl of the saturated aliphatic/alkane compounds (Bergougnou et al., 2009 and Bradley, 2015). Other functional groups present here are the C – H vinyl of alkene group with 1406.78 cm⁻¹ frequency and CH in-plane bending vibration and strong intensity. This cis olefinic functional group is usually found within the frequency range of 1450 – 1380 cm⁻¹. The C – O alkoxy ester with C – O stretching vibration at 1269.43 cm⁻¹ and the C – O alkoxy ester with a C – O – C stretching vibration at 1101.09 cm⁻¹ were also represented as well as the overlapping (CH₂)_n rocking vibration and the out – of – plane of cis-disubstituted olefins (Lerma Garcia et al., 2010; Oyerinde and Bello, 2016). The C – H out-of-plane bending vibration of 601.26 cm⁻¹ represented =C – H cis – disubstituted alkene. There are no aromatics present in biodiesel, it consists of alkyl esters (Knothe, 2001 and Bradley, 2015).

The FTIR area (1446 – 1428 cm⁻¹) under the methyl (O-CH₃) peak (1436 cm⁻¹) was measured and it showed the progress of

the transesterification reaction. This area showed the methyl esters of all types of acids in the biodiesel (Bergougnou et al., 2009 and Donnell et al., 2013). One way to differentiate biodiesel from pure vegetable oil is to measure this FTIR area.

4. Conclusion

It can be concluded that Fourier Transform Infrared (FTIR) spectroscopy at mid infrared region $4000 - 400 \text{ cm}^{-1}$ can be used to quantitatively analyze rubber seed oil and biodiesel samples. The method was fast, environmentally friendly and economical. The FTIR method shows the functional groups and vibrations present in the oil and biodiesel samples and the biodiesel purity and stability were also confirmed. Hence, the produced and tested biodiesel can be used for running diesel engines.

References

- Bergougnou, M. A., Chinmoy, B. and Ernest, K.Y. 2009. Biodiesel production from *Jatropha curcas* oil using potassium carbonate as an unsupported catalyst. *International Journal of Chemical Reaction Engineering*, Vol.7, No. 12:72.
- Bradley, M. 2015. Biodiesel (FAME) analysis by FTIR. Thermo Fisher Scientific, Modison, WI, USA: 1–3.
- Coates, J. 2000. Interpretation of infrared spectra. A practical approach in encyclopedia of analytical chemistry in R. A. Meyers (Editor) Pp. 10815 – 10837, John Wiley and Sons Limited, Chichester.
- Crouch, S. and Skoong, D. A. 2007. Principles of Instrumental Analysis. Australia: Thomson Brooks / Cole
- Donnell, S.O., Demshemino, I., Yahaya, M., Nwadike, I. and Okoro, L. 2013. A review on the spectroscopic analyses of biodiesel. *European International Journal of Science and Technology*, Vol. 2. No. 7: 137– 146.
- Fatima Bezerra de Lira, L.D., Cruz de Vasconcelos, F. V., Pereira, C. F., Silveira Paim, A. P., Stragevitch, L. and Pinnentel, M. F. 2010. Prediction of properties of diesel / biodiesel blends by infrared spectroscopy and multivariate calibration. *Fuel* 89: 405 – 409.
- Gullein, M. D. and Cabo, N. 1997. Characterization of edible oils and lard by fourier transform infrared spectroscopy, relationship between composition and frequency of concrete bands in the fingerprint region, *Journal of the American Oil Chemists Society*, Vol. 74, No. 10:1281 – 1286.
- Jahirul, M. I., Brown, R. J., Senadeera, W., O' Hara, I. M. and Ristovski, Z. D. 2013. The use of artificial neural networks for identifying sustainable biodiesel feedstocks. *Energies*, 6: 3764 – 3806.
- Knothe, G. 2001. Determining the blend level of mixtures of biodiesel with conventional diesel fuel by fiber – optic near infrared spectroscopy and H nuclear magnetic resonance spectroscopy, *Journal of American Oil Chemists Society*, Vol. 78, No. 10:1025 – 1028.
- Lerma-Garcia, M. J., Ramis-Ramos, G., Herrero-Martinez, J.M. and Simo Alfonso, E.F. 2010. Authentication of extra virgin olive oils by fourier-transform infrared spectroscopy. *Food Chemistry*, Vol. 118, no 1:78-83.
- Oyerinde A. Y. and Bello, E. I. 2016. Use of fourier transformation infrared (FTIR) spectroscopy for analysis of functional groups in peanut oil biodiesel and its blends, *British Journal of Applied Science and Technology* 13(3): 1-14.
- Perston, Ben 2015. Rapid analysis of biofuels and biofuel blends with fourier transform infrared spectrometry, *American Laboratory Articles Application Note*. No. 61.
- Pikolov, Aleksandr A. 2014. The Analysis of biodiesel blends by fourier transform infrared spectroscopy (FTIR) in Proceedings of the National Conference on Undergraduate Research (NCUR) University of Kentucky, Lexington, KY; USA: 9 – 16.
- Pinentel, M.F., Ribeiro, C., Cruz, R.S., Stragevitch, I., Filho, G., Teixeira, I. 2006. Determination of biodiesel content when blended with mineral diesel fuel using infrared spectroscopy and multivariate calibration. *Microchemistry Journal*, 82: 201-206.
- Rohman, A., Che Man, Y. B., Ismail, A. and Puziah, H. 2011. FTIR spectroscopy combined with multivariate calibration for analysis of cod liver oil in binary mixture with corn oil. *International Food Research Journal* 18: 757– 761.
- Zhang, Wei-Bo 2012. Review on analysis of biodiesel with infrared spectroscopy. *Renewable and Sustainable Energy Reviews*, 16: 6048-6058