J. Basic. Appl. Chem., 1(9)80-84, 2011

ISSN 2090-424X
Journal of Basic And Applied Chemistry
www.textroad.com

Composition and Characterization of Crude Glycerol from Biodiesel Production Using Neem Seed Oil

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ABSTRACT

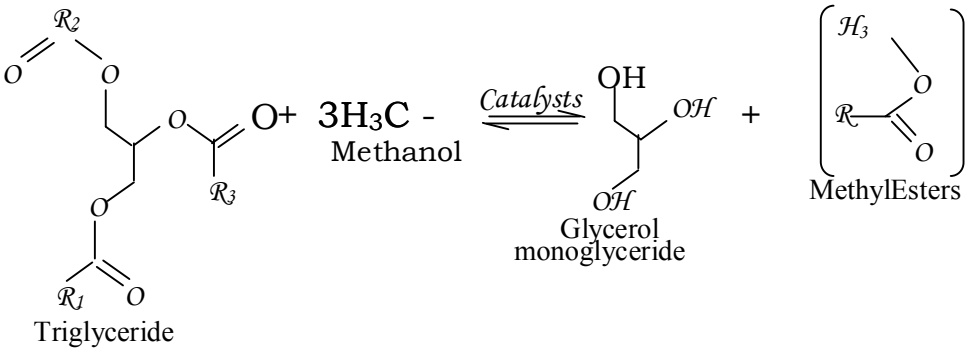
Crude glycerol from biodiesel production using neem seed oil was analyzed for Free Fatty Acid, Acid value, Safonification value, Iodine value, Refractive Index, Viscosity, Color and Density using standard methods. Results show 1.54mgKOH/g, 3.08meq/g, 6.02meqKOH/g, 45.1meqKOH/g, 1.560, 127rpm/Pa, unpleasant, 1.78g/cm^3 respectively. Fatty acids profile by GCMS showed predominance of glycerol (58.10) and fatty acids Linoliec (24.31), Linolenic (20.70), Erucic (12.43), Behinic (11.06) and Oleic acids (10.11). It showed the presence of other fatty acid acids such as Palmitic, Stearic and so on. The UV-VIS scanning showed the absorption at characteristic of the OH bond while the FTIR analysis showed the presence of functional groups of –COO-, -OH and C=O. This will contributing in effective conversion of crude glycerol into useful products and will be useful in setting up a refinery for glycerol refining.

Key words: neem, glycerol, FFA and GCMS.

INTRODUCTION

Neem (*Azadirachta indica*) has been used in India since 2000-4000 BC, and was referred to in ancient Indian text as "the curer of all ailments". The leaves, twigs, and oil from the nuts (www.neemfoundation.org). All parts of the tree are used; the cake is used in improving soil organic matter, the roots and bark is used in controlling pest and tick and the oil is used for insecticidal and medicinal uses.

Neem seed oil is one of the potential oils in biodiesel production because its non edible thus does not affect the food chain. The transesterification of vegetable oils with an alcohol mainly methanol in the presence of a catalyst produce biodiesel and glycerol as a major by-product (Thompson and He, 2006; Hossein et.al, 1998; Sneha et.at, 2009; Naresh Pachauri, Brian He, 2006).



R_1, R_2 and R_3 are alkyl groups, which are long chain carbon

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Glycerol produced by transesterification is only about 50% pure. It contains a significant amount of contaminants including methanol, soap, and catalyst. It is generally treated and refined through filtration, chemical additions, and fractional vacuum distillation to yield various commercial grades, dynamite grade, yellow distilled and chemically pure glycerol (Yong et.al, 2001)

There is a vast literature on the use of crude glycerol from biodiesel for conversion into valuable products. The conversion of the glycerol to any product depends on the quality and purity of the crude glycerol. However, there is a limited literature on the use of neem seed oil for biodiesel production and subsequently the conversion of its glycerol into valuable products. This work characterizes crude glycerol obtained from biodiesel production using neem seed oil, with a view to contributing in effective conversion to useful products and will be useful in setting up a refinery for glycerol refining.

MATERIALS AND METHODS

The sample was obtained at by a PhD student of the department. It was a dark viscous liquid with choking smell. The sample is believed to contain the methanol and the catalyst even though the methanol content was not determined. All the tests were conducted on the sample without further treatment. The chemicals and reagents used were analytical grades except otherwise stated.

Free Fatty Acids (AOCS methods; Ca 5a-40), Safonification Value (AOAC method 920:160/AOCS method cd 3-25), Iodine value and Acid value were determined by standard methods. The viscosity (at 37^0C) was determined using a viscometer (MJ 800S), Refractive index was determined with a refractometer and density was also determined. All measurements were in duplicates.

The Fatty Acid Composition (FAC) of the crude glycerol was determined by Gas Chromatography coupled to Mass spectrophotometer (GCMS-QP2010 Shimadzu). The temperature of the program was initially at 60^oC and the final temperature of 280^oC for total of 15mins and about 1.0 µl of the derived crude fatty acids was injected into the gas chromatograph. The sample was first methylated by dissolving 0.125gm of the oil in 5.0 ml of N-hexane. This was then followed by the addition of 0.5 ml of 5M sodium methoxide and vigorously shaken (Oladiji, et.al, 2010). The analysis was conducted at the National Research Institute for Chemical Technology, Zaria-Nigeria.

Additionally, the crude sample was scanned using UV-VIS spectrophotometer (UV-2500PC series, Shimadzu) for a range of 200-800nm for absorbance, using 1g of the sample in a 3ml cuvette. The sample was also analyzed using FT-IR (8400S Shimadzu, Japan) with a Happ-Genzel apodization module and resolution of 2.0 for the functional group analysis. The range was 340-4700cm^{-1}. The result was presented as the percentage transmittance.

RESULTS

Table 1.0: Physicochemical parameter of the sample

s/no	parameter	value
1.	Free Fatty Acid (mgKOH/g)	1.54
2.	Acid Value (meq/g)	3.08
3.	Iodine value (mgKOH/g)	45.1
4.	Safonification value (mgKOH/g)	6.02
5.	Viscosity (rpm/Pa) at 37^0C	127
6.	Color	Dark brown
7.	Refractive index at 25^0C	1.560
8.	Odor	Unpleasant
9.	Density (g/cm^3) at 28^0C	1.78

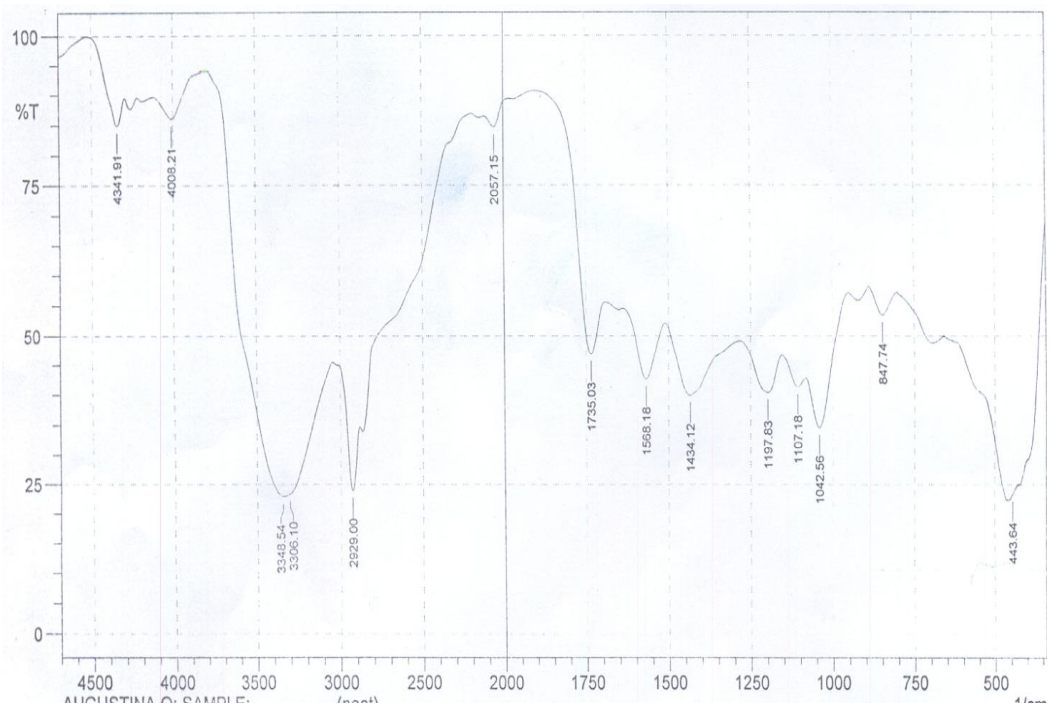

Fig 1.0: FITR Spectrum of the sample showing the peaks corresponding to different functional groups in the sample analyzed.

Table 2.0: Fatty acid profile of the sample, their corresponding retention times and area to height ratio of the various peaks in the GCMS spectrum.

Peak No	retention time	A/H	fatty acid
1	13.411	58.10	glycerol
2	24.984	3.60	Di-OH propional
3	25.332	7.18	Palmitc acid
4	25.613	8.32	Stearic acid
5	27.385	4.72	Arachidic acid
6	27.637	6.29	Elaidic acid
7	28.033	12.43	Erucic acid
8	28.298	10.11	Oleic acid
9	30.129	6.55	Pentadecanoic acid
10	30.535	5.14	Eicosanioc acid
11	32.558	24.31	Linoleic acid
12	33.857	20.70	Linolenic acid
13	43.593	8.05	6-nonenal
14	44.314	11.06	Behinic acid

DISCUSSION

The result (table 1.0) presents the results of the physicochemical analysis of the sample. The free fatty acid, Acid value, Iodine value, Safonification value, refractive index, color density and viscosity were presented. Table (2.0) presents the analysis of the sample by using GCMS and results presented as a percentage of the area/height ratio. Figure 1.0 showed the spectrum for FTIR analysis.

The low free fatty acid value of 1.54mgKOH/g shows that there was no significant destruction of the triglyceride from the neem oil. Sneha et.al (2009), reported the factors that could affect the quality of the vegetable oil to include; the extraction process and the maturity of the seed. The free fatty acid is an important property in determining the quality of the crude glycerol from the transesterification reaction and the pure glycerol from the purification technology. In the chemistry of the transesterification, the triglyceride molecule is broken down into lower glycerides (i.e. diglycerides, monoglyceride and glycerol) by losing one, two or all the three fatty acids. There are some fatty acids however, that are lost from the triglyceride which could not form either of the products. Hence, they are released as free fatty acids. Acid Value (3.08meq/g) from the table (1.0) also corresponds to the low free fatty acid value. Acid value is an important index of physicochemical property of oil which is used to indicate the quality, age, edibility and suitability of oil for use in industries such as paint (Olatunji, 2010). This means that, there was little FFA to be neutralized, consequently, little soap is formed as it was indicated by the safonification value (6.02meqKOH/g) which is basically the hydrolysis of triglyceride to glycerol and FFA. The actual safonification value of the sample would have been lower if the analysis was done earlier than Nine to ten day. This had however, shown that the deteroration of the sample after this time was not so much. The Iodine value is another quality parameter indicating from the table (45.1meqKOH/g). This result may be subjected to scrutiny as it has shown a high value but it could possibly be as a result of the presence of the soap and impurities in the sample from the transesterification process, thus making the glycerol looking more saturated.

The color intensity is due to accumulation of non-volatile decomposed compounds such as oxidized triacylglycerols and FFA (Alireza, et.al, 2010).The color of crude glycerol is mostly dark or brown. This could be confirmed by the determination of the refractive index which showed a value of 1.56. The viscosity of the sample from the table (127rpm) at 37^0C was significantly higher than viscosities (8.80, 8.67, 8.50, 8.46, 8.65, 8.50 and 26.50) for Rapeseed, Canola, Soy bean, Crambe and Waste Vegetable oils respectively all at 40^oC reported by Thompson and He, (2006). This could be attributed to the methanol content of the sample and the temperature of the sample. The glycerol phase is much denser than biodiesel phase and the two can be gravity separated with glycerol simply drawn off the bottom of the settling vessel. The density (1.78g/cm^3) of glycerol from the table was higher than biodiesel.

The spectrum from FTIR (fig 1.0), showed absorption frequency 3348.54cm^{-1} corresponding to an –OH stretching in an alcohol and 1760cm^{-1} characteristic of C=O stretching. The result also showed the peak 2929cm^{-1} indicated the presence of a carbonyl compound (esters). The functional group – COO^- detected at the frequency 3306.1 cm^{-1} corresponded to a tertiary alcohol.

The fatty acid composition of the crude sample showed the presence of glycerol (58.10) in relative abundance. The sample also contained significant amount of polyunsaturated fatty acids of linoliec (24.31) and linolenic (20.70) acids. The presence of oleic, eruric and other medium chain fatty acids present were characteristic of vegetable oils. The presence of linoliec and oleic acids in the oil samples could account for the high iodine value (Oladiji, 2010). In general, the fatty acid composition of the sample suggested that the neem seed oil contained low fatty acid composition (FAC) hence, this makes it a suitable feedstuff for biodiesel production.

Conclusion

The analysis of the crude glycerol sample from biodiesel production using neem seed oil was evaluated for physicochemical properties such as free fatty acid, acid value; safonification value, refractive index, viscosity, iodine value and color were found to be present. Additionally, fatty acid profile revealed the presence of monounsaturated, polyunsaturated and medium chain fatty acids, while the FTIR revealed the presence of –COO, C=O and –OH groups in the sample.

Acknowledgement

The authors are grateful to Mr. Okunola, O.J and Miss Aina Olubukola of the National Research Institute for Chemical Technology, Zaria-Nigeria.

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