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"Characterization of Biodiesels Produced using Mixed Base Catalyst by Gas Chromatography & FTIR Spetroscopy"

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Abstract- In this study, fish oil & cottonseed oils were used to produce their individual methyl esters using a mixed base catalyst (Sodium hydroxide & di-sodium phosphate). The produced biodiesels were characterized to check the quality of biodiesel and to establish the feasibility of using the mixed base catalyst for production of biodiesels. The biodiesel was characterized by FTIR (Fourier Transform infrared spectrometry) and GC (Gas Chromatography) tests and the other important properties of biodiesel were found out and compared with that of diesel. FTIR test confirms complete conversion of biodiesel from individual oils and the fuel properties were found to be within the range prescribed in ASTM standards. GC analysis has shown presence of more unsaturated fatty acids in cottonseed oil and less in fish oil biodiesel throwing some light on the stability of the fuels. The present characterization studies has established the potential use of mixed base catalyst during transesterification reactions.
Keywords: FTIR, GC, RSM, Mixed base catalyst.

I. INTRODUCTION:

In day today's life fossil fuels have become the major source of energy which fulfill most of the human demands such as transportation, industrialization & agricultural needs etc. The derivatives of fossil fuels are petrol, diesel & kerosene which are mainly used as fuel for basic needs. But growing industrialization, increasing population & rapid urbanization are causing the depletion of fossil fuels [1]. Many researchers have suggested the use of biodiesel as an alternative for the depleting fossil fuels as it has better efficiency, sustaining ability and energy conservation [2,3]. Less Vapor pressure, large biodegradability, decreased emission of exhaust gas & less toxicity are some of the important properties of bio diesel increasing its usage in large scale [4,5]. The fundamental downside of vegetable oils is their high viscosity which does not allow the biodiesel diesel to be used in CI engines. It was also observed that high viscosity cause less volatility & improper combustion, which will lead to the formation of large emission of oxides of carbon. This problem can be overcome by a process called transesterification, which removes glycerol and thus improves the quality of biodiesel by reducing its viscosity [1].

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Thus, transesterification is a significant process which is carried out on vegetable oils to increase its usage in diesel engines [6]. There are many tropical countries which are growing trees such as Mahua, Simarouba, Cotton & Honge all yielding oil bearing seeds. India is the world's second highest producer of cottonseed with about 22% of the world's production [7]. Oil is extracted from the seeds of cotton plant after the removal of cotton lint. Some of the physical & chemical properties of cottonseed oil matches with the vegetable oils and also highlight the presence of triglycerides [8,9]. The molecules of triglyceride forms long chain fatty acids and these esters are bonded to single molecule of glycerol [13].

According to the report from Food and Agriculture Organization, around 141.6 million tons of Fish is obtained out of which 50% will go as waste (as on 2006) [10]. An average of 40 to 60% of oil can be obtained from the waste [11]. The composition of biodiesel produced from vegetable oils & animal fats are same. The difference is that animal fats having more saturated fatty acid compositions [16].

II. MATERIALS & METHODS:

A. Materials:

The fish oil which was dark brown in color was purchased from Mangalore district, Karnataka. Care was taken to collect fresh oil having less free fatty acid to avoid esterification. The fish oil was heated at 100°C and then it was allowed to cool to room temperature. The top layer of cooled oil was collected for transesterification process. The transesterification process was carried out with a mixed base catalyst consisting of a mixture of sodium hydroxide (homogeneous catalyst) and sodium di phosphate (heterogeneous catalyst) dissolved in methanol. The cottonseed oil was collected from Tumkur, Karnataka, which was light yellow in color.

B. Methods:

The FFA (Free Fatty Acid) value of the fish and cottonseed oils were determined by titration method. If the FFA value is more than 4 then esterification process should be carried out, otherwise the oil sample can be subjected to transesterification process. The FFA value of fish and cottonseed oil were determined to be 2.6 and 2.0 respectively (less than 4). Using Response Surface Method the transesterification reaction parameters such as reaction temperature, reaction time & methanol to oil ratio were optimized.

In accordance with the RSM method about 20 trials were taken to optimize reaction parameters. The reaction procedure for a single trial is explained.

About 250ml of oil sample was poured into a three neck flask and heated to 60°C. A mixture of sodium hydroxide and sodium di phosphate powders (mixed catalyst) is dissolved in methanol and the mixture is poured into the heated oil sample and the sample is continued to heat for the next 1 to 1.5 hours. During this process a condenser is used so that no methanol escapes from the mixture. The magnetic stirrer present in the flask will continuously mix the oil and allow the catalyst to react, which leads to the formation of glycerol. The solution is then poured into the settling funnel and different layers of solution were observed. The bottom layer is heterogeneous catalyst, next to it is glycerol and the top layer is biodiesel. The catalyst is collected for next reaction & glycerol is removed from the funnel. The biodiesel contains some amount of methanol in it, which is recollected through distillation process. Now the biodiesel is allowed to wash with water (of pH 7) to remove base content in it. After 2 to 3 wash the pH of biodiesel is checked using pH paper. If the pH characteristic is basic then it is allowed for further wash otherwise washing is stopped. The left out biodiesel is heated till it loses all water content in it and cooled to room temperature. Now the biodiesel is ready to use by blending with commercial diesel. By following this procedure, the yield obtained for fish oil biodiesel and cottonseed oil biodiesel are 94.6% and 97.8% respectively [18].

III. RESULTS & DISCUSSION:

A. Fuel Properties:

The quality of biodiesels produced from fish oil & cottonseed oil were assessed through physical & chemical properties, such as viscosity, flash point, density, corrosion, ash content, carbon residue, pour point & cloud point. "Table-I" shows the obtained fuel properties of fish oil and cottonseed oil biodiesels. The properties are compared with diesel and biodiesel ASTM standards. The result shows that the biodiesel properties are in the range of ASTM standards and hence the obtained biodiesel is considered to be of good quality.

B. Fatty Acid Composition (FAC):

The *FAC* of fish oil and cottonseed oil was determined by Gas Chromatograph using GC-6890N (model AGILENT) equipped with a flame ionization detector (FID) and DB wax was filled in column of cross section 30 mm X 0.25 mm. The temperature maintained at injector port and detector port were 270°C & 280°C respectively. Hydrogen gas was used as a carrier gas to carry the sample [12]. The results of Gas Chromatograph are shown in "Table II". The fatty acid profile of fish oil biodiesel were mysteric acid 6.48%, palmic acid 25.42%, stearic acid 8.13%, behenic acid 9.51%, Oliec acid 15.32%, erucic acid 0.42%, recenoleic acid 2.06%, linoleic acid 2.55%, linolenic acid 0.77% and arachdonic acid 1.02%. The total saturated and unsaturated fatty acid compositions of fish oil biodiesel were 49.51% & 22.14% respectively.

Fatty acid profile of cottonseed oil biodiesel were mysteric acid 1.08%, palmatic acid 25.76%, stearic acid 3.34%, behenic acid 0.46%, lignoceric acid 0.26%, oleic acid 19.22%, erucic acid 0.26%, linoliec acid 48.99%, linolenic acid 0.33% and arachidonic acid 0.30%. The total saturated & unsaturated fatty acid compositions of cottonseed oil biodiesel were 30.90% & 69.10% respectively.

Among the considered oils, fish oil biodiesel has maximum saturated fatty acid composition (49.51%) and cottonseed oil has maximum unsaturated composition (69.10%). The maximum amount of unsaturated fatty acid composition leads to the formation of oxidation in a rapid rate. This requires usage of antioxidants or by avoiding exposure to heat & light, to preserve the biodiesel for a long time [17].

C. Characterization of Fish Oil & Cottonseed Oil Biodiesels through FTIR Analysis:

Spectroscopy is a device which analyses the interaction between matter and radiation. This equipment works on the principle of measuring the radiation produced or absorbed by the molecular species. As spectroscopy is a precise and suitable analytical method for quality control analysis, it can be used in the analysis of biodiesels. There are 6 types of infrared spectroscopy employed in the analysis, namely, Fourier Transformation Infrared (FTIR) Spectroscopy, Mass Spectroscopy (MS), Near Infrared (NIR) Spectroscopy, Thermal lens spectroscopy (TLS), Nuclear Magnetic Resonance Spectroscopy (NMR) & Ultraviolet Spectroscopy (UV). Out of these FTIR can be considered as a modern analytical tool to find out biodiesel conversion because it is fast & easy detecting method. The methyl esters and oils are the strong absorber in infrared regions, which helps in identifying C=O, C=C, C=H, CH_2 & CH_3 groups [14].

Infrared spectra were recorded on Brucker Alpha-T FTIR spectrometer (KBr windows, 2 cm^{-1} resolution) and spectra were analyzed using OPUS/MENTOR software. "Fig. 1" and "Fig. 2" show the FTIR Spectrum for fish oil and cottonseed oil respectively. The result is in the form of variation of percentage of transmittance of IR with the wavelength of the radiation are as shown in Table-III.FTIR spectrum of fish oil biodiesel shows sharp bands at 2946–2854 cm^{-1} & for cottonseed oil biodiesel sharp bands are observed at 2948–2857 cm^{-1}, confirming the C= H stretching vibration of methylene groups. The sharp bands at 1743 cm^{-1} for fish oil biodiesel & 1746 cm^{-1} for cottonseed oil biodiesel are attributed to C=O stretching frequency, which confirms the conversion of triglycerides into methyl esters. Absorption at 1463 cm^{-1} & 1436 cm^{-1} for fish oil biodiesel and 1460 cm^{-1} & 1432 cm^{-1} for cottonseed oil biodiesel are assigned to asymmetric CH_3 or CH_2 bending vibrations. Bands at 1245 cm^{-1}, 1193 cm^{-1} & 1169 cm^{-1} for fish oil biodiesel and 1249 cm^{-1}, 1198 cm^{-1}& 1170 cm^{-1} for cottonseed oil biodiesel are due to C=O stretching of esters respectively. The bands obtained at 1118 cm^{-1}, 1017 cm^{-1} & 865 cm^{-1} for fish oil biodiesel and 1121cm^{-1}, 1019cm^{-1} & 870 cm^{-1} for cottonseed oil are due to C=O stretching. From the observation it is seen that the fish oil biodiesel and cottonseed oil spectrum were in the specified range, hence we can consider fish oil & cottonseed oil biodiesels as a good quality biodiesels [15].

IV. CONCLUSION:

The fish oil & cottonseed oil biodiesels produced from mixed base catalyst have been characterized and compared with standards. The high yield of fish oil & cottonseed oil biodiesels produced from mixed based catalyst shows effectiveness of the used catalyst and reaction parameters. The FTIR test confirms the presence of methyl esters indicating complete transesterification of fish oil & cottonseed oil. The fuel properties are within the range of ASTM standards indicating the potential use of these biodiesels as blends with diesel in Compression Ignition engines. GC analysis has revealed a presence of 22.14 % of unsaturated fatty acid in fish oil biodiesel. Hence, fish oil biodiesel produced from mixed base catalyst can be stable with less rate of oxidation. However, in cottonseed oil biodiesel, 69.10 % of unsaturated fatty acid is observed indicating the instability of this oil with a higher rate of oxidation. The present study has established the feasibility of using of mixed base catalysts for production of biodiesels.

Table-I: Fuel Properties of Diesel, Fish oil biodiesel & Cottonseed oil biodiesel

Sl. No.	Properties	Units	Testing Procedure ASTM	Fish oil Biodiesel	Cottonseed oil Biodiesel	Diesel	Biodiesel Standard ASTM D6751
1	Viscosity @ 40^{o}C	mm^2/s	D-445	5.4	4.8	2.36	1.9-6.0
2	Density @ 15^{o}C	Kg/m^3	D-93	880	872	830	870-900
3	Flash point	^{o}C	D-4052	170	156	64	>130
4	Copper Strip Corrosion, 50^{o}C, 3 h	-	D-130	1a	1a	--	No. 3 max
5	Calorific value	kJ/kg	D-240	37587	39019	42440	-
6	Cloud Point	^{o}C	D-2500	+9	+10	5	-3 to 12
7	Pour point	^{o}C	D-97	+4	-2	-10	-15 to 10
8	Ash content	% mass	D-874	0.006	Nil	Nil	0.050
9	Carbon Residue	% mass	D-4530	Nil	Nil	Nil	0.020

Table-II: Properties of Fatty acid Composition of Fish oil & Cottonseed Oil Biodiesels

Sl. No.	Fatty Acid Composition (wt%)	Fish Oil Biodiesel %	Cottonseed Oil Biodiesel %
	Saturarted fatty acids:		
1	Myristic Acid	6.48	1.08
2	Palmitic Acid	25.42	25.76
3	Stearic Acid	8.13	3.34
4	Behenic Acid	9.51	0.46
5	Lignoceric Acid	Nil	0.26
	Mono Un saturated fatty acids:		
6	Oleic Acid	15.32	19.22
7	Erucic Acid	0.42	0.26
8	Recenoleic Acid	2.06	Nil
	Poly un saturated fatty acids:		
9	Linoleic Acid	2.55	48.99
10	Linolenic Acid	0.77	0.33
11	Arachidonic Acid	1.02	0.30

Table-III: IR Absorption ranges of fish oil & cottonseed oil biodiesels

Functional Group	Absorption Location range (cm^{-1})	Absorption Intensity	Fish Oil Biodiesel Absorption Location (cm^{-1})	Cottonseed Oil Biodiesel Absorption Location (cm^{-1})
Alkane (C-H) [For methylene Group]	2975-2850	Strong to Medium	2946–2854	2948–2857

Ester (RCOOR) [For conversion of Triglycerides to Methyl Esters]	1735-1750	Strong	1743	1746
Methyl/Ethyl (CH_3 or CH_2)	1470-1430	Strong to Medium	1463 & 1436	1460 & 1432
Carbonyl (C=O)	-	-	1245, 1193 & 1169	1249, 1198 & 1170

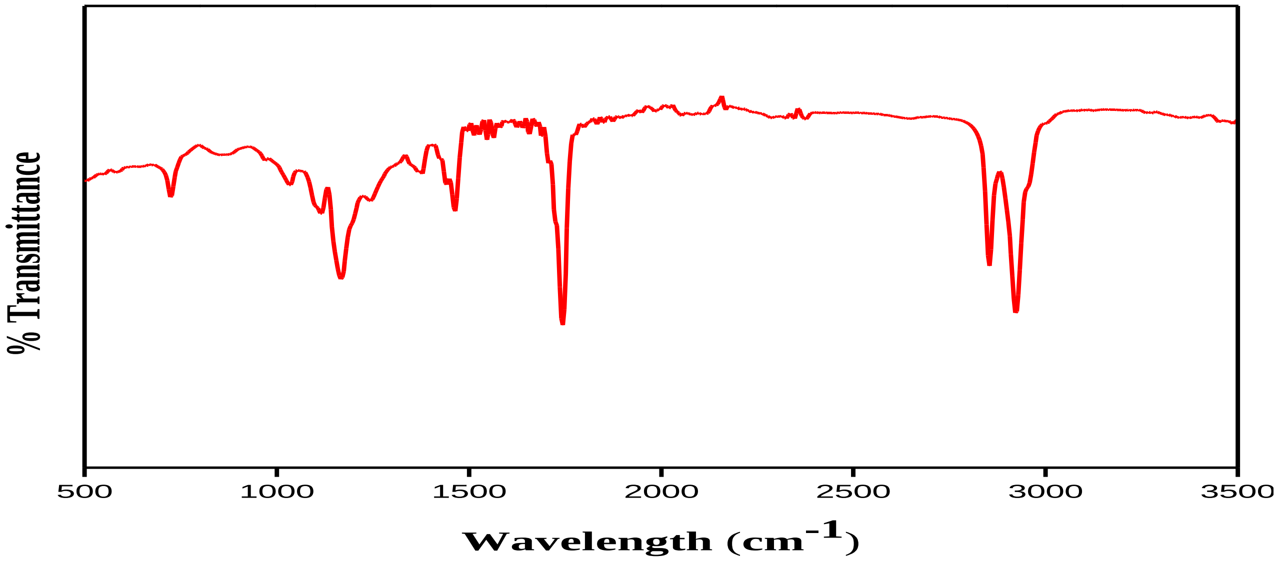

Fig.1. FTIR of Fish oil Biodiesel

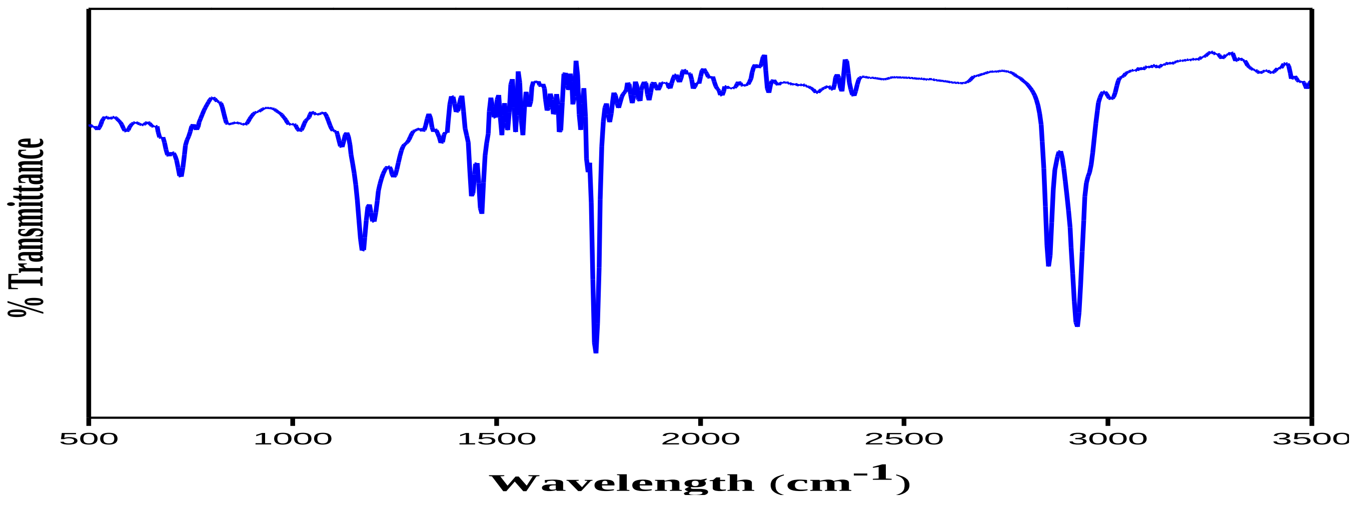

Fig.2. FTIR of Cottonseed oil Biodiesel

REFERENCES:

1. Basha, S. A., K. R. Gopal, and S. Jebaraj. 2009. A review on biodiesel production, combustion, emissions and performance. *Renewable and Sustainable Energy Reviews* 13:1628–34.
2. Agarwal, A. K. 2007. Biofuels (alcohos and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science* 33:233–71.
3. Manjunath H, Omprakash Hebbal & Hemachandra Reddy K., Process Optimization for Biodiesel Production from Simarouba, Mahua, and Waste Cooking Oils, *International Journal of Green Energy* (2015) **12**, 424–430 Copyright © Taylor & Francis Group, LLC ISSN: 1543-5075 print / 1543-5083 online DOI: 10.1080/15435075.2013.845100.
4. Margaroni, D. 1998. Fuel lubricity. *Industrial Lubrication and Tribology* 50(3):108–18.
5. Knothe, G. and K. S. Steidley. 2005. Kinematic viscosity of biodiesel fuel component and related compounds: Influence of compound structure and comparison to petrodiesel fuel components. *Fuel* 84:1059–65.

6. Yamane, K., A. Ueta, and Y. Shimamoto. 2001. Influence of physical and chemical properties of biodiesel fuels on injection, combustion and exhaust emission characteristics in a direct injection compression ignition engine. *International Journal of Engine Research* 2:249–61
7. Manish Jain, Amit Pal, Vineet Kumar, Life cyle management of Cottonseed oil, International Journal of Current engineering and Scientific Research (IJCESR), ISSN: 2393-0697, Volume 2, Issue 8, 2015.
8. F D Gun Stone, J L Harwood, The lipid hand book third edition CRC Press, Boca Raton, FL 2007.
9. Umre Rashid, Farooq Anwar, Gerhard Knothe, Evaluation of biodiesel obtained from cottonseed oil, Fuel Processing Technlogy 90(2009) 1157-1163.
10. FAO-Food & Agricultural Organization. The state of world Fisheries and aquaculture, Rome: 2006.
11. V R Wiggers, A. Wisniewski Jr, L.A.S. Madureira, A.A.Chivanga Barros, H. F. Meier, Fuel 88 (2009) 2135-2141.
12. K. V. Yatisha, H. S. Lalithambaa, R. Sureshb and B. R. Omkareshb,, Synthesis of biodiesel from Garcinia gummi-gutta, Terminalia belerica and Aegle marmelos seed oil and investigation of fuel properties, ISSN: 1759-7269 (Print) 1759-7277 (Online) Journal homepage: http://www.tandfonline.com/ loi/tbfu20, 2016.
13. Leonardo S.G, Teixeira, Marcelo B. Couto, Giancarlos S. Souza, Miguel Andrade Filho, Julio C. R. Assis, Paulo R.B. Guimarates, Luiz A.M. Pontes, Selmo Q. Almeida, Josanaide S.R. Teixeira, Characterization of beef tallow biodiesel and their mixtures with soybean biodiesel and mineral diesel fuel., Biomass and Energy 34(2010) 438-441.
14. Sylvester O'Donnell, Innocent Demshemino, Muhammad Yahaya, IsiomaNwadike, Linus Okoro. A review on the spectroscopic Anallyses of Biodiesel, European International Journal of Science & Technology 2013: 2(7): 137-146.
15. William Kemp, Organic Spectroscopy, 3rd Edition, Macmillan, 2009.
16. Lang X. Dalai AK, Bakhshi NN, Reany MJ, Hertz PB. Preparation and characterization of Bio-diesels from various bio-oils, Bioresour Technol 2001;80:53-62.
17. http://people.umass.edu/~mcclemen/581Lipids. html.
18. "Optimization of Transesterification Reaction Parameters For Fish Oil Biodiesel Production: A Response Surface Methodology Approach".Journal of Physics: Conference Series: 2019 J. Phys.: Conf. Ser.1240 012140, Conf. Series1240 (2019) 012140IOP Publishingdoi:10.1088/1742-6596/1240/1/012140, NFEST-2019, NIT,Kurukshethra.

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