International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075; Impact Factor: RJIF 5.22
Received: 26-01-2019; Accepted: 01-03-2019
www.chemicaljournals.com
Volume 3; Issue 3; May 2019; Page No. 07-10

Assessment and optimization of biodiesel production from neem seed oil using sulfated zirconia catalyst

AU Muhammad[1*], C Muhammad[2], BU Bagudo[3], M Mukhtar[4], B Magaji[5], M Musa[6]
[1-5] Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto, Nigeria
[6] Sokoto Energy Research Center, Usmanu Danfodiyo University Sokoto, Nigeria

Abstract
Response surface based on Box-Behnken design was used to investigate and optimize the reaction conditions for conversion of neem seed oil in to biodiesel. The oil was extracted from the seed using n-hexane and trans esterified using methanol and sulfated zirconia catalyst to biodiesel. The oil extracted and biodiesel produced were analyzed for physicochemical and fuel properties using ASTM methods and are in conformity with ASTM D6751. The fatty acid methyl ester was estimated using Gas Chromatography- Mass Spectrophotometry (GC-MS). The results obtained showed percentage oil yields of 40.64 ± 1.01%. The optimum yield of 89% was obtained at the reaction temperature, reaction time, molar oil to methanol ratio and catalyst concentration, 60°C, 1:12, 90 minutes and 1% wt. respectively. The model obtained has good predictive power, Methanol to oil molar ratio and reaction time followed by temperature were the major parameters that determine the response output (biodiesel yield).

Keywords: optimize, biodiesel, box-behnken design, transesterification, model

1. Introduction

Energy is an essential driving factor to socioeconomic development in our present society. Its impact touches all aspect of human endeavours [1]. Petroleum based fuels are the major fuel source used in transportation sector in most of the developing nations. Its combustion generates emissions which are nuisance to environment and adversely affect human health [2]. However, these nonrenewable sources will be exhausted in near future. Recent assessments of remaining petroleum reserves show the world will soon face relentless oil supply crisis [3]. Subsequently, various alternative energy sources are under intense investigation. Among these, biofuels have been identified to be sustainable alternative with promising long-term positive impact on the environment [4]. Large scale engagement of biofuels into the energy mix will further provide a platform for large scale job creation at both agricultural production and biofuel production sectors of industry [5,6]. Biodiesel, in particular is recognized to be greener as well as alternative to fossil diesel due to its properties such as higher cetane number, lower smoke and particulates, and lower carbon dioxide and hydrocarbon emissions than fossil diesel. In addition, it is biodegradable and nontoxic [7, 8]. Biodiesel is produced from different mechanism such as transesterification process, in which mono alkyl ester of long chain fatty acid is produced when triglyceride chemically react with alcohol (such as methanol or ethanol) in the presence of acid or base catalyst [9]. Recently homogeneous transesterification with NaOH and KOH catalyst is major technologies involved in production of biodiesel [10]. Heterogeneous solid acid catalyst have been used as an alternative to basic and enzyme catalysts since they can be used in both transesterification and esterification reaction [11]. Sulfated zirconia showed high activity and selectivity for esterification of fatty acids with alcohols [12]. Developing countries such as Nigeria have a comparative advantage for biofuel production because of greater availability of land, favourable climatic conditions for agriculture and lower labour costs [13]. However, the major problem to extensive commercial production of biodiesel is its relatively high cost of feed stock. It is preferable to use available local raw materials for the country where biodiesel plant will be installed [14]. Neem seeds are oil rich and have been shown to be viable source of oil for biodiesel production [15, 16, 17]. On the other hand, due to higher high free fatty acid levels of the oil from neem seeds sulfated zirconia which is classified as super acid catalyst due its thermal stability, resistance to catalyst poison and strong acidic properties to promote simultaneous esterification and transesterfication reaction and prevent undesirable product was used in the production of biodiesel from neem seed oil [18, 19].

Thus, the aim of this study is to use response surface methodology based on Box-Behnken statistical design to study and optimize the process variable in biodiesel production using Sulfated zirconia catalyst.

2. Materials and Methods

2.1 Chemical reagents

The chemicals are used as procured without further purification.

2.2 Sample preparation and oil extraction

The neem seeds were obtained from Bodinga Local Government area of Sokoto state, Nigeria. The seeds were sorted out, dehulled, ground into powder and the oil was extracted by soxhlet extraction method using n-hexane solvent.

2.3 Catalyst preparation

The solvent – free method by Sun – *et al.* [20]. was adopted.

2.3.1 Catalyst Characterization:

Infrared spectroscopy and thermo gravimetric was used to characterize the catalyst prepared. The absorption peak at 748 cm^{-1} represent $Zr\text{-}O_2$ stretching vibrations and the absorption peaks at 1017 and 1140 cm^{-1} are due to stretching frequencies of O-S-O (Appendix F). However, the TGA and DTA curves of prepared sulfated Zirconia catalyst show the weight loss at 100 ^0C and 750 ^0C due to loss of physically adsorbed water and SO_4^{2-}bounded to the surface of S-Zr (Appendix G).

2.4 Neem seed oil, biodiesel physicochemical characterization

The iodine value, acid value, free fatty acid, and saponification value were determined according to AOAC 1997 [21] methods. The physicochemical properties were determined according to standardized methods: the viscosity (ASTM D 445), the flash point (ASTM D 93), the pour point (ASTM D 97), the specific gravity (ASTM D 1298) and water and sediments (ASTM D 2709).

2.5 Experimental design

Response surface (Box-Behnken) statistical experimental design was used to design the optimization experiments. Four independent variables namely reaction time, temperature, methanol to oil ratio and catalyst were selected. Appendix A shows the lower and upper levels of the factors employed based on experience and literature survey [22]. The runs were completely randomized and a total of 27 runs were obtained. The experiment was designed using MINITAB 17 statistical software and data that was collected from the experiment was analyzed using same software at $\alpha = 0.05$ (95% confidence level).

2.6 Description of experimental runs

Each run involved 10g of neem oil in test tube, the amount of methanol and catalyst were added as specified in the design matrix. The mixture was then refluxed at appropriate temperature (60, 62.5 or 65ºC) for the specified period (60, 90, or 120 minutes) as in design matrix (Appendix A). At the end of stipulated time the test tube containing the mixture, was allowed to cool and the mixture was centrifuge to remove the catalyst. The mixture was transferred in to separating funnel to separate under gravity overnight. The separated upper layer was placed into an evaporating dish and heated in water bath at 90 ^OC for 30 minutes to remove the residual methanol, then neutralized with dilute phosphoric acid (pH 4.0). The methyl esters were then washed with hot distilled water (1:5 v/v) until the washed water had a pH of 7.0. The residual water was removed by drying the methyl esters over heated (100 ^0C) anhydrous sodium sulphate [23]. The percentage yield was calculated using equation 1.

$$\text{Yield} = \text{weight of Biodiesel}/\text{weight of sample} \times 100 \quad ..1$$

2.7 Analyses of the biodiesel Produced using GC-MS

The fatty acids methyl esters (FAMEs) mixture from the produced biodiesel was analyzed using a QP-2010 model GC-MS machine. Two microliters (2 µl) of the produced biodiesel sample was injected into the gas chromatograph at injection temperature of 250 0C. The column oven temperature was programmed between 60-280 0C at 5 ^0C/min; hold 5 min at 280 ^0C. The acquired chromatographs were scanned and the components identified based on software matching with mass spectra.

3. Results and discussions

3.1 Physicochemical properties of the neem oil

The percentage Oil yield of the plant seeds is one of factors for assessing the economic viability of a feedstock for biodiesel production. Table 2 showed the oil content of 40.64 ± 1.01%.

Free fatty acids (FFA) content of the raw oil is a parameter that affects the optimal conversion of the triglycerides to biodiesel (FAMES) and also dictates the selectivity of a suitable catalyst for the transesterification reaction [24]. Iodine value is the measure of average amount of unsaturation of fats and oils which indicate the suitability of oil use as biodiesel. The result obtained 82.45 ± 1.60 $gI_2/100g$ as presented in Table 2 (Appendix B) is within the range reported by [25] for neem seed oil.

3.2 Effect of process on the mean biodiesel yield

Figure 1 gives a summary of the biodiesel yield obtained from the 27 experimental runs conducted different levels of the four process variables investigated. The biodiesel yield varies from minimum of 59.54% to maximum of 89%. There is predominant increase in yield with increase in methanol to oil ratio. Notably the yield increases with increase in reaction time from 60 min to 90 min, but then decreases when the reaction time raised to 120 min.

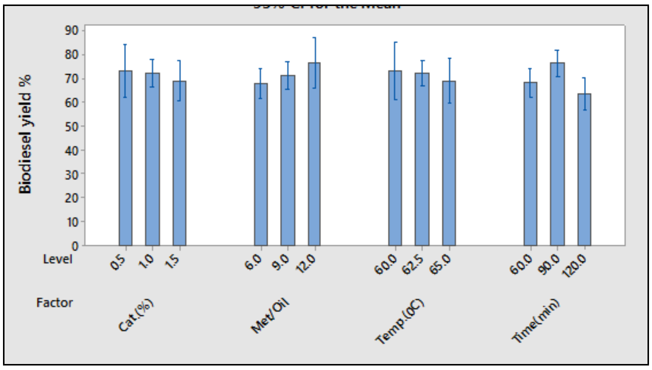

Fig 1: summary of the effect of the process variables on the biodiesel yield from neem seed oil.

Figure 2 is contour plots describing the relationship between any two of the process variables as they affect biodiesel yield while holding the other two variables constant. The biodiesel yield increases with increase in methanol to oil ratio and decreases with increase in temperature beyond the boiling point of methanol. Interestingly, the biodiesel yield increases with increase of both catalyst concentration and temperature when time and methanol to oil ratio are hold constant at 90 minute and 9:1 respectively.

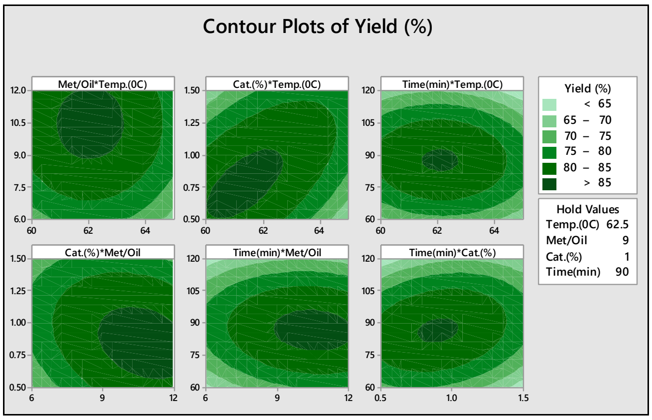

Fig 2: contour plots showing the relationship between biodiesel yield and process variables.

3.3 Properties of biodiesel

The fuel property of the produced biodiesel is shown in Table 4. Acid value is a measure of free fatty acids in a given product [26]. Acid number of the biodiesel produced from neem seed oil indicates that it contains higher fatty acid composition of 0.44 mgKOH/g but is within the acceptable range (0 -0.50 max) specified by the ASTM [27] Iodine Value determines the chemical stability of biodiesel fuels [28]. Higher iodine value indicates less stability of biodiesel. Neem oil fatty acids methyl esters had iodine values of 36.54 ± 0.10 g/100g (Table 4). The results infer that the produced biodiesel may have higher oxidation stability due to relatively lower iodine value. Kinematic Viscosity is one of the required parameters regarding fuel atomization, combustion as well as fuel distribution [29]. Kinematic viscosities of the produced biodiesel is within ASTM specification. Cetane number is fuel quality parameter that is related to the ignition delay time and combustion quality of a fuel, it measures the readiness of a diesel fuel to auto ignite when injected into the diesel engine [30]. The results obtained (Table 4) above are higher than 23.65 reported for *lagenaria vulgaris* oil biodiesel [31]. Flash point is the lowest temperature at which a combustible mixture will be formed above the liquid fuel. However, higher than 55ºC reported for bottle gourd [32]. Specific gravity is an important fuel quality parameter that is related to fuel injector system. Its value must be maintained within a tolerable limit to allow optimal air to fuel complete combustion [33]. The higher the specific gravity of a fuel the greater the mass of fuel injected into the engine and hence more power [34]. Water and Sediment content is the measure of fuel cleanness. According to ASTM D 6751 standard the percentage of water and sediment content for B100 biodiesel must not exceeds 0.05% [35].

The profile of fatty acids methyl esters in neem biodiesel shown in Table 5 (Appendix E), shows methyl-11-octadecadienoate (linoleic acid ester) as the dominant ester. This compound has one level of unsaturation which may accords it likelihood to undergo a peroxidation. Therefore, a biodiesel produced from this feedstock could deteriorate on long storage due its susceptibility to the attack of oxygen. However, the presence of methyl hexadecanoate and methyl octadecanoate the second and third most abundant methyl esters in the produced biodiesel will enhance the stability of the diesel been them saturated compounds and less susceptible to peroxidation. Interestingly, the biodiesel produced may have higher stability due to absence of polyunsaturated esters with double and triple bonds that causes blockage in engine injection system [36].

4. Conclusion

The methyl ester of biodiesel produced from neem seed oil has acceptable properties approved by the American Society of Testing Material (ASTM) with high energy content while the high acid value can be reduced by pretreatment such as neutralization before the oil transeterification. The production of biodiesel from neem seeds oil should be encourage not only for reducing the overwhelming energy crisis but also serve as means of relieving the environment from carbon dioxide emissions.

5. Acknowledgement

he first author thanks Sokoto state ministry of science and technology for the study leave to pursue his postgraduate studies.

6. References

1. Sokoto AM, Hassan LG, Salleh MA, Dangoggo SM, Ahmad HG. Quality Assesment And Optimization of Biodiesel from Lagenaria Vulgaris Seeds Oil. International Journal of Pure and Applied Science Technology. 2013; 15:55-65.
2. Mussatto SI. A Closer Look At The Developments And Impact Of Biofuels In Transport And Enviroment; What Are The Next Steps? Biofuel Research Journal. 2016; 9:31-36.
3. Ogunsiyi HO. Acid and Base Catalyzed Transesterification Of Mango (*Mangiferaindica*)Seed Oil To Biodiesel. IOSR Journal of Applied Chemistry. 2012; 2:18-22.
4. Muhammad AB, Muyibat O, Hassan LG, Aliero AA. Optimization of Process Variables In Acid Catalyzed In Situ Transesterification Of Hevea Bransillensis (Rubber Tree) Seed Oil Into Biodiesel. Biofuels. Taylor And Francis Group, 2016. Available Online at http://dx.doi.org/10.1080/17597269.2016.1242689. Accessed on 18/10/2016.
5. Antolin G, Tinaut FV, Briceno Y. Calcium oxide as a solid base catalyst for tranesterification of soybean oil. Bioresource technology. 2003; 83:111-114.
6. Bajpai, D, Tyagi VK. Biodiesel: Source, production, composition, properties and its benefits. 2006; 55:487-500.
7. Al Zuhair S. Production of biodiesel:properties and challages. Biofuels. 2007; 1:57-66.
8. Encinar JM, Gonzalex JFRA. Rodriguez Ethanolysis of used frying oil: Biodiesel preparation and characterization. Fuel process technology. 2007; 88:513-522.
9. Yusuf NA, Kamarudin S, Yaakub Z. Overview on the current trends in biodiesel production. Energy Conversion and Management. 2003; 52:2741-2751.
10. Lee HV, Juana JC, Taufiq Yap YH. Preparation and application of binary acid–base CaO–La 2O3 catalyst for biodiesel production, Renewable Energy. 2015; 74: 124-132.
11. Kim HJ, Kang BS, Park JM. Transesterification of

vegetable oil to bio diesel using heterogeneous base catalyst. Catalysis Today. 2004; 93:315-320.
12. Anton AC, Dimian G. RothenbergSolid acid catalyst for biodiesel production – towards sustainable energy. Advance synthesis catalysis. 2006; 8:75-81.
13. Balat M. Potential alternatives to edible oils for biodiesel production. Energy Conversion and Management. 2011; 52:1479-1492.
14. Anastasov A. Biodiesel-Basic characteristics, technology and perspectives, Biotecnol&Biotechnol Anniversary scientific conference, 2009. available online at www.diagnosisp.com/dp/journals /view_pdf.php?...id..., Accessed on 14/03/2015
15. Muthu H, Sathyaselvabala V, Varathachary T, Kirupha Selvaraj D, Nandagopal J, Subramanian S. Synthesis Of Biodiesel From Neem Oil By Two-Step Tranesterification. Braziliian Journal Of Chemical Engineering. 2010; 27:601- 608.
16. Muhammad C, Alhassan Y, Bello ZAI. Ifeyinwa Composition and Characterization of Crude Glycerol from Biodiesel Production Using Neem Seed Oil. Journal of Basic Applied Chemistry. 2011; 1:80-84.
17. Diedhiou Djibril, Diatta ML, Faye M, Vilarem G, Sock O, Rigal L. Biodiesel production from neem seeds (*Azadirachta indica A.Juss*) oil by its base-catalyzed Transesterification and its Blending With Diesel. Research Journal of Chemical Sciences. 2015; 5(10):13-19.
18. Galadima A, Muraza O. Biodiesel Production From Algae By Using Heterogeneous Catalysts: A Critical Review. Energy 2014; 78:72-83.
19. Yadav GD, Nair JJ. Sufated zirconia and its modified versions as promising catalysts for industrial processes. Micro Pormes opormater, 1999, 1- 10.
20. Sun Y, Ma S, Du Y, Yang J. Solvent – free preparation of nanosized sulfated zirconia with bronsted acidic sites from a simple calcinations. Journal of physical Chemistry. 2005; 109:2567-2572.
21. Association of Oil Chemist, Method Cd 3d-63, Acid value, Sampling and Analysis of Commercial Fats and Oils, Arlington, Virginia. 15 ed, 1997.
22. Hawash SI, Abdel Kader E, Joseph YF, El Diwani. Biodiesel Production By Esterification /Transesterification Of Jatropha Oil Over Sulfated Zircona. International Journal Of Innovative Science, Engineering & Technology. 2014; 1:86-103.
23. Muhammad AB, Kabiru B, Tambuwal AD, Aliero AA. Assessment And Optimization Of Conversion Of L. Siceraria Seed Oil Into Biodiesel Using Cao On Kaolin As Heterogeneous Catalyst. International Journal Of Chemical Technology. 2015; 7:1-11.
24. Deshmukh SJ, Bhuyar LB. Transesterified higan (Balanites) oil as a fuel for compression ignition engines. Journal of Biomass and Bioenergy. 2009; 33: 108-112.
25. Aransiola EF, Betiku E, Ikhuomoregbe D, Ojumu TV. Production Of Biodiesel From Crude Neem Oil Feedstock and Its Emissions From Internal Combustion Engines. African Journal of Biotechnology. 2012; 11:6178-6186.
26. Knothe G. Analyzing Biodiesel: Standards and Other Methods, Review. Journal Of American Oil Chemist Society. 2006; 83:823-25.
27. Gerpen JV, Chanks B, Pruszo R, Clements D, Knoth G. Biodiesel Analytical Methods Subcontractor Report, National Renewable Energy Laboratory, 2004. available at; http://www.bentlybiofuels.com/ pdfs/NREL_BD_Analytical. pdf accessed on 16/01/2016,
28. Mukhtar M, Dangoggo SM, Ross AB. Low Temperature/Pressure Hydrothermal Microwave as a Potential Alternative Method of Processing Microalgae, Proceeding of the 35th Chemical Society of Nigeria, Annual and International Conference. 2012; 1:510-515.
29. Salaheldeena M, Aroua MK, Mariod AA. Physico Chemical Characterization and Thermal Behavior Of Biodiesel And Biodiesel-Diesel Blends Derived From Crude Moringa Peregrinased Oil. Journal Of Energy Conversion and Management. 2015; 92:532-542.
30. Fakhary EM, El Maghraby DM. Fatty Acids Composition And Biodiesel Characterization Of Dunaliella Salina. Journal of Water Resource and Protection. 2013; 5:894-899.
31. Sokoto AM, Hassan LG, Dangoggo SM. Influence of Fatty Acid Methyl Ester On Fuel Properties Of Biodiesel Produce From *Curcubita Popo. Nigerian* Journal Basic and Applied Science. 2011; 19:81-86.
32. Hassan LG, Sani NA. Preliminary Studies On Biofuel Properties of Bottle Gourd (Lagenaria Siceraria) Seeds Oil. Nigerian Journal of Renewable Energy. 2010; 11:20-25.
33. Galadima A, Garba ZN, Ibrahim BM. Homogeneous and Heterogeneous Trans- Esterification of Groundnut Oil For Synthesizing Methyl Biodiesel International Journal of Pure and Applied Sciences. 2008; 2:138-144.
34. GL N Rao, Ramadhas AS, Nullusamy N, Sakthivel P. Relationship Among The Physical Properties of Biodiesel and Engine Fuel System Design Requirement. International Journal of Energy and Environment. 2010; 1:919-926.
35. Mukhtar M, Muhammad C, Dabai MU, Mamuda M. Ethanolysis Of Calabash (*Lageneria Sinceraria*) Seed Oil For The Production Of Biodiesel. American Journal of Energy Engineering. Available Online at http://www.Sciencepublishinggroup.com/j/ijrse. 2 (2015) 141 -145.
36. Knothe G. Analyzing Biodiesel: Standards and Other Methods, Review. Journal of American Oil Chemist Society. 2006; 83:823-25.