



Production of Biodiesel and Glycerol from Shea Butter Seed Oil at Different Operational Conditions

M. N. Yaro*, I. A. Bashir, Aminu Dauda, Hamza Badamasi

Department of Chemistry, Federal University, P.M.B 7156, Dutse, Jigawa State, Nigeria

*Email: yaro_n@yahoo.com G.S.M. +2347032863036

Abstract Shea butter seeds were collected and processed. 500.000 g of the processed seeds were subjected to soxhlet extraction for 5 hours at 85°C using n-hexane (as extracting solvent). The extract (seed oil) was recovered from the extracting solvent by rotary evaporation and concentrated to a constant weight at 37 °C. A solution mixture of volume ratio, 1: 9(seed oil to methanol) was prepared and subjected to transesterification reaction under different operational conditions of temperature, catalyst (NaOH) and reaction time for biodiesel production. The biodiesel produced was separated from the associated product (glycerol) and concentrated to constant weight. The saponification value of the glycerol component was determined. The work showed that the optimum operational conditions for maximum biodiesel production were 65°C, 1.00 M of NaOH (as catalyst) and 65 minute. The work also showed that: temperature' above 65°C led to decomposition of biodiesel; catalyst concentrations above 1.00 M led to formation of soap as by-product and; prolonging of reaction time beyond 65 minute led to hydrolysis of the biodiesel formed.

Keywords Shea butter seed oil; biodiesel, reaction time; temperature; concentration of catalyst

Introduction

The interest in adopting the use of renewable energy came to the fore during the worldwide energy crisis of the 1970s when high fuels (oil and gas) demand highlighted the world's dependence on fossil fuels in which the rate of consumption was much faster than it was drilled from the earth crust, which may result in the depletion of fossil fuels supply all over the world [1]. In addition, the hike price of fossil fuels (petrol, diesel, kerosene, liquefied natural gas, e.t.c.), which are difficult to get by the majority of common people also contributes nuisance in using these fuels [2]. Population growth worldwide, which led to high energy demand, environmental problem and health hazards associated with the use of fossil fuels also fronted the search for renewable energy sources as alternative to popular conventional fossil fuels [3].

In order to overcome or minimize the problems associated with the drilling, refining and combustion of fossil fuels, as well as to succeed in achieving alternative renewable energy sources (biodiesel inclusive), there is the need to embark on research and exploitation of the available renewable biomass resources in our natural environment for the energy generation. This can be achieved by domesticating and growing viable plants as energy crops on our endowed vast land [4].

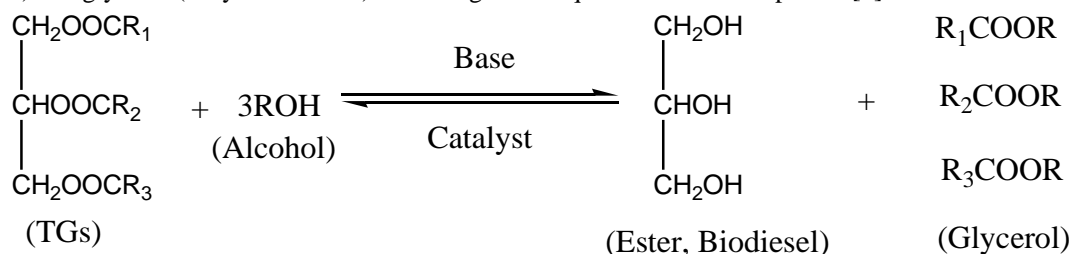
Biofuels are generally alternative renewable energy sources, which are environmentally-friendly due to their biodegradability and low emission of carbon (ii) Oxide, sulphur-free quality and non-toxic nature [3]. Biodiesel was found to be promising alternative to popular fossil fuels, as it possesses all the properties of the conventional diesel,



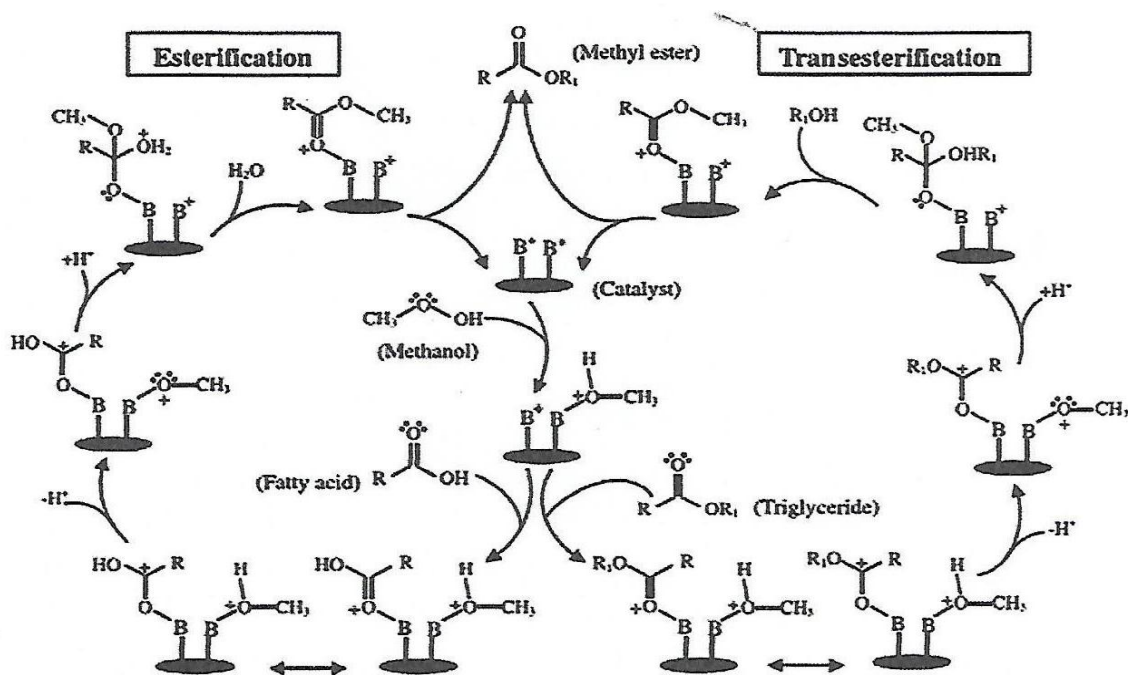
such as high flash point and improved cetane number [5]. Biodiesel is a clean burning fuel produces through transesterification reaction between triglycerides (TGs) and short chain alcohol (methanol or ethanol) in the presence of catalyst. The process of biodiesel production (i.e. transesterification reaction) is achieved through various methods such as base catalyzed transesterification, direct acid catalyzed transesterification or conversion of oil to fatty acid and subsequently to biodiesel [1].

Some common raw material for biodiesel production include: soya beans, palm oil, shea butter oil, poultry oil, fish oil, groundnut oil, algae, *Jatropha curcas* seed oil, *Gossypium hirsutum* seed oil, sesame oil and sorghum [6].

The chemistry of biodiesel production through transesterification reaction involves deprotonation of alcohol with a base and become a very strong electrophile. The base serves as a catalyst, which helps the transesterification reaction between TGs and short chain alcohol (usually methanol) to quickly occur and form ester of fatty acid (biodiesel) and glycerol (trihydric alcohol) according to the equation below as reported [7].



During transesterification of TGs into biodiesel, some of the biodiesel formed decomposed into glycerol at temperature above 65°C; more TGs participate in saponification reaction with the catalyst at high concentration of base catalyst and; extension of reaction time leads to hydrolysis of ester into TGs, which subsequently produces soap [4].



B^+ = Bronsted acid site on the catalyst surface

R = alkyl group of fatty acid

R_1 = alkyl esters of triglyceride



The major focus of recent advancement is the development of recyclable heterogeneous solid acid catalyst (SACs) for easier production of biodiesel. These catalysts have been established as favorable alternative to commercially used catalyst for biodiesel production [7]. SACs both the Bronsted-type (such as sulphonic acid containing materials) and Lewis-type (such as mixed sulphated oxides) combined the advantages of heterogeneous base catalysts and mineral acids [8]. The exceptional advantages to this particular class of catalyst (SACs) are insensitivity to moisture and simultaneous esterification and transesterification reactions as can be seen in the following schematic reaction diagram as reported by Nasar *et al* [7]:

Elimination of the final biodiesel washing step, minimizing of corrosion problem even in the presence of acid species, selectivity, recyclability and easy regeneration of catalyst after use are also advantages of SACs [9]. Another advantage of SACs is its ability to sterically hinder salvation of the catalytic active sites from the action of water, which helps in minimizing catalyst deactivation, minimizing of product (biodiesel) contamination as a result of easy separation from the reaction medium [10]. In addition, the applicability and hydrophobic surface of SACs, which prevents the polar by-products (water and glycerol) from deactivating the active sites, which in return enhances selectivity adsorption of oily hydrophobic molecules to the surface of the catalyst as reported by Choundan and Sharma [8]. These advantages among many others attracted attention in considering solid acid catalysed biodiesel production much over base catalysed process on low grade feedstock [7].

However, very little has been done on the mechanism and reaction pathways of TGs on SACs during the production of biodiesel. These short comings together with some other technological challenges necessitated the adoption of predominantly conventional method of biodiesel production. (i.e. base catalysed transesterification method) in the present work. This work reports studies on the extraction of shea butter seed oil, as well as the effects of temperature, reaction time and concentration of catalyst on the production of biodiesel and glycerol from shea butterseed oil. The work also reports studies on the saponification value of the glycerol generated under these operational conditions.

Materials and Methods

Collection and Processing of Experimental Sample

Mature and dried shea butter seeds were collected from Dawakin-Tofa Local Government Area, Kano State, Nigeria. The epicarp (outer cover) of the seeds was cracked and removed and the seeds were ground using wooden pestle and mortar.

Extraction of Shea Butter Seed Oil.

A mass (500.00 g) of the ground seeds was placed in a round bottomed flask connected to a Merckham still apparatus (soxhlet extraction set apparatus) and subjected to soxhlet extraction for 5 hours at 85°C using n-hexane. The extract (shea butter oil) was recovered from extracting solvent (n-hexane) by rotary evaporation and concentrated to a constant weight at 37°C on hot plate in fume cupboard.

Preparation of Solution Mixture

A solution mixture was prepared by mixing the extract (shea butter oil) with methanol in the volume ratio, 1:9 of extract to methanol according to the method described by Garba *et al* [4] with few adjustments.

Effect of Temperature on Biodiesel Production

This was carried out in the light of the procedure adopted by Yaro [11] with few adjustments. The temperatures used were 45°C, 55°C, 65°C and 75°C. The process was carried out in triplicate and the average volume of biodiesel generated at each reaction temperature was evaluated.

Effect of Concentration of Catalyst (NaOH) on Biodiesel Production

The effect of concentration of catalyst was also carried out in the light of the procedure described by Yaro [11] with few adjustments. The volumes of reaction mixture and catalyst used were 400.000 cm³ and 10cm³, respectively. The



concentrations of the catalyst (NaOH) used were 0.50 M, 1.00 M, 1.50 M, 2.00M and 2.50 M, which were added into five (5) different reactors of equal capacity (i.e. 500.00 cm³ round bottomed flasks) each containing 400.00 cm³ of the solution mixture earlier prepared. The reactor were labeled A, B, C, D and E, respectively.

The catalysed solution mixtures in the reactors were heated at 65°C along with stirring at the rate of 450 rpm using magnetic stirrer. (The heating temperature, 65°C used was based on the findings of the effect of temperature carried out earlier in the present work).

The effect of reaction times was investigated using 10.00cm³ of 1.00M NaOH at 65°C according to the method adopted by Garba *et al* [4] with few adjustments.

Determination of Saponification Value

The saponification value was determined using the method described by Yaro [11] with few modifications. The saponification value was evaluated (in mol/dm³) using the modified form of equation adopted by Alabi [12] below.

$$S_y = \frac{(S - B) \times C \times \text{mass of 0.1 M KOH}}{\text{volume of glycerol used}}$$

where S_y = Saponification Value

S = Sample titre Value

B = Blank titre value

C = Molar concentration of HCl

Results and Discussion

Results

The results of all the experiments carried out in this work are shown in Tables 1-3 below. Table 1 shows the effect of temperature on transesterification of TGs into biodiesel and glycerol. Table 2 gives the results obtained under the effect of concentration of base catalyst (NaOH) during the transesterification of TGs into biodiesel at 65°C. Table 3 shows the effect of reaction time on transesterification of TGs into biodiesel and glycerol at 65°C.

Table 1: Effect of Temperature on Biodiesel and Glycerol Production from

Temperature (°C)	35	45	55	65	75
Volume of biodiesel (cm ³)	118.00	144.00	162.00	240.00	184.00
Volume of glycerol (cm ³)	54.00	58.00	92.00	120.50	132.00
Saponification value (mol/dm ³)	0.00	0.00	0.00	0.00	0.46

Table 2: Effect of Concentration of Catalyst (NaOH) on the Production of Biodiesel and Glycerol

Concentration of KOH (mol/dm ³)	0.50	1.00	1.50	2.00	2.50
Volume of biodiesel (cm ³)	132.00	208.00	200.00	192.00	189.00
Volume of glycerol (cm ³)	82.00	104.80	115.00	103.00	101.50
Saponification value (mol/dm ³)	0.00	0.00	0.12	0.22	0.31

Table 3: Effect of Reaction Time on the Production of Biodiesel and Glycerol from

Reaction time (minute)	35	45	55	65	75
Volume of biodiesel (cm ³)	183.00	191.00	204.50	211.00	198.00
Volume of glycerol (cm ³)	80.50	83.00	95.00	101.00	109.50
Saponification value (mol/dm ³)	0.00	0.00	0.011	0.00	0.22

Discussion

The result of the effect of temperature on the production of biodiesel and glycerol from Shea butter seed oil is shown in Table 1. The result (Table 1) showed that transesterification reaction significantly varied with temperature, in the which low yield of biodiesel and glycerol was observed at 35°C, 45°C, 55°C and the high yield of biodiesel and glycerol was achieved at 65°C. The low and high yield observed may be connected to incomplete and complete



transesterification reactions, respectively. These findings is in accordance with the findings of Yaro [11]. The low quantity of biodiesel and high quantity of glycerol observed at 75°C may be associated with the decomposition of biodiesel into glycerol as reported by Senoz *et al* [13]. The little saponification value observed at 75°C could possibly be connected to side saponification reactions of TGs, which led to formation of soap (as by-product). This is in accordance with the findings of Garba *et al* [4].

Table 2 presents the effect of catalyst concentration on the amounts of biodiesel and glycerol, as well as the soap obtained at 65 °C. The result showed that 1.00M was the optimum concentration of catalyst. The low yield observed at catalyst concentration (0.50 M) and high yield recorded at catalyst concentration (1.00 M) may be connected to the incomplete and complete conversions of TGs, respectively during transesterification reaction as reported by Yaro [4]. The decrease in the amount of biodiesel and the corresponding increase in the amounts of glycerol and saponification values observed at catalyst concentrations above 1.00 M (ie 1.50 M, 2.00 M, and 2.50 M) may be associated with the over participation of more TGs in the saponification reaction with the NaOH [4, 14].

Table 3 shows the result of the effect of reaction time on biodiesel and glycerol yield, as well as the saponification value at 65 °C. From the result (Table 3), it could be said that 65 minutes was the optimum reaction time for biodiesel production because it was the time at which highest collection of biodiesel was achieved. The increase in the volumes of biodiesel and glycerol at reaction times range 35-65 minutes observed may be connected to progressive increase in transesterification reaction as reaction time increases to a maximum product yield at 65 minutes. This is because during transesterification, biodiesel production continues with the reaction time up to completion provided that there are enough reactants (oil and alcohol) in the reactor. The decrease in biodiesel and the corresponding increase in glycerol observed at reaction 75 minutes may be associated with the hydrolysis of ester (the biodiesel formed). This is because after complete transesterification of TGs into biodiesel, extension of reaction time leads to hydrolysis of biodiesel formed into fatty acid, which causes formation of more soap (by-product) [4]. The relative high saponification value observed at 75 minutes reaction time could be connected to the formation of more soap from the hydrolysis of the ester formed into fatty acid. This is because fats and oils undergo hydrolysis with caustic alkali to form propane 1,2,3- triol and the corresponding sodium or potassium salts (soap) of the component fatty [15].

Conclusion

Favourable transesterification reaction conditions for appreciable production of biodiesel and glycerol by base catalysed transesterification reaction were established. From the experimental findings of the present work, it could be concluded that large scale production of cheaper and environmentally-friendly biodiesel as alternative to non-renewable environmentally-aggressive petrodiesel can be achieved from shea butter seed oil.

References

- [1]. Ndana, M. and Manko, M. U (2010): Biodiesel Production: A future energy option for automobiles and power generating plants in Nigeria. *Kontagora Journal of Science and Technology*, 8(1): 22- 30
- [2]. Ewenchi, M. M. and Yaro, M. N. (2010): Gaseous fuel production by anaerobic fungal degradation of banana leaves. *Chemsearch Journal*, 1 (1): 28-32.
- [3]. Sani, Y. M. Wan, D. W. and Abdulaziz, A. R. (2014): Activity of Solid acid catalyst for biodiesel production, a critical review. *Applied Catalyst A*; 470: 140-161.
- [4]. Garba, B. Gumel, S. M. and Babayo, M. B. (2012): Effects of Operational Parameters on Biodiesel Production. *Dynamic in Science and Technology*; a publication of Kano University of Science and Technology, Wudil. Pp 11-20
- [5]. Shajaratun, N. Z. A., Taufiq-Yap, Y.H, Rabiah, N. M. F., (2014): A production of Biodiesel from Palm Oil using modified Malaysian natural dolomites. *ELSEVIER: Energy Conservation and Management*, 78:738-744
- [6]. Pinto, A. C., Guariero, L. L. N., Rezende, M. J. C., Rineiro, N., M., Torres, E. A and Lopes, W. A. (2005): An overview, *Brazil Chemical Society*, 13: 13-30.



- [7]. Nasar, M., Taufiq, Y. H., Rashid, U and Lokman, T. B. (2012): Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production; A review, *ELSEVIER: Energy, conservation and Management*. (In press).
- [8]. Choundan, A. P. S. and Sarma, A. K. (2011): Modern Heterogeneous Catalyst for biodiesel production; Comprehensive review. *Renewable Sustainable Energy*, 15: 4378-4399.
- [9]. Guo, F., Fang, Z., Xu, C. C. and Smith, R. L. (2012): Solid acid mediated hydrolysis of biomass for producing biofuel. *Prog Energy Combustion Sci.* 38: 672-690
- [10]. Nusterer, E. Biochi, P. E. and Schuwarz, K. (1996): Interaction of water and methanol with a zeolite at high coverages *Chemical Physics Lett.*, 253:448- 455.
- [11]. Yaro, M. N. (2018): Effect of temperature, concentration of catalyst and reaction time on biodiesel production from Gossipium Hirsutum Seed. *International Journal of Science & Engineering Research*, 9 (5): 2124 – 2129.
- [12]. Alabi, K. A. (2014): Chemical Characterization of Soluble Soap Prepared from Milkbush (Theretia peruviana) Seed oil. Proceedings of 37th Annual International Conference, Workshop and Exhibition of Chemical Society of Nigeria (CSN), Vol. 2 Held at Ibom Hall, IBB Way, Uyo, Akwa Ibom State, Nigeria, Pp. 558-563.
- [13]. Sensoz, S. Angin, D. and Yargin, S. (2000): Influence of particle size on the pyrolysis of repeseed (*Barassica napus L.*) fuel properties of bio-oil. *Biomass and Bioenergy*, 19: 271-279.
- [14]. Mohibbe, A.M. and Waris-Naher, N. M. (2008): Prospects and Potentials of fatty acid methyl ester of some non traditional seed oils for use as biodiesel in India. *Boimas and Bioenergy*, 29.
- [15]. Ababio, O. Y. (1985): New School Chemistry Certificate Science Series (Revised edition), Africana FEP Publishers Limited, in association with FEP International Private Limited, Hamzat Building, 22/26 Park Road, Sabongari, Zaria Pp. 495-499

