

Full Length Research Article

CATALYTIC SYNTHESIS OF ETHYL ESTER FROM SOME COMMON OILS

*GALADIMA, A¹. & GARBA, Z. N².

¹Surface Chemistry and Catalysis Group, University of Aberdeen, AB24 3UE, Aberdeen, UK.

²Department of Chemistry, Ahmadu Bello University, P.M.B. 1044, Zaria, Nigeria

*ahmadgldm@yahoo.com

ABSTRACT

Catalytic conversion of ethanol to fatty acid ethyl esters (FAEE) was carried out by homogeneous and heterogeneous transesterification of melon seed, shea butter and neem seed oils using NaOH, KOH and 5wt%CaO/Al₂O₃ catalyst systems respectively. Oil content of the seeds from n-hexane or hot water extract ranged from 25.0-33.3% and increased in the order melon seed < shea butter seed < neem seed. The heterogeneous catalyst maintained an optimal activity after 5 cycles of reusable applications and produced higher FAEE of 95.63% than 91.2% and 92.8% obtained with KOH and NaOH respectively. After purification by distillation of excess ethanol and neutralisation and separation of the homogeneous catalysts, the FAEE was subjected to qualitative analysis to determine its potential application as commercial biodiesel based on international specifications. With the exception of neem seed oil FAEE that shows high acid value and total ash content the esters could be used directly or as blend in diesel engines to give good performance.

Key words: Ethyl ester, synthesis, catalytic activity, common oils, biodiesel potential.

INTRODUCTION

Reaction of a low molecular weight alcohol (usually methanol to butanol) with either fresh or used vegetable oil/fat is an industrial chemical process that transforms the triglyceride esters in the oil feedstock to corresponding fatty acid alkyl esters and glycerol. The transesterification reaction therefore serves as an alternative for eliminating the viscosity problems associated with direct use of vegetable oils in diesel engines. It is similarly a greener technology recommended by international organisations due to good potential for climate change mitigation (IPCC, 2007). The resulting alkyl esters from the reaction are totally biodegradable substances that can be used directly or blended with petroleum diesel to reduce greenhouse gases emissions and ensure sustainable environmental management. Developed countries like United Kingdom have implemented a regulatory policy requiring 5.75% blend in diesel fuel (Anderson *et al.*, 2009). In developing countries

like Nigeria the recent biofuels policy seeks to ensure 20% blend ratio by 2010 (NNPC, 2007).

Various Literature studies indicated the transesterification reaction to be an equilibrium process that can be carried out either catalytically or non-catalytically at different temperatures (Abigor *et al.*, 2000; Galadima *et al.*, 2009). Catalysts involved include homogeneous substances such as KOH, NaOH, their corresponding alkoxides and mineral acids like HCl or heterogeneous catalysts ranging from pure metals to supported oxides such as CaO/MgO, SiO₂/ Al₂O₃ e.t.c. (Alamu *et al.*, 2007; Liu *et al.*, 2008). The homogeneous catalysts are reported to show faster conversion but are difficult to be separated at the end of the reaction causing increased production costs and environmental concerns due to disposal problems. Heterogeneous catalysts on the other hand can be recycled, reused and yield good purity glycerol at certain temperatures. For example Liu *et al.*, (2007) reported SrO to show long catalyst lifetime and could maintain sustained activity even after being repeatedly used for 10 cycles. The study proved the transesterification of soybean oil to biodiesel using SrO as a catalyst to be a commercially viable way to decrease the costs of biodiesel production. Similarly, Yan *et al.* (2008) reported 92.0% conversion at 64.5°C during transesterification of rapeseed oil over CaO/MgO catalyst system. However, activity decay may be a problem.

The current study reports the catalytic conversion of three common oils (melon seed, shea butter and neem seed oils) with the aim of investigating the activities of some homogeneous and heterogeneous materials as transesterification catalysts and ascertaining the potential of the oils as commercial biodiesel feedstock.

MATERIALS AND METHODS

Transesterification reactions were monitored in a Pyrex type all glass reactor (250 cm³ size) equipped with magnetic stirrer, thermometer, and with adequate isolation from the environment to prevent heat lose from the system. Measurements were carried out using an electrical Lenton Model weighing balance that was previously calibrated with known weight of samples. Chromatographic characterisations where applicable were carried out using PE Auto-system GC-MS.

Ethanol, potassium hydroxide and sodium hydroxide used in this study were BDH, England chemicals with purity range of 97.5 to 99.20% provided by Chemistry Department Usmanu Danfodiyo University Sokoto, Nigeria. CaO and Al₂O₃ used were Fischer type

Laboratory grade chemicals of about 98% purity. The seeds (melon, neem and shea butter) were obtained locally in Sokoto, oven dried followed by n-hexane and hot water oil extractions, distillation and storage in Pyrex glass containers for few days prior to ethyl ester synthesis. All other reagents used were of Analytical grade purity from BDH England.

Ethyl ester synthesis and analysis: The melon seed and Shea butter seed oils were transesterified by homogeneous method while the neem seed oil was transesterified heterogeneously. Exactly 0.5g of KOH was added slowly to 20g of ethanol and stirred until both dissolved to form a homogeneous mixture. 100g of melon seed oil was transferred into the reactor and pre-heated to 55°C. The earlier prepared solution was added to the oil; the mixture was stirred vigorously and kept in a water bath at 67.5° for two hours until two clear distinct layers (upper amber yellow and lower dark brown layers) were observed.

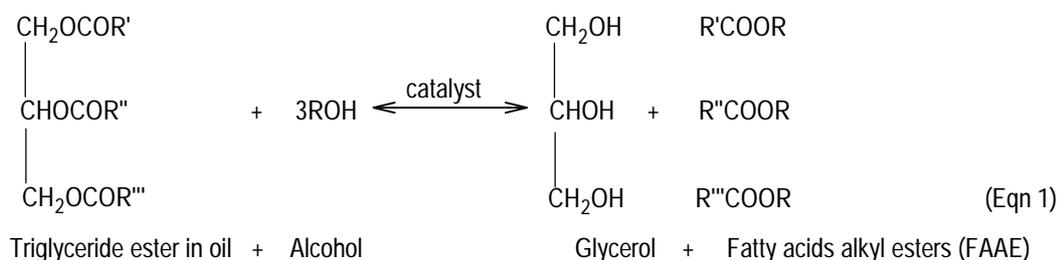
For the shea butter seed oil; 0.5g of NaOH was accurately measured, and readily mixed with 20cm³ of ethanol to dissolve the NaOH pellets by stirring and swirling to get a single phase solution,

which was quickly transferred to the reactor containing 50g of the oil at 40°C and the resulting mixture maintained at the same temperature for 2 hrs. In the transesterification of neem seed oil, 1g of 5wt% CaO/Al₂O₃ calcined at 400°C was quickly transferred into the reactor containing a mixture of ethanol and oil (1:4 v/v ratio) pre-heated to 42°C. Ethanol conversion to ethyl ester was carefully monitored at the same temperature for 2 hrs.

In all cases the two distinct layers formed were separated for further analyses. The ethyl ester product was analysed for parameters such as density, moisture content (water and sediments), Pour point, acid value and total ash content using standard American Society for Testing and Materials (ASTM) procedures previously adopted elsewhere (Galadima *et al.*, 2008).

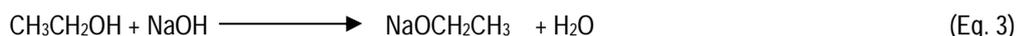
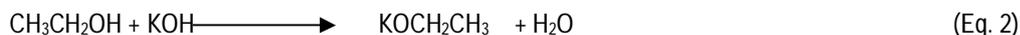
RESULTS AND DISCUSSION

Reaction Chemistry: Under normal conditions a low molecular weight alcohol interacts with triglyceride esters of oil/fat forming corresponding fatty acid alkyl ester (FAAE) and glycerol (GL) as the only reaction products (Equation 1).



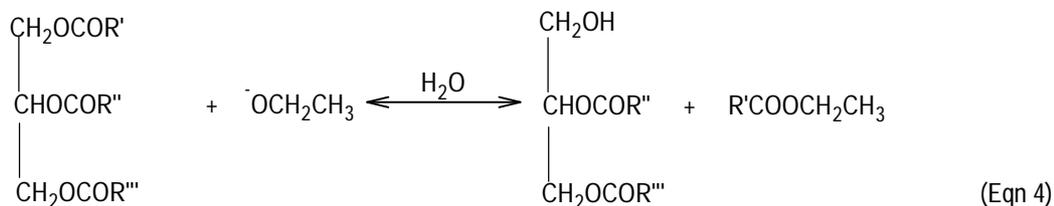
The choice of the catalyst and the nature of the alcohol determine the type of initial specie(s) and the nature of FAAE to be formed. In this study, the homogeneous reaction involved an initial separate

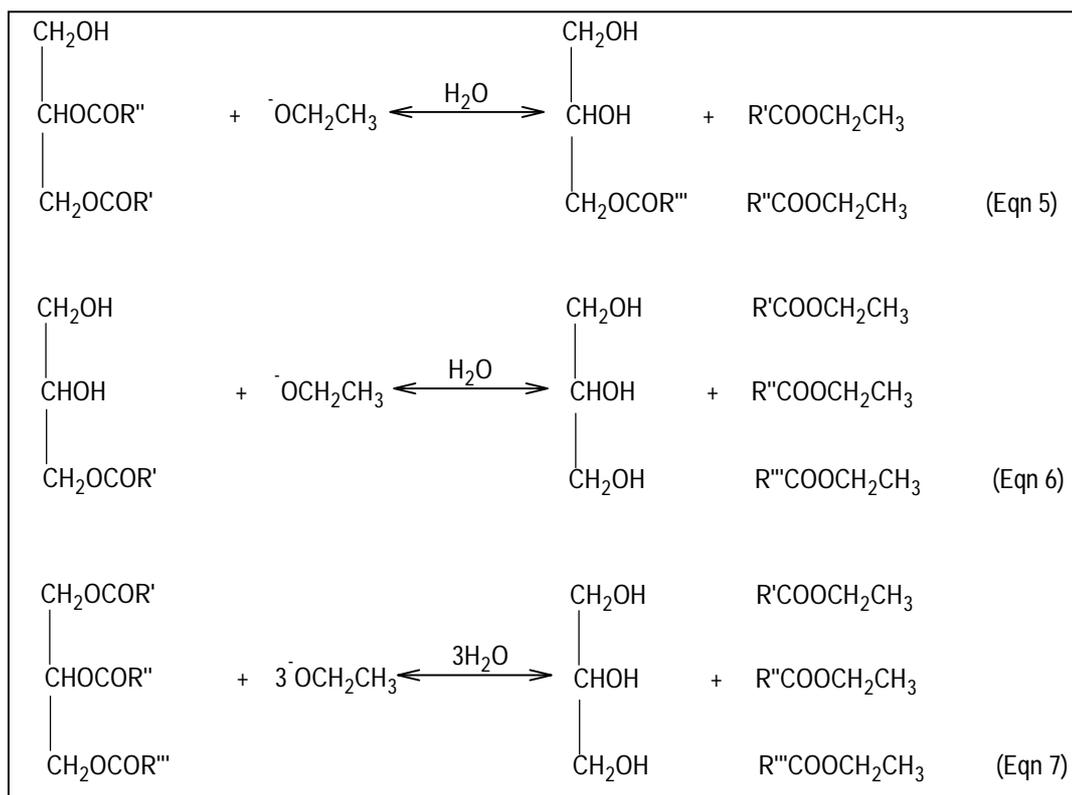
interaction between KOH and NaOH with ethanol producing potassium ethoxide and sodium ethoxide (Equations 2 and 3) respectively.



These room temperature reactions aided by employing high surface area KOH and NaOH crystals and continuous swirling were immediately followed by the interaction of ethoxide molecules, water and oil (melon seed or shea butter seed oil) at the reaction temperature (55°C or 40°C) for 2 hrs, yielding glycerol and fatty acid ethyl esters (FAEE) as the final reaction products (Equation 7).

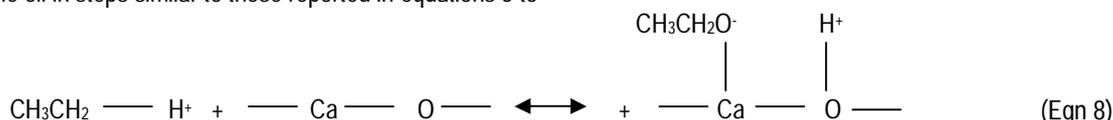
The latter reaction was reported from chromatographic studies by Galadima *et al.*, (2008) and Anderson *et al.*, (2009) to involved sequential conversion of the triglyceride esters to diglyceride and monoglyceride esters (Equations 4 and 5) and consequently to the desired reaction products (Equation 6).





In the heterogeneous reaction three initial ethanol, oil and CaO/Al₂O₃ layers were formed. With constant stirring the ethanol interacts with basic sites of calcium oxide to form surface ethoxide anions (Equation 8) due to proton extraction from the hydroxyl group of ethanol (Liu *et al.*, 2008). These ionic species generated react with the oil in steps similar to those reported in equations 5 to

7. Contrary to the homogeneous method involving KOH and NaOH that produced two distinct FAEE and glycerol layers at the end of the reaction, an additional solid CaO/Al₂O₃ layer was obtained with the heterogeneous system accounting for non catalyst decay by physical lose or dissolution.



Although there are many experimental evidences that KOH and NaOH catalysts allow faster conversion of the reactants due to approximately equal availability of the catalyst particles to the reactant molecules the catalysts are associated with separation problems resulting to increased industrial biodiesel production cost. A shift to the heterogeneous catalysts could therefore offer advantages such as easy separation, non-corrosive, reusability, recyclability and cheaper production cost. Calcium oxide was reported in some studies to show promising activity. Liu *et al.*, (2008) found 8% CaO (wt% of oil) to maintained a longer catalyst life time than K₂CO₃/Al₂O₃ and KF/Al₂O₃ in the same reaction and the catalyst remained active after 20 cycles of repeated applications. Similarly, the activity of the pure catalyst could be enhanced by the introduction of appropriate support material. Yan *et al.*, (2008) reported 92.0% conversion at 64.5°C during methanolysis of rapeseed oil over CaO/MgO catalyst system. This value is lower than 95.63% obtained from this study when MgO is replaced with Al₂O₃. It can therefore be interpreted that good dispersion of CaO over Al₂O₃ was achieved at 5wt% CaO loading and with negligible interference by the alumina support as an acidic

carrier. Decay of catalyst material previously reported with pure CaO (Albuquerque *et al.*, 2008) was not encountered in the present study after 5 cycles of repeated applications.

Percentage Yield: The average values obtained as percentage oil and FAEE yields of each seed from chromatographic studies are shown in Figs 1 and 2. Neem and melon seeds have the highest and lowest oil yield respectively. This is probably due to different in the triglyceride esters content of the seeds and the drying method employed coupled with the nature of the extracting solvents. Although these yields (25.0, 29.1 and 33.3%) may be considered low, the resulting FAEE yields >91% (Fig 2) are commercially attractive and are larger than values obtained with cotton seed oil by Galadima *et al.*, (2009). An interesting finding is that the reaction temperatures of 40-55°C employed contributed in shifting the equilibrium position sufficiently to the products side allowing very high reactants conversion. The highest percentage yield of 95.63% for the neem seed oil over the heterogeneous catalyst could similarly be attributed to 1:5 molar ratio of oil to ethanol and high degree of stirring used.

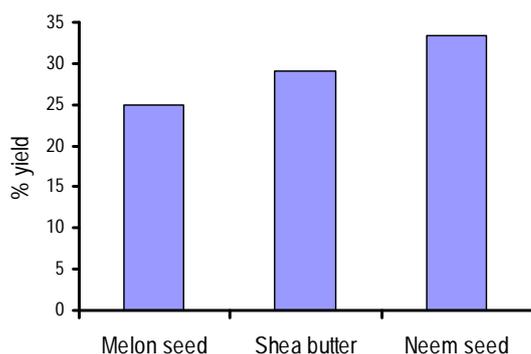


FIG. 1. PERCENTAGE YIELD: OIL

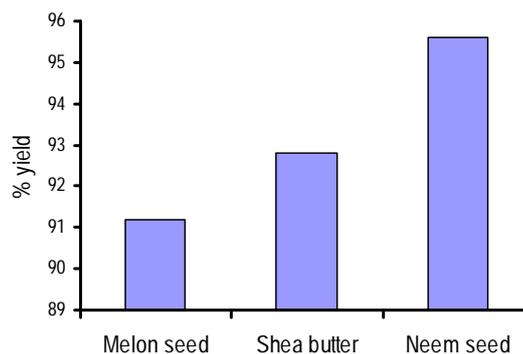


FIG. 2. PERCENTAGE YIELD: ETHYL ESTER

Biodiesel Potential of the FAE: Application of alkyl ester biodiesel as substitute or blend to petroleum diesel is subject to the ester meeting important international criteria. Although these specifications may vary from region to region the guidelines approved by American Society for Testing and Materials (ASTM) is widely accepted as applicable to all regions (Reynolds *et al.*, 2007; Galadima *et al.*, 2009). Result of the parameters evaluated in comparison to the standard guidelines for B100 biodiesel is shown in Table 1.

Appropriate limit of density (0.80-0.90 gcm⁻³) is required to ensure sufficient air to fuel ratio and prevent incomplete combustion that

could lead to particulate matter emissions and coke deposition (Galadima *et al.*, 2009). Water and sediment specification is necessary to strike a balance between good storage and storage tank protection because water can react with the esters to form free fatty acids and can also lead to microbial growth in storage tanks. Similarly, biodiesel fuels with values exceeding the maximum permissible limit (0.05 vol%) can cause serious engine problems such as filter plugging and damage, injector wear and increased corrosion. A value of 0.2wt% (maximum) is required to ascertain proper removal of alcohol from the manufacturing process. The cetane number of at least 47.0 measures the ignition quality of the alkyl ester.

Parameter	Melon seed oil FAE	Shea butter seed oil FAE	Neem seed oil FAE	*ASTM Specifications
Density (gcm ⁻³)	0.89	0.84	0.834	0.80-0.90
Water-sediments (%volume)	0.033	0.04	0.032	0.050 max
Total Ash (wt%)	0.045	0.011	0.08**	0.070max
Flash point (°C)	190	200	180	130min
Acid Number (mgKOH/g)	0.36	0.048	0.574**	0.50 max
Cetane number	75.0	78.0	80.0	47.0min
Alcohol content (wt%)	0.10	0.12	0.11	0.20max

*ASTM Specifications are reported for B100 biodiesel in ASTM D6751 guidelines.

**Values larger than maximum permissible limit.

TABLE 1. RESULTS OF FAE QUALITATIVE ANALYSIS

From Table 1, the values obtained for the three oils ranged from 0.834-0.89gcm⁻³, 0.032-0.04vol%, 0.10-0.12wt%, 75.0-80.0 and 180-200°C for density, water and sediment, alcohol content, cetane number and flash point respectively and are within the approved specifications. However, acid number (0.574mg KOH/g) and total ash content (0.08wt%) for the neem seed oil FAE are above the permissible limits reported in Table 1, indicating potential corrosion, fuel system and engine deposition problems. The larger value for the acid number is an indication of high free fatty acids in the FAE product (Galadima *et al.*, 2009).

CONCLUSION

The study indicates successful homogeneous and heterogeneous synthesis of FAE from some common oils at lower temperatures

of 40-55°C for 2 hrs reaction time. Both KOH and NaOH showed good activities involving initial ethoxides formation but posed purification problems at the end of the reaction. The heterogeneous method proceeds via formation of surface protons and ethoxide anions and the CaO/Al₂O₃ catalyst maintained good activity without any decay by physical lose or dissolution after repeated applications. FAE from melon seed and shea butter oils showed complete compliance with international biodiesel specifications but the neem seed oil FAE have potential engine problems due to high free fatty acids and total ash content. The former could be employed as good biodiesel feedstock.

ACKNOWLEDGEMENT

The Authors are grateful to the Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto Nigeria for providing some chemicals and analytical equipment. Contribution to the practical studies by the following undergraduate students; Nura Sabo, Grace Obaro and Auwal Ahmed is immensely acknowledged.

REFERENCES

Abigor, R. D., Uadia, P. O. Foglia, T. A. Haas, M. J., Jones, K. C., Okpefa, E., Obibuzor, J. U., & Bafor, M. E. (2000). Lipase-catalysed production of biodiesel fuel from some Nigerian lauric oils. *Biochemical Society Transactions*, 28(6):976-981.

Alamu, O. J., Waheed, M. A. & Jekayinfa, S. O. (2007). "Alkali-catalysed Laboratory Production and Testing of Biodiesel Fuel from Nigerian Palm Kernel Oil". *Agricultural Engineering International: The CIGR Ejournal*. Manuscript Number EE 07 009. Vol. IX. July, 2007.

Albuquerque, M. C. G., Urbistondo, I., González, S. J. Mérida-Robles, M. J., Moreno-Tost, R., Rodríguez-Castello, E., Jiménez-López, A., Azevedo, D.C.S., Cavalcante Jr., L.C., Maireles-Torres, P. (2008). CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. *Applied Catalysis A: General*, 334:35-43

Anderson, J. A., Beaton, A., Galadima, A., Wells, R. P. K. (2009). Role of Baria Dispersion in BaO/Al₂O₃ Catalysts for Transesterification. *Catalysis Letters*, 131: 213–218 DOI 10.1007/s10562-009-0051-7.

Galadima, A. Garba, Z. N., Ibrahim, B. M. (2008). Homogeneous and Heterogeneous Transesterification of Groundnut Oil for synthesizing methyl Biodiesel. *International Journal of Pure and Applied Sciences*, 2(3)138-144.

Galadima, A., Ibrahim, B. M., Umar, K. J., Garba, Z. N. (2009). Homogeneous and Heterogeneous Methanolysis of cotton seed oil locally produced in northern Nigeria. *Biological and Environmental Science Journal for the Tropics* 6(3):71-75.

IPCC (2007). Climate Change 2007. Intergovernmental Panel on Climate Change (IPCC). 4th Assessment Report (AR4). Released 17th November, Valencia Spain.

Liu, X., He, H., Wang, Y., Zhu, S. (2007). Transesterification of Soybean oil to biodiesel using SrO as a solid base catalyst. *Catalysis Communications*, 8(2007):1107-1111.

Liu, X., Huayang H, Yujun, W., Shenlin, Z., Piao, X. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, 87:216-221

NNPC, (2007) Official Gazette of the Nigerian Biofuels Policy and Incentives: Renewable Energy. Nigeria National Petroleum Corporation. <http://www.nnpcrd.com/images/policy.pdf> Accessed 08 July 2008.

Reynolds, R. E., Herwick, G., Mccornick, R. L., Kasperson, A., Hochhauser, A. M., Jewitt, C. (2007). Changes in diesel fuel Service Technician's Guide for compression ignition fuel quality. National Institute for Automotive Service Excellence (NIASE).

Yan, S., Lu, H., & Liang, B. (2008). Supported CaO Catalysts Used in the Transesterification of Rapeseed Oil for the Purpose of Biodiesel Production. *Energy & Fuels*, 22: 646–651.