Biodiesel Production in Nigeria Using Cocoa Pod Ash as a Catalyst Base

Adeola G. Olugbenga[1], Abubakar Mohammed[2], Olumuyiwa N. Ajakaye [3]

[1]Department of Chemical Engineering, Federal University of Technology Minna, Nigeria
[2]Department of Mechanical Engineering, Federal University of Technology Minna, Nigeria
[3]Department of Chemical Engineering, The Federal Polytechnic Bida, Nigeria

Abstract- This investigation was carried out to ascertain the possibility of enhancing the activity of potash participated from cocoa pod husk (CPH). A single promoted catalyst, CPH/MgO, was developed to be capable of promoting transesterification reactions. For the production of the biodiesel from waste vegetable oil, the potash K_2CO_3 from CPH was first leached out and subsequently impregnated with Magnisium oxide and the green catalyst was supported CPH/MgO. BET and X-ray diffraction were used to characterize the catalyst. The reactor used was fabricated and coupled with a thermometer and a reflux unit having a 3liter capacity. During the transesterification reaction of waste oil on the prepared catalyst, after optimization of a 5hours reflux reaction, 35% K_2CO_3 was required at 630°C. However at 50°C of a 3hours reaction, the methanol: oil ratio of 50:1 was observed at the molar scale. The catalyst can be classified as a suitable catalyst for transesterification reactions with or without MgO loading. The supported catalyst was effective even at lowest percentage loading of MgO. The impressive biodiesel yield was 94% indicative of an industrial breakthrough in the production of green heterogeneous base catalyst for Nigeria economy.

Keywords: Biodiesel, Cocoa Pod Ash, Transesterification Reaction, Supported Catalyst.

I. INTRODUCTION

The application of potash form CPH for heterogeneous base catalyst for waste oil transesterification reaction has been carried out to convert waste to wealth. The cocoa pod husk is a major source of waste in the Idanre cocoa plantation in Nigeria. The use of single promoted catalyst has been successful and reported in transesterification reactions containing oils. Mono–alkyl esters productions of biodiesel by transesterification of triglyceride using mono-alkyl alcohols, generally known methanolysis process, are also a major breakthrough in biofuel industry. In fact, biodiesel fuels have been produced with reactions normally carried out with homogenized base and acid catalysts where hydrochloric and sulfuric acids are used. The drawback to these oil production routes is that the reaction time is as long as two days and a higher methanol to oil range is involved (40–140:1 mol%) [1-3]. The base catalysts used are sodium alky oxides (NaOCH₃), sodium hydroxide, Potassium hydroxide, and their carbonates.

Since the analytical graded K2CO3 were loaded on MgO and K2O have shown effective and large yield of biofuels [4] achieving a yields as high as 99% biodiesel, then working with the optimized data of the reacting temperature, methanol-oil ratio and optimum time of reaction was a major step forward in the use of the organic counterpart of K2CO3. The inorganic K2CO3 are either mined or their processing route is somewhat expensive counterpoising their organic K2CO3 counterpart. Potash form palm kernel, coconut and palm tree bud have been used as organic source of potash for biodiesel production with an excellent catalyst recovery [5, 6].

This era has shifted attention to alternative source of energy due to an increase in greenhouse gases. The mono-alkyl esters of fatty acid obtained from vegetable oils and animal fat is a biodiesel which is both renewable and biodegradable [7]. Rudolph Diesel produced biofuel from vegetable oil in 1911. The outcome of the act or processes was that vegetable oils will conveniently drive a diesel engine [8]. Most interestingly biodiesel can conveniently drive compression ignition engines without a change in the engine configuration [9]. This was a first major breakthrough. It has emerged that biodiesel has wider applications due to its brilliantly low viscosity, high cetane number, high flash point and high lubricity. Its low carbon emission (when used in its pure state or blended state), and its biodegradability makes it environmentally friendly [10, 11]. Dalai et al [12] used canola oil and produced biodiesel from vegetable oils using heterogeneous catalysts and their applications as lubricity additives. Baroutian et al [13] took advantage of the density of palm oil-based methyl ester and produced biodiesel. Tiwari et al [14] produced biodiesel from jatropha oil (Jatropha curcas) with high free fatty acids: an optimized process in biomass and bioenergy. Li et al [15] carried out transesterification of soybean oil to obtain biodiesel with Zn/I2 catalyst. These oil were all edible oil and so the competition between food supply and fuel production has motivated the approach in this work where waste oil was preferred for the diesel production. The use of edible oil can result into a soaring cost in food also. Over 95% of biodiesel has been produced from vegetable oils, Suppes et al [16] reported that calcium carbonate from rock

acted as a base catalyst, 78% biofuel was obtained by others with diver heterogeneous catalyst developed from laboratories using catalyst based from plants [16-19]. However, in this work the cocoa pod hausk from Idanre in Nigeria is a major waste in that was effective enough to be converted to wealth saving the cost of disposal and environmental sanitation. Kim et al [19] also used hydrotalcite and achieved a lower conversion from oil to biodiesel at a percentage as low as 34% requiring a high temperature for biodiesel conversion to be improved. The current work is a giant step forward to eliminate these drawbacks and obtain an organic catalyst aimed towards achieving an economical production route. The study has proved that the K2CO3 from CPH is evidently feasible and the quantity of K2CO3 is a large enough catalyst for biodiesel production using waste oil.

II. METHODOLOGY

A. Catalyst Preparation.

Analytical grade methanol with 99.5% concentration, orthophosphoric acid, benzoic acid and hydrochloric acid was obtained industry, while Phenolphthalein, toluene and MgO were available in Laboratory. Cocoa pod husk were obtained from Idanre in Ibadan, Nigeria. The MgO was mixed with distilled water. The cocoa pod was sun dried and later placed in an open metallic container and ashed by setting the oven to 200oC. The dried cocoa pod was grinded into powder and calcinated in a furnace at 490oC for 6 hours. 2 litres of distilled water was used to leach out the potash by adding 500g of the calcinated cocoa pod husk. The extract solution was seen as brown in colour which is the resulting potash. The filtrate solution was placed in a large crucible and evaporated in the oven at 100oC. The resulting brown crystals were placed in a reflux and washed with distilled water several time until a white crystal was seen. The white crystals were loaded with MgO and a ratio of 0.5 was maintained. The crystals were also calcinated at 450oC for 4hrs. Out of several trials of suitable grams of cocoa ash, 40g of ash equivalent to 0.812M of crude potassium hydroxide was found optimum and was used to produce 500mls of Cocoa ash of crude potassium methoxide. Thereafter, 500mls of cocoa methoxide was mixed with 1000ml of waste vegetable oil in a suitable local reactor of 3 litres capacity. The mixture was stirred continuously for 2-4 minutes to get a homogenous mixture. The mixture was later transferred into separating funnel and allowed the distinct layer of biodiesel to separate after 6-8 hours. As soon as the 3 layers were observed the glycerine, which was the bottom layer was selectively run off the separating funnel and biodiesel layer was washed with 50% volume of warm water. The washing was done for 3-4 times after which it was transferred to silica gel desiccated bathe for drying. After the biodiesel was heated to temperature of 110oC and maintained for 45minutes so as to get rid of the water trapped in the biodiesel during washing. Subsequently, the biodiesel was cooled and transferred for physio-chemical determination.

Another batch was produced using sodium hydroxide. Catalyst (0.0125M of sodium methoxide) was used and same procedure was followed from washing to drying of the waste oil Biodiesel from cocoa ash and its physio-chemical properties.

The solution was dried in an over at $100^{\circ}C$. The slurry was solid catalyst, the solid was grinded and calcinated at $800^{\circ}C$. The catalyst was dried in a desiccator containing silica gel in order to avoid water and CO_2 going into companions with the prepared catalyst. The structure of the catalyst was determined. The X-Ray Powder Diffraction (XRD) was used to identify distinctive peaks to define double promoted catalyst. Brunauer-Emmet-Telle (BET) was used to determine pore diameter, pore volume and specific surface area.

B. Transesterification Reaction

Transesterification reaction was made to proceed inside a fabricated reactor coupled with relux condenser and a thermometer using vegetable oil and methanol with a molar ratio of 1:50 was filled with 5% amount of catalyst with respect to weight of oil. The mixture was refluxed at $60^{\circ}C$ and 5 hours of reaction time under stirring at a constant speed of magnetic stirrer inside the reactor. The catalyst was filtered off the solution. A separating funnel was used to separate into three layers, top layer was methanol, the middle was fatty acid methyl ester and the bottom layer is glycerine.

III. RESULTS

Table 1 shows the reduction in the values of the surface area and pore volume with MgO. It was excellently clear because the initial surface area of the 92 m^2/g cocoa pod husk ash was occupied with MgO. This was an indication that the pore has been occupied with the calcium oxides.

TABLE 1: CATALYST PROPERTIES USING THE BET TECHNIQUES

Catalyst Properties	MgO/ash	MgO/ K_2CO_3 with 40% add of MgO
Mean pore size (A^o)	35.311	40.211
Pore volume(cm^2/g)	0.201	0.112
Specific surface area (m^2/g)	92.00	20.001

A. Effect of loading MgO

In Figure 1, the active site of MgO was agglomerated by the covering of the basic site, which lowers the surface area and reduced over 40% loading amount of MgO, the excessive addition of MgO making biodiesel yield significant at about 40% MgO. Addition of activity of the catalyst in the sorption process of MgO/ash in literature show clear agreements with this percentage. An optimum addition can be taken to lie between 40%-50% MgO addition. This optimum value was used to obtain the duration temperature of calcination shown in Figure 2 and Figure 3, which are impressive for an optimum production route for the double promoter catalyst. The optimum biodiesel yield was achieved when the calcination temperature was between 600^0C and 700^0C (Figure 2) and maximum yield was achieved after 5 hours of calcination (Figure 3). Figure 4 represent percentage catalyst concentration defined by biodiesel yield and reaction

temperature. Beyond the 1.25% molar concentration of the MgO, the biodiesel yield was retarding back to 80% showing that catalyst concentration is sufficient at 1.25% for 95% biodiesel production.
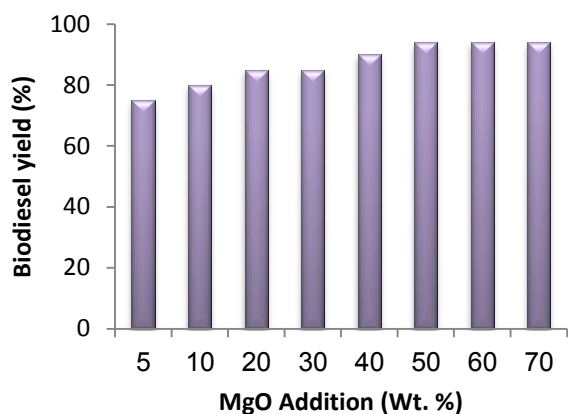

Figure 1: Yield of Biodiesel (%) versus addition of MgO addition (wt %) during transesterification reaction
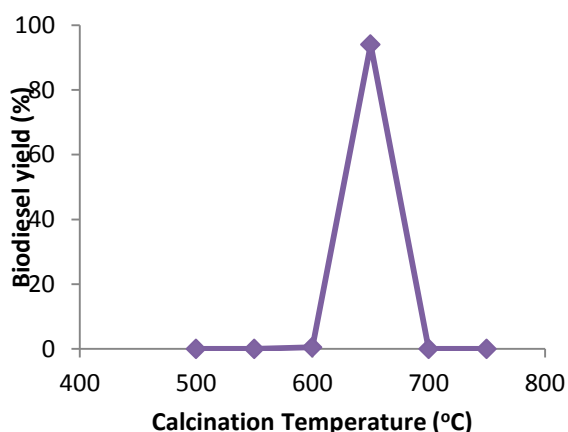

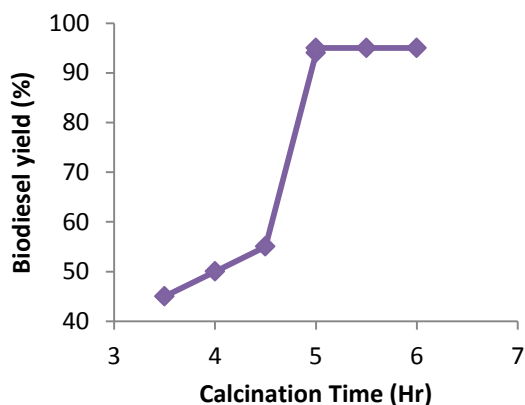Figure 2: Yield of Biodiesel (%) versus Temperature during transesterification reaction

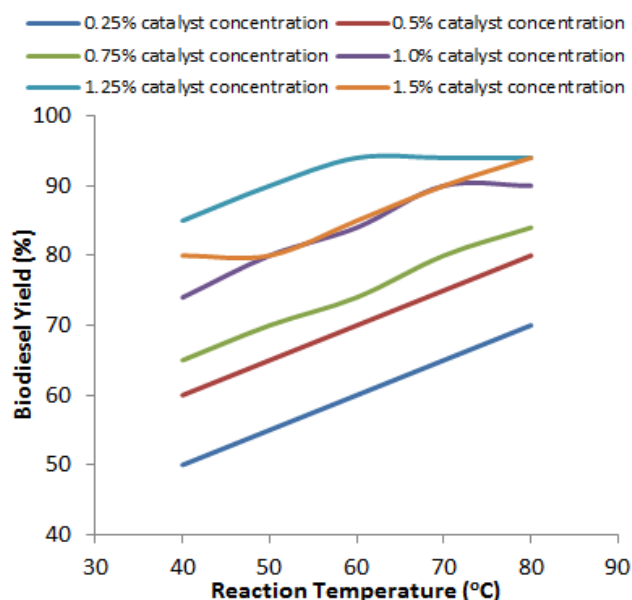Figure 3: Yield of Biodiesel (%) versus Calcination time during transesterification reaction

Figure 4: Percent Catalyst Concentration Defined by Biodiesel Yield and Reaction Temperature

B. XRD oriented slide Diffraction of the Catalyst

Figure 4 shows the XRD. The characteristic peaks of MgO observed indicate a satisfactory dispersion of MgO on CPH. As the amount of addition MgO was increasingly loaded at 25 to 30% MgO loading, the distinguished peaks were seen at 2θ with values 42°, 46°, 48° and 58° within the amorphous phase curve (a-d). No other distinguishing characteristics peaks were seen, in fact the intensities increases significantly. The characteristic XRD peaks of MgO appeared on the XRD patterns peaks intensities increases as the amount of loaded MgO increases indicates that an uncovered phase of the phase of CPH was available for occupying. A well-defined dispersion capacity of MgO on CPH was between 35 and 40 wt. %. The monolayer seen in the XRD shows the distinctive phase of MgO on CPH which clearly dispersed on CPH curve (a). The sites loaded with MgO at greater than the spontaneous dispersion on alumina beyond it capacity, on the composite only the residual bulk phase of K_2CO_3 is left unoccupied. Accordingly, since MgO has interaction with the K_2CO_3 surface only a portion of MgO decomposed during activation indicating very reliable characteristics peaks. A new pattern gradually evolved at curve (e) where the MgO was not pronounce because of the low 20% addition, the K_2CO_3 phase also shows clearly and with a much reduction in the percentage loading of MgO the MgO peaks will extinct at zero loading and the effectiveness/activity of the K_2CO_3 is still potent, an indication that with or without the MgO addition, the potash obtained from the CPH can reliably enhance transesterification reaction.
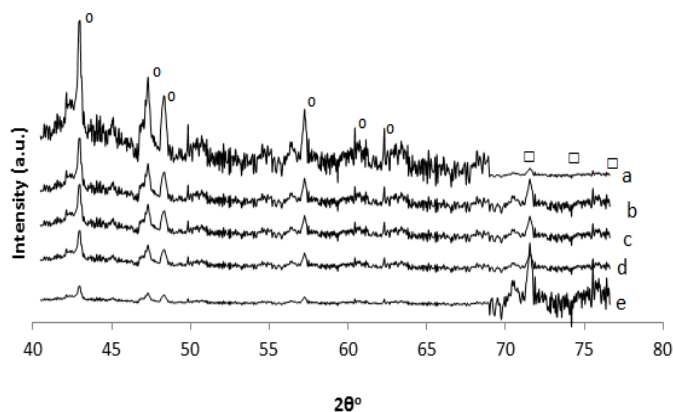
Figure 4: XRD patterns calcined at 700°C; (a) 40% MgO/ash, (b) 35% MgO/ash, (c) 30% MgO/ash, (d) 25% MgO/ash, (e) 20% MgO/ash.

IV. CONCLUSIONS

Magnesium loaded potash from cocoa pod husk shows a stronger solid based promoted catalyst used for biodiesel production. At high degree of 630°C calcination, a calcination route was defined and a 5hr reaction time having a 35% wt addition of potash. A good conversion was achieved as 94% biodiesel yield emerged. Considering a corresponding basic properties the activities the base catalysts show a reliable relationship. The precipitated K_2CO_3, developed allowing the impregnation of MgO species in the composite, were the active basic sites.

REFERENCES

[1] K.J. Harrington, C. D'Arcy-Evans, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 314.

[2] K.J. Harrington, C. D'Acry-Evans, J. Am. Oil Chem. Soc. 62 (1985) 1009.

[3] S. Siler-Marinkovic, A. Tomasevic, Fuel 77 (1998) 1389.

[4] X. liang, S. Gao, H. Wu, J. yang, highly efficient procedure for the synthesis of 1317 biodiesel from soyabean oil Fuel process. Technol. 90 (2009) 701-704.

[5] G.A.R. Wood, R. A. Lass cocoa, fourth ed., Longman England. 1985.

[6] A.S. lopez, Chemical change occurring during the Processing of cocoa, in: P.S. Dimick (Eds.), in Cocoa Biotechnplpgy-Proceedings, Pennsylvania state University, 1986, pp 19-55

[7] C.-Y. Lin, H.-A. Lin, L.-B. Hung, Fuel structure and properties of biodiesel produced by peroxidation process, Fuel 85 (2006) 1743–1749.

[8] A.C. Pinto, L.L.N. Guarieiro, M.J.C. Rezende, N.M. Ribeiro, E.A. Torres,W.A. Lopes, P.A. de Pereira, J.B. de Andrade, Biodiesel: an overview, Journal of the Brazilian Chemical Society 16 (2005) 1313–1330.

[9] M.A. Dubé, A.Y. Tremblay, J. Liu, Biodiesel production using a membrane reactor, Bioresource Technology 98 (2007) 639–647.

[10] M.P. Dorado, E. Ballesteros, J.M. Arnal, J. Gómez, F.J. López, Exhaust emissions from a diesel engine fueled with transesterifiedwaste olive oil, Fuel 82 (2003) 1311–1315.

[11] J.P. Szybist, J. Song, M. Alam, A.L. Boehman, Biodiesel combustion, emissions and emission control, Fuel Processing Technology 88 (2007) 679–691.

[12] A.K. Dalai, M.G. Kulkarni, L.C. Meher, Biodiesel productions from vegetable oils using heterogeneous catalysts and their applications as lubricity additives, IEEE EIC Climate Change Technology Conference EICCCC art 057358, 2006.

[13] S. Baroutian, M.K. Aroua, A.A.A. Raman, N.M.N. Sulaiman, Density of palm oil-based methyl ester, Journal of Chemical and Engineering Data 53 (2008) 877–880.

[14] A.K. Tiwari, A. Kumar, H. Raheman, Biodiesel production from jatropha oil (Jatropha curcas) with high free fatty acids: an optimized process, Biomass and Bioenergy 31 (2007) 569–575.

[15] H. Li, W. Xie, Transesterification of soybean oil to biodiesel with Zn/I2 catalyst, Catalysis Letters 107 (2006) 25–30.

[16] G.J. Suppes, K. Bockwinkel, S. Lucas, J.B. Mason, J.A. Heppert, J. Am. Oil Chem. Soc. 78 (2001) 139.

[17] E. Leclercq, A. Finiels, C. Moreau, J. Am. Oil Chem. Soc. 78 (2001) 1161.

[18] C.R. Beynese, H. Hinnekens, J. Martene, US Patent 5,508,457 (1996).

[19] H.J. Kim, B.S. Kang, M.J. Kim, Y.M. Park, D.K. Kim, J.S. Lee, K.Y. Lee, Catal. Today 93–95 (2004) 315.