Heterogeneous Catalyzed Transesterification of Refined Cottonseed Oil to Biodiesel.

C.N. Ude, M.Eng.[1*]; E.J. Ahmed[2]; M.I. Onyiah, M.Eng.[1]; O.E. Anisiji, M.Eng.[1]; and E.N. Ude[1]

[1]Engineering Research Development and Production Department, Projects Development Institute (PRODA), Emene-Enugu, Nigeria.
[2]Material and Energy Technology Department, Projects Development Institute (PRODA), Emene-Enugu, Nigeria.

E-mail: nony24real@yahoo.com*
Telephone: +2348039353284

ABSTRACT

Transesterification of refined cottonseed oil was carried out using heterogeneous catalysts (CaO and MgO) with methanol using different conditions. The parameters investigated were the reaction time (1, 2, 3, 4, and 5 hours), catalysts concentration (2, 4, 6, 8, 10, and 12 % wt), methanol/oil molar ratio (4:1, 6:1, 8:1, 10:1, 12:1 and 14:1), reaction temperature (25, 45, 65, 75 and 85^oC) and agitation speed (150, 200, 250, 300 and 350rpm). The physical and chemical properties of the oil and biodiesel were determined in order to investigate the effects of the properties of the triglyceride and the reaction parameters on the product characteristics, yields and purity. The low acid value, iodine value and saponification value of the oil enabled it to undergo direct transesterification without treatment. The methyl ester was produced by transesterification of cottonseed oil.

Transesterification of the refined cottonseed oil using heterogeneous catalysts reduced the viscosity from 63.9 to 5.6mm^2/s. and this achievement paved way to use the produced biofuel as diesel engine fuel without any engine modifications. The biodiesel high flash point makes possible its easy storage and transportation. The heating value of the FAME will produce high brake power that can give a reasonable thermal efficiency for a diesel engine. Increase in process parameters such as reaction time, catalyst concentration, methanol/oil ratio, reaction temperature and agitation speed increased the yield of methyl ester to a reasonable point before it decreased. CaO produced higher yield than MgO in all the parameters studied. The highest yield produced by the both catalysts at different parameters was above 70%.The result showed the potential of CaO and MgO in production of biodiesel.

(Keywords: heterogeneous catalysis, transesterification, biodiesel, calcium oxide, magnesium oxide)

INTRODUCTION

Biodiesel is the most promising alternative diesel fuel which has attracted attention worldwide [1]. This is primarily due to its outstanding benefits over the conventional petro diesel. It is renewable, biodegradable, non-toxic, with high flash point and good reduction in greenhouse emissions [2], [3], [4], [5]. Biodiesel is the free fatty acid methyl esters, popularly referred to as FAME, derived from oil sources. There are various processes that have been adopted in production of biodiesel from vegetable oils and animal fats namely; micro-emulsification with alcohols, catalytic cracking, pyrolysis and transesterification [2], [6], [7], [5]. Among these methods, transesterification is the key and foremost important process to produce the cleaner and environmentally safe fuel [8], [9].

Transesterification of vegetable oil to biodiesel can be catalyzed by base, acids and enzymes [10]. Base catalysts include homogeneous base catalysts and heterogeneous base catalysts. Homogeneous alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification. However, a large amount of water is required to transfer the catalysts from the organic phase to a water phase after the reaction. Therefore, it is considerably more costly to separate the catalyst from the produced solution [11].

Heterogeneous base catalysts have many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. Meanwhile, they are much more easily separated from the liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [12; 13].

Recently, many types of heterogeneous catalysts have been explored for transesterification of vegetable oils to biodiesel, such as alkaline earth metal oxides, various alkali metal compounds supported on alumina or zeolite [14; 15; 16]. However, for most supported alkali catalysts, the active ingredients are easily corroded by methanol and they exhibit short catalyst lifetimes [16].

Calcium oxide (CaO) and magnesium oxide (MgO) have attracted attention among researchers worldwide for the development of biodiesel owing to their low cost and easy preparation. Huaping et al., [17], used CaO as heterogeneous catalyst for biodiesel synthesis from Jatropha curcas oil and obtained 93%. Xuejun et al., [16], studied the transesterification of Soybean oil to biodiesel with 93% yield. Di serio et al., [18], reported the catalytic activity of MgO where 92% yield was achieved. Dossin et al., [19], reported that MgO was found to work efficiently in batch reactor at ambient temperature during the transesterification reaction.

In this study, transesterification of refined cottonseed oil using CaO and MgO as solid based catalysts were studied experimentally considering the effects of the process variables on the biodiesel yield.

MATERIALS AND METHODS

Materials

The commercial refined, edible grade cottonseed oil was purchased from Shoprite Enugu, Nigeria. The methanol, CaO and MgO were purchased from De-Cliff Integrated Services Ltd., Enugu, Nigeria and they were of analytical grade.

Preparation of Catalyst

The catalysts were calcined in a muffle furnace at temperature of 550^oC for 5h to remove any absorbed water. They were stored in a desiccator in the presence of silica and KOH pellets in order to avoid water and CO_2 contact with the catalysts.

Characterization of Refined Cottonseed Oil

The physiochemical properties; relative density, moisture content, melting point, free fatty acids content, iodine values, peroxide value, saponification value and viscosity of the oil were determined using the American Oil Chemists Society methods [20].

Characterization of Free Acid Methyl Ester

The physiochemical properties; density, acid value, flash point, cetane number, heating value and viscosity of the FAME were determined using the American Oil Chemists Society methods [20].

Transesterification Reaction

The transesterification was carried out in a batch reactor. A 200ml round-bottom flask was equipped with a reflux condenser. The reaction temperature was controlled by a hotplate with temperature sensor and stirring rate of 500rpm. The refined cottonseed oil was precisely quantitatively transferred into the reactor. Then specific amount of each catalyst, CaO and MgO (by weight of refined cottonseed oil) dissolved in the required amount of methanol was added.

The reaction flask was kept on a hot magnetic stirrer at a particular temperature with defined agitation throughout the reaction. At the defined time, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e. the glycerol in the lower layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of layer biodiesel with the weight of refined cottonseed oil used.

Biodiesel Yield (%) =

$$\frac{weight\ of\ fatty\ acid\ methylester}{weight\ of\ oil\ used} \times 100\% \quad (1)$$

RESULT AND DISCUSSION

Characterization of the refined cottonseed oil

From Table 1, the FFA value of the refined cottonseed oil is less than 1%. This is an acceptable level for transesterification reaction. The density and high viscosity of the oil will make it difficult to be atomized in internal combustion engine, hence it cannot be used directly as bio-fuel. The acid value, iodine value, and saponification value show that the oil will form less soap and improve separation of the biodiesel from the glycerol, thus increase the yield. The low pour point shows that the oil will hardly solidify at room temperature hence can be stored for a long time.

Table 1: The Summary of Characterization of Refined Cottonseed Oil.

Properties	Units	Values
Specific gravity		0.912
Kinematics viscosity at 40°C	Centistokes	63.9
Acid value	mgKOH/Oil	0.29
Iodine	g I_2/100g oil	22.1
Saponification value	mgKOH/g oil	63.19
Free fatty acid	%	0.145
Pour point	°C	-4.9
Refractive index		1.467
pH		3.64

Characteristics of Biodiesel

Transesterification of the refined cottonseed oil using heterogeneous catalysts reduced the viscosity from 63.9 to 5.6mm^2/s. This achievement paved way to use the produced biofuel as diesel engine fuel without any engine modifications. The biodiesel high flash point makes possible its easy storage and transportation. The heating value of the FAME will produce high brake power that can give a reasonable thermal efficiency for a diesel engine. The fuel properties are mentioned in Table 2.

Table 2: Fuel Properties of Cottonseed Methyl Ester compared with ASTM Limits.

Properties	Refined Cottonseed Oil FAME	ASTMD-6751
Free Fatty Acid (%)	0.05	≤0.4
Acid Value (mgKOH/g)	0.29	≤0.8
Ash Content (%)	Nil	
Specific Gravity	0.867	0.83-0.88
Kinematic Viscosity (cst) at 40°C	5.6	1.6-6.0
Flash Point (°C)	180	≥120
Cloud Point (°C)	13	
Pour Point (°C)	-0.7	
Water Content (%)	Nil	
Heat Value (MJ/kg)	40.1	

Analysis of FAME

Effect of Time on Biodiesel Yield: The conversion rate increased with reaction time. In this work, the effect of reaction time from 0.5h to 5h on the reaction yield using heterogeneous catalysts (CaO and MgO) was investigated. It was found that the optimal reaction time was 4h and beyond it the yield decreased (as shown in Figure 1). The reaction was very slow due to the mixing and dispersion of methanol and catalysts into cottonseed oil and the decreased in the yield after the optimal time is due to reversible reaction of transesterification resulting in loss of esters. The yield obtained by CaO was found to be greater than the yield by MgO.

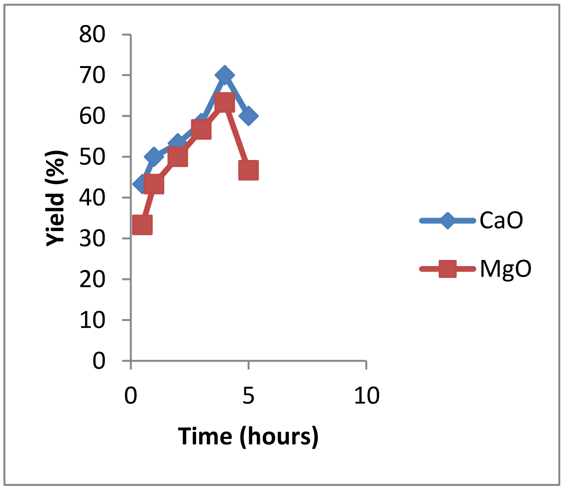

Figure 1: Effect of Time on Biodiesel Yield. Reaction conditions: Catalyst conc.:8%; reaction temperature: 65^{o}C; speed:300rpm; methanol/oil molar ratio:10:1.

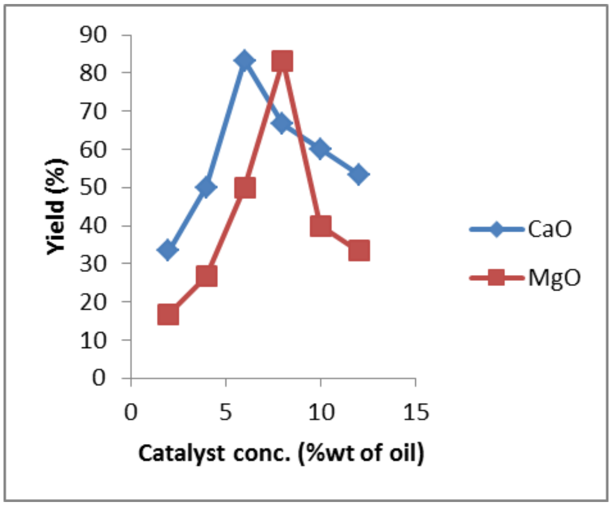

Figure 2: Effect of Catalyst Concentration on Biodiesel Yield. Reaction conditions: reaction temperature:65^{o}C; speed:300rpm; methanol/oil molar ratio; 10:1; reaction time: 4h.

Effect of Catalyst Concentration on Biodiesel Yield

In a chemical reaction, the bonds holding the reactants together must first be broken before the reaction can begin. Breaking bonds requires energy, and the minimum energy needed to start a reaction is referred to as activation energy. Catalysts provide alternative reaction pathways for breaking and remaking of bonds. The activation energy for this new pathway is often less than the activation energy of the normal pathway. Calcium oxide and magnesium oxide were used as solid base catalysts for the transesterification reaction in this work.

The effect of CaO and MgO concentrations expressed as weight percentage of the oil on the production yield is presented in Figure 2. The yield of methyl ester increased with increase in catalyst weight up to 6% for CaO and 8% for MgO and then began to decrease. Initially the amount of catalyst helped to accelerate the reaction by increasing the reaction rate. The higher yield of ester with increase in catalyst weight is due to the higher availability of catalyst in the reaction medium. Increasing the catalyst weight beyond the optimum weight of 6% for CaO and 8% for MgO led to the decrease in ester yield. This may be due to excess catalyst causing dispersion and mixing problems, thereby inhibiting the formation of end product.

Effect of methanol/oil molar ratio on biodiesel

The amount of substance involved in a reaction determines how much product will be formed. This is because in order for any reaction to occur, particles must first collide. This is true whether both particles are in solution, or whether one is in solution and the other a solid. If the concentration is higher, the chances of collision are greater.

The alcohol to oil molar ratio is one of the most important factors that can affect the yield of esters. The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3 moles of ester and 1 mole of glycerol, but most researchers have found that excess alcohol was required to drive the reaction close to completion. In this research, methanol was preferred alcohol and the effect of its molar ratio in the range of 4:1 to 14:1 was investigated, keeping other process parameter fixed.

The yield of methyl esters to the different molar ratio of methanol/oil is shown in Figure 3. The results indicated that methanol oil molar ratio has significant impact on biodiesel yield. The maximum ester yield was obtained at a methanolysis of oil molar ratio of 6:1 for CaO and 8:1 for MgO. The higher molar ratio than the stoichiometric value results in higher rate of ester formation and could ensure complete reaction.

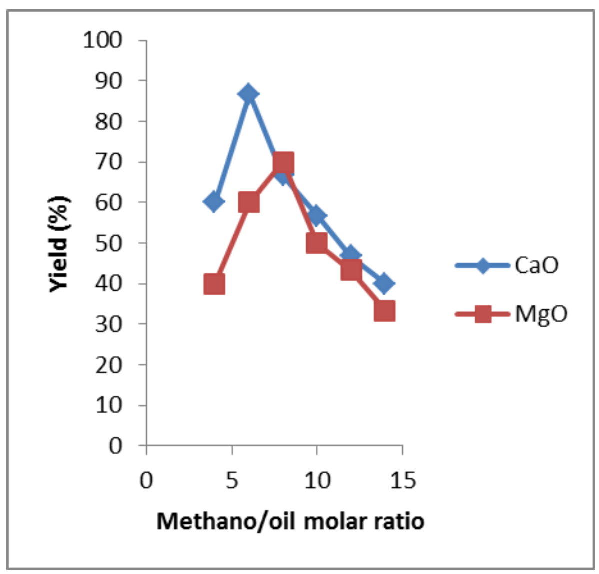

Figure 3: Effect of Methanol/Oil Molar Ratio. Reaction Conditions: Reaction temperature: 65^{o}C; speed:300rpm; catalyst conc.6%; reaction time: 4h.

The yield reduced when the molar ratio was higher than 6:1 for CaO and 8:1 for MgO. This could be as a result that the catalyst activity decreased with increased in methanol content and glycerol separation becomes difficult.

Effect of Temperature on Biodiesel Yield

In the presence of heterogeneous catalysts, the reaction mixture constitutes a three-phase system, oil-methanol-catalyst, in which the reaction would be slowed down because of the diffusion resistance between different phases. However the reaction rate can be accelerated at higher reaction temperatures. For studying the effect of temperature on the yield of the transesterification reaction, the reaction temperature was varied as 25, 45, 55, 65, 75, and 85^{o}C, while the other parameters were kept constant.

As shown in Figure 4, the reaction rate was slow at low temperatures, but biodiesel yield first increased and then decreased with the increased of the reaction temperature beyond 65^{o}C.

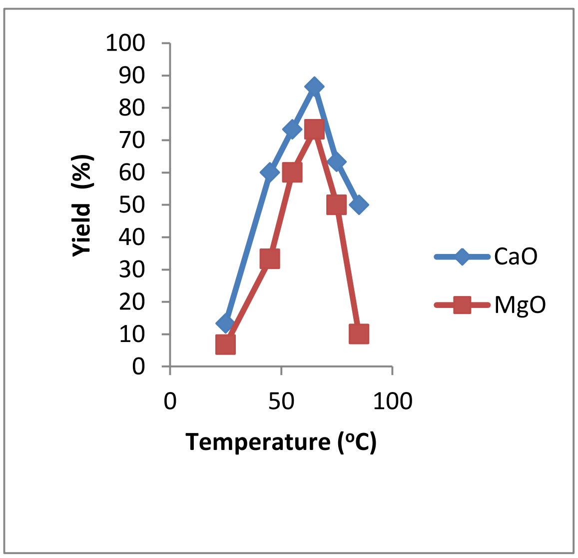

Figure 4: Effect of Reaction Temperature. Reaction conditions: Methanol/oil molar:6:1(CaO) and 8:1(MgO); speed:300rpm; catalyst conc.6%; reaction time: 4h.

Generally, a more rapid reaction rate could be obtained at high temperatures, but at high temperatures, methanol was vaporized and formed a large number of bubbles, which inhibited the reaction on the three-phase interface. Therefore, the optimum reaction temperature was 65^{o}C.

Effect of agitation speed on biodiesel

The mixing appears to be of particular importance for the transesterification process: it ensures homogeneity within the reaction mixture. It increased the contact area between oils and catalyst or methanol solution. Mixing facilitates the initiation of the reaction. Without mixing, the reaction occurred only at the interface of the two layers and considered too slow to be feasible. In this study, methanolysis was conducted with different rate of stirring such as 150, 200, 250, 300, and 350 revolutions per minutes (rpm).

The yield of methyl esters at different rate of mixing is shown in Figure 5. It was observed that the reaction of methanolysis was practically incomplete at 150rpm and only exhibited a yield which was difficult to separate. The yield was observed to decrease as the stirring rate went above 250rpm for CaO and 300rpm for MgO; the backward reaction may have been favored when mixing intensity was accelerated. The yield of methyl esters at 250rpm (CaO) and 300rpm (MgO) were 85 and 75% respectively. Stirring can play an important role in the yield of biodiesel production. It promoted the homogenization of the reactants and thus lead to higher yields.

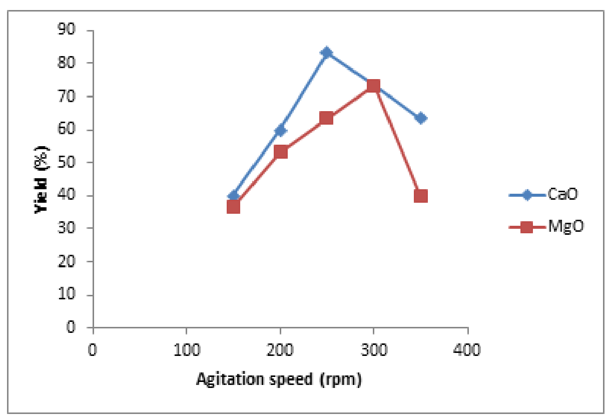

Figure 5: Effect of Agitation Speed. Reaction conditions: Methanol/oil molar ratio: 6:1(CaO) and 8:1(MgO); reaction temperature:65^{o}C; catalyst conc.6%; reaction time: 4h.

CONCLUSION

The production of biodiesel from cottonseed oil using heterogeneous catalysts (CaO and MgO) was carried out. The low acid value, iodine value and saponification value of the oil enabled it to undergo direct transesterification without treatment. The methyl ester was produced by transesterification of cottonseed oil.

Transesterification of the refined cottonseed oil using heterogeneous catalysts reduced the viscosity from 63.9 to 5.6mm^2/s. This achievement paved way to use the produced biofuel as diesel engine fuel without any engine modifications. The biodiesel high flash point makes possible its easy storage and transportation. The heating value of the FAME will produce high brake power that can give a reasonable thermal efficiency for a diesel engine. Increase in process parameters such as reaction time, catalyst concentration, methanol/oil ratio, reaction temperature and agitation speed increased the yield of methyl ester to a reasonable point before it decreased. CaO produced higher yield than MgO in all the parameters studied. The highest yield produced by the both catalysts at different parameters was above 70%. The result showed the potential of CaO and MgO in production of biodiesel.

REFERENCES

1. Fan, X., X.Wang, and F. Chen. 2011. "Biodiesel Production from Crude Cottonseed Oil: An Optimization Process using Response Surface Methodology". *The Open Feuls and Energy Science Journal*. 4, 1-8.

2. Demirbas, A. 2009. "Progress and Recent Trends in Biodiesel Fuels". *Energy Conversion and Management*. 50:14-34.

3. Kaya, C., C. Hamamei, A. Baysal, O. Akba, S. Erdogan, and A. Sayduct. 2009. "Methyl Ester of Peanut (*Arachis hypogeal* L.) Seed Oil as Potential Feedstock for Biodiesel Production". *Reneweable Energy*. 34:1257-1260.

4. Ghetsi, G.F., J.L. De Macedo, V.C. Parente, J.A. Dias, and S.C.L. Dias. 2009. "Synthesis, Characterization and Reactivity of Lewis Acid/Surfactant Cerium Trisdodecylsulfate Catalyst for Transesterification and Esterification Reaction". *Appl. Cat. A*; Gen 355:139-147.

5. Aderemi, B.O. and B.H. Hameed. 2010. "Production of Biodiesel from Palm Oil". *Nigeria Society of Chemical Engineers Proceedings*. 40: 135-143.

6. Leng, T.Y., A.R. Mohamed, and S. Bhatia. 1999. "Catalytic Conversion of Palm Oil to Fuels and Chemicals". *Canad. J. Chem. Eng*. 77:156.

7. Li, H., B. Shen, J.C. Jabalu, and M. Nchare. 2009. "Enhancing the Production of Biodiesel from Cottonseed Oil by Fixed-Fluidized Bed Catalytic Cracking". *Renewable Energy*. 34: 1033-1039.

8. Younis, M. N., M.S. Saeed, S. Khan, M.U. Furqan, R.U. Khan, and M. Saleem. 2009. "Production and Characterization of Biodiesel, from Waste and Vegetable Oils". *Journal of Quality and Technology Management*. 5(1):111-121.

9. Attanatho, L., S. Magmee, and P. Jenvanitpanjakul. 2004. "Factors affecting the Synthesis of Biodiesel from Crude Palm Kernel Oil". *Proceedings of the Joint International Conference on Sustainable Energy and Environment (SEE)*. 1-3 December, 2004. Hua Hin, Thailand; 359-361.

10. Ma, F. and M.A. Hanna. 1999. "Biodiesel Production: A Review". *Bioresour. Technol*. 70, 1–15.

11. Ebiura, T., T. Echizen, A. Ishikawa, K. Murai, and T. Baba. 2005. "Selective Transesterification of Triolein with Methanol to Methyl Oleate and Glycerol using Alumina Loaded with Alkali Metal Salt as a Solid-Base Catalyst". *Appl. Catal. A*. 283:111-115.

12. Gryglewicz, S. 1999. "Rapeseed Oil Methyl Esters Preparation using Heterogeneous Catalysts". *Bioresour. Technol*. 700:249-253.

13. Tanabe, K. and W.F. Hölderich. 1999. "Industrial Application of Solid Acid-Base Catalysts". *Appl. Catal. A*. 181: 399-434.

14. Xie, W., H. Peng, and L. Chen. 2006. "Transesterification of Soybean Oil Catalyzed by Potassium Loaded on Alumina as a Solid Catalyst". *Appl. Cat. A*; Gen 300: 67-74.

15. Suppes, G.J., M.A. Dasari, and E.J. Doskocil. 2004. "Transesterification of Soyabean Oil with Zeolite and Metal Catalysts". *Appl. Catal. A*. 257: 213-223.

16. Xuejun, L., H. Huayang, W. Yujun, Z. Shenhin, and P. Xianglan. 2008. "Transesterification of Soybean Oil to Biodiesel using CaO as a Solid Base Catalyst". *Fuel*. 87: 216-221.

17. Huaping, Z., W. Zongbin, C. Yuanxiong, Z. Ping, D. Shijie, and L. Xiaohua. 2006. "Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and its Refining Process". *Chin J. Catal*. 27: 391-396.

18. Di Serio, M., M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser, and E. Santacesaria. 2006. "Transesterification of Soybean Oil to Biodiesel by using Heterogeneous Basic Catalysts". *Industrial and Engineering Chemistry Research*. 45: 3009-3014.

19. Dossin, T.F., M.F. Reyniers, R.J. Berger, and G.B. Marin. 2006. "Simulation of Heterogeneously MgO-Catalyzed Transesterification for Fine-Chemical and Biodiesel Industrial Production". *Appl. Catal. B*: Gen. 67:136–148.

20. AOCS. 1996. *Sampling and Analysis of Commercial Fats and Triglycerides*. Official methods of Analysis of the American Triglyceride Chemist Soc. pp: 80-855.

SUGGESTED CITATION

Ude, C.N., E.J. Ahmed, M.I. Onyiah, O.E. Anisiji, and E.N. Ude. 2013. "Heterogeneous Catalyzed Transesterification of Refined Cottonseed Oil to Biodiesel". *Pacific Journal of Science and Technology*. 15(2):71-77.

Pacific Journal of Science and Technology