



Valorization of Biodiesel Production: Focus on Crude Glycerine Refining/Purification

O. S. Muniru^{1*}, C. S. Ezeanyanaso¹, T. K. Fagbemigun¹, E. U. Akubueze¹,
A. O. Oyewole¹, O. J. Okunola¹, G. Asieba¹, A. O. Shifatu¹, C. C. Igwe¹
and G. N. Elemo¹

¹Federal Institute of Industrial Research, 3, FIIRO Road, Oshodi, Lagos, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author OSM designed the study, performed the experiments and wrote the first draft of the manuscript. Authors CSE and CCI supervised the running of the project. Authors TKF and AOO managed the literature searches, analyses of the study. Author AOS provided technical assistance. Author GA performed the spectroscopy analysis and author EUA also helped manage the experimental process and author OJO assisted with raw materials and technical assistance. Author GNE provided financial and workspace. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2016/27982

Editor(s):

(1) Milan Stankovic, Department of Biology and Ecology, University of Kragujevac, Serbia.

Reviewers:

(1) Joao Fernando Pereira Gomes, ISEL–Lisbon Polytechnic, Portugal.

(2) K. Varatharajan, Velammal Engg. College, Chennai, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history/15709>

Original Research Article

Received 28th June 2016
Accepted 30th July 2016
Published 9th August 2016

ABSTRACT

Biodiesel production in Nigeria is gaining more level of awareness but the cost of production is still on the high side. This is largely due to the cost of raw materials, mainly vegetable oil or fat. Fortunately, a very efficient way to reduce this cost and increase profitability is the purification of the crude glycerol by-product of the biodiesel production process. Hence, this research was carried out using crude glycerol from biodiesel production of Neem Seed Oil (N. S. O.) and Waste Cooking Vegetable Oil (W.C.V.O) and it also provides a cost effective, domesticated process technology for the purification of the crude glycerol from any biodiesel production facility. Neutralization and phase separation was carried out using dilute phosphoric acid, followed by separation of the glycerol rich layer, concentration and methanol recovery, glycerol extraction using iso-propanol (IPA) and then colour removal with activated charcoal. The effect of pH during

*Corresponding author: E-mail: segunmunir@yahoo.com;

neutralization on the purification level was investigated using a pH range of 3.0 – 7.0 at steps of 0.5. The optimal pH was found to be about 6.5 for both crude glycerol sources. Also, the IPA: glycerol ratio was varied using 1:1, 1:2, 2:1, 3:1 and extraction was found to be optimum at 2:1 (v/v) to achieve average glycerol purity level of about 97%. Both the refined glycerol and crude glycerol samples were analyzed using the Gas Chromatograph Mass Spectrometer (G. C. M. S.). Other analyses were also extensively carried out and all conformed to quality standard.

Keywords: Biodiesel; crude glycerine; purification; phosphoric acid; GCMS.

1. INTRODUCTION

Oil and gas exploration and production has become a dominant sector of the world energy and other economic sectors since the last century. In the Nigerian perspective, since the discovery of commercial reserves in the Delta region in the mid-1950s, the sector has increasingly dominated the agriculture and solid minerals exploitation for both the source of energy and revenue to the [1]. Within the last 20 years, about 75% of human made CO₂ emissions were from burning of fossil fuels. Nigeria is the largest emitter of these undesirable gases from the sub-Saharan Africa, and particularly, the second worlds' biggest gas flarer, contributing immensely to the global atmospheric pollution [2]. In an attempt to mitigate these problems, Nigerian government have recently indicated the incorporation of biofuels production, particularly bioethanol and biodiesel to be a good option. The production of these fuels could enhance fuel use in automotive industry, electric power generation and rural development, including agricultural mechanization and light industrial goods development, and in ensuring that the common man is fully benefitted from the country's economy [3].

Biodiesel is a proven alternative to the petroleum diesel fuel. Biodiesel is renewable, biodegradable, non-toxic and has almost very close property to that of fossil-based diesel and hence is one of the most promising alternative fuels. Biodiesel, a mixture of long chain fatty acid methyl or ethyl esters, does not contribute to the increase of the net atmospheric CO₂ level and allow a reduction of the emissions of several pollutants such as particulate matter, carbon monoxide, sulfur and polycyclic aromatic hydrocarbons [4]. It can be produced from vegetable oil as well as animal fats. Biodiesel is commonly produced via transesterification process and the triglycerides are converted into

esters (biodiesel) by the transesterification reaction.

The production of 10 kg of biodiesel by the transesterification process yields approximately 1 kg of crude glycerol as by-product [5-7]. Currently the world's capacity for biodiesel production is increasing dramatically and further increase in biodiesel production rates will significantly raise the quantity and surplus of crude glycerol and may have environmental effect because the glycerol obtained contains several impurities, such as water, organic and inorganic salts, soap and alcohol, traces of mono and di-glycerides and vegetable colors [6].

High purity glycerol, an alcohol with three hydroxyl groups (-OH), is a very important industrial feedstock. Its applications are found in foods, drugs, cosmetics, tobacco industries and a host of others. However, crude glycerol originating from biodiesel industry is expensive to be purified to above 99% for use in food, pharmaceuticals, or cosmetics industries and isn't a favorable option for small and medium scale producers so, cheaper efficient refining methods are still required [8,9]. Therefore, certain purification steps are necessary for the crude glycerol recovery prior to its use as a raw material in many industries and as a potential feedstock for the production of bio lubricants.

Different purification processes have been developed and reported in the literature, among which the most common processes include those using ion exchange resin, nano-cavitation technology, membrane separation technology (MST), simple distillation under reduced pressure, and acidification, followed by neutralization and solvent extraction, etc. Nevertheless, the purification processes using ion exchange resin and simple distillation are limited because of these processes generally produce a very low yield of pure glycerol (<15 wt.%). The use of nano-cavitation technology for the purification of crude glycerol has been

demonstrated, but its large-scale operation is very challenging. MST could yield ultra-high purity glycerol provided that the crude glycerol undergoes prior purification that reduces salts and matter organic non glycerol (MONG, such as methyl ester). Compared with other processes, the processes using acidification/neutralization demonstrated to be more promising due to higher yields and their relatively low costs [10].

Kongjao et al. [5], reported the purification of crude glycerol (30 wt.% glycerol content) from a waste used-oil methyl ester plant using 1.19 M H_2SO_4 followed by neutralization and solvent extraction to get glycerol of around 93 wt.% purity. In a similar work, [11] demonstrated that crude glycerol was upgraded from purity of 34 wt.% to 52 wt.% by using sulphuric acid. However, the main issue in these processes is the use of sulphuric acid that has corrosive nature of sulphuric acid and the non-biodegradability of the produced sulfate salts [10].

In this work, purification of crude glycerol obtained from a biodiesel plant and also from biodiesel produced from waste cooking vegetable oil in the lab, was carried out using dilute phosphoric acid and investigating the effect of pH value and extraction solvent ratio on crude glycerol purification.

2. MATERIALS AND METHODS

Crude glycerol was collected from the biodiesel plant at the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria, which uses neem seed oil and also from biodiesel production using waste cooking vegetable oil (W.C.V.O), both via alkali catalyzed transesterification.

The refining procedure is based on the procedure used by [12,10] with some modifications.

2.1 First Stage: Neutralization

About 50 g of crude glycerol from each source was neutralized using dilute Phosphoric acid (85% H_3PO_4 , Sigma Aldrich) from its initial pH of about 9 to a pH in the range of pH 3 – 7 in steps of 0.5, with continued stirring, and then left for 2 hours until the solution had phase separated into two or three distinct layers, that is a top layer of free fatty acids, the middle glycerol-rich layer

and, the bottom inorganic salt-rich layer (which was absent in the glycerol from waste cooking vegetable oil). The top layer was removed by decantation and the middle glycerol-rich layer was separated from the bottom inorganic salt-rich layer by filtration. The optimal pH for neutralization was then determined using the pH with the highest glycerol content in the extracted glycerol rich layer.

2.2 Second Stage: Glycerol Layer Concentration and Methanol Recovery

The glycerol rich layer obtained from stage one was concentrated by simple distillation to remove water and also recover the methanol present in the mixture. This caused some of the phosphate salt formed as a result of the catalyst reacting with the dilute H_3PO_4 , to crystallize out of the solution.

2.3 Third Stage: Glycerol Extraction with IPA

The concentrated glycerol rich layer was mixed with Isopropyl Alcohol (99.5% IPA, Sigma Aldrich) to extract the glycerol out of the mixture (solvent extraction) and then allowed to stir on the magnetic stirrer for about 30 minutes to allow proper contact. The mixture was then allowed to settle for about 2 hours to enable proper separation of the two layers formed; the glycerol-alcohol phase on the top and the crystallized salt on the bottom. The upper layer was separated by slow decantation to eliminate the crystallized salt and then filtered to remove any traces of salt or solids in it.

2.4 Fourth Stage: Adsorption with Activated Carbon

Finally, the color, as well as some fatty acids and other components, of the refined crude glycerol was reduced by adsorption with commercial powdered activated carbon (PAC, 300 microns particle size, Burgoyne Burbidges & Co.). Prior to use, the activated carbon was dried at 105°C for 30 min to eliminate free moisture. In the adsorption stage about 10 g of activated carbon was mixed with about 300 ml of the glycerol-alcohol mixture obtained in stage 3, mixed at 200 rpm for 5 hours and then filtered to remove the activated carbon.

2.5 Fifth Stage: Glycerol Refining and IPA Recovery

The decolorized glycerol-alcohol mixture was then refined by distilling and recovering the IPA at 85°C and the resulting refined glycerol was also heated at about 105°C for 3 hours to reduce the moisture content and further concentrate the refined glycerol.

2.6 Test and Analysis

The concentration of glycerol was analyzed by Gas Chromatography Mass Spectrometer (GCMS). The water content was measured following the Standard method (ISO 2097-1972) by using the volumetric Karl Fisher titration. Ash content was analyzed according to the Standard method (ISO 2098-1972) by burning 1 g glycerol in a muffle furnace at 750°C for 3 h [13]. The MONG levels were calculated by the difference from a hundred of the previous three compositions (100 - (% glycerol content+% water content+% ash content)). The pH of the glycerol solution was measured with a pH meter. The color of glycerol was measured by a UV/Vis spectrophotometer at a wavelength of 457 nm.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Crude Glycerol Samples

The crude glycerol obtained from biodiesel plant using neem oil as feedstock was a dark brown liquid and that obtained from the waste cooking vegetable oil biodiesel process was also brown coloured but lighter with both having a high pH. As also reported by [12], the crude glycerol is a dark brown liquid with a high pH. It contained a low content of glycerol (just over one-third by volume) and ash, but it had a relatively high water and MONG (Matter Organic Non Glycerol) content (Table 1).

Table 1. Physico-chemical properties of the crude glycerol

Parameter	Crude glycerol (Neem)	Crude glycerol (W.C.V.O.)
pH	9.82	9.20
Glycerol content (%)	41.33	35.66
Ash (%)	4.31	4.08
Moisture (%)	15.4	12.2
Colour	Dark brown	Brown
MONG (%)	38.96	47.86

The ash content was largely composed of inorganic matter, such as sodium salts that originated from the utilized catalyst (NaOH) in the transesterification process, whilst the water content might be attributed to the absorption of moisture from its surroundings during the production process. Another large contaminant was MONG, which indeed was close to the glycerol levels, was generated by the contamination of soap, methanol and methyl esters in the glycerol residue from the biodiesel production process.

During the transesterification process, some of the methyl esters get dissolved or suspended in the glycerol solution. The free fatty acids and the dissolved methyl esters then react with the excess NaOH subsequently to form soap which remained in the glycerol residue. Besides glycerol, crude glycerol contains various compounds, including fatty acids and their derivatives, such as methyl oleate, methyl palmitate, palmitic acid, methyl stearate, oleic acid, methyl taurate, methyl myristate, methyl palmitoleate, amongst others, which are the main components of vegetable oil.

3.2 Neutralization Step

The addition of the dilute phosphoric acid to the crude glycerol automatically caused the crude glycerol to phase separate into two or three distinct layers comprised of free fatty acid layer on the top, a glycerol-rich layer in the middle and, an inorganic salt layer on the bottom. For the waste cooking vegetable oil biodiesel crude glycerol, the organic salt layer was absent probably because the phosphate salt produced dissolved in the solution because of the high water content.

The optimal pH of was determined by the GCMS analysis of the glycerol rich phase obtained from various pH values obtained from pH 3 – 7 and was found to be 6.0 for the crude glycerol from waste cooking vegetable oil biodiesel process and 6.5 for that from the neem biodiesel process. 99.5% analar grade glycerol was used to prepare the calibration curve.

The glycerol rich layer was obtained by first heating up the mixture to about 60°C and then allowed to cool. This caused the FFA layer to solidify on cooling, which was then removed using a spatula, and the glycerol-rich layer was then slowly decanted and analyzed using the GCMS. As depicted in Fig. 2, the amount

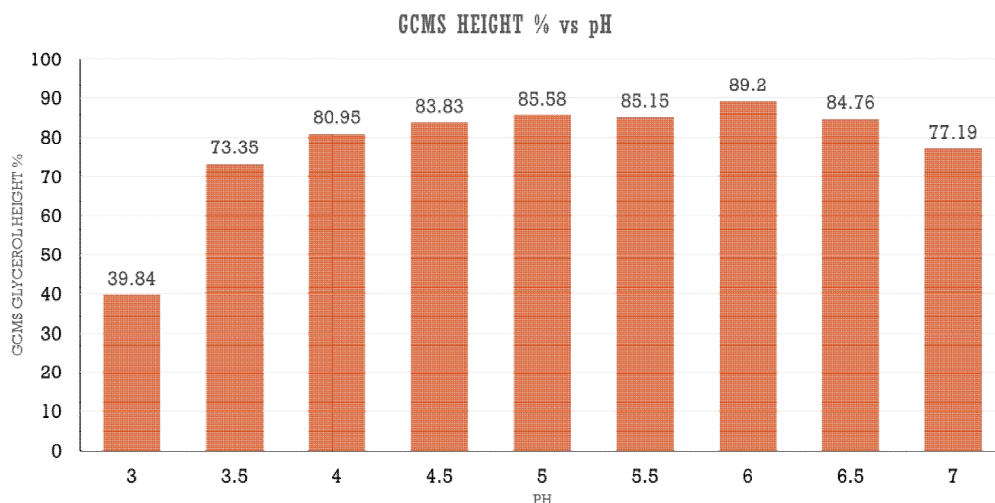


Fig. 1. GCMS result for acidification step for used waste cooking vegetable oil crude glycerol

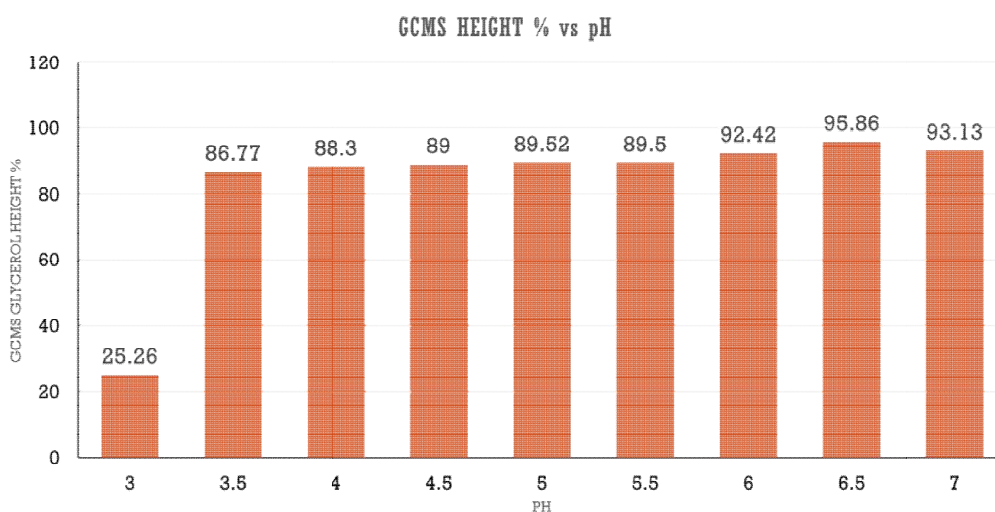


Fig. 2. GCMS result for acidification step for neem oil crude glycerol

of glycerol in the glycerol-rich layer after pH of 3, showed that though close, the optimal value could be approximated to be between 6.0 and 6.5.

3.3 Extraction of Glycerol with IPA

Prior to solvent extraction, the decanted glycerol-rich layer was heated to about 100°C for twenty (20) minutes to recover a large part of the dissolved methanol and also, reduce the water level in the mixture.

Because the phosphate salt formed during the neutralization step is dissolved in mixture with the glycerol-water system, Isopropyl Alcohol

(IPA) was used to solvent extract the glycerol from the mixture. This is because glycerol is very soluble in IPA while the phosphate salt formed is very insoluble in the IPA thus precipitating out the salt crystals at the bottom with the glycerol-IPA layer at the top. The Glycerol: IPA ratio of 1:1, 1:2 and 1:3 were used and it was observed that above ratio of 1:2, there was no difference thus the optimal ratio used was 1:2 as also reported by [12].

3.4 Adsorption with Activated Carbon

The IPA-Glycerol layer decanted after the extraction stage was having a golden yellow colour and was decolourized using commercial

activated carbon. The decolorization was carried out in two steps and each step with about 34 g/l of powdered activated carbon to glycerol. At the end of the process, the solution gave a clear liquid.

3.5 Glycerol refining and IPA recovery

After the decolorization stage, the glycerol was separated/refined by distilling off the IPA at about 85°C and the distilled IPA collected for reuse. The properties of crude glycerol after

purification in comparison with commercial analar glycerol are listed in Table 2, and it can be seen that the performance of purified crude glycerol reached basically the quality level of commercial glycerol.

The GCMS spectra of both the refined glycerol and the glycerol standard produced using 99.9% pure analytical grade glycerol, shows the refined glycerol have same peaks as that from the analar grade glycerol.

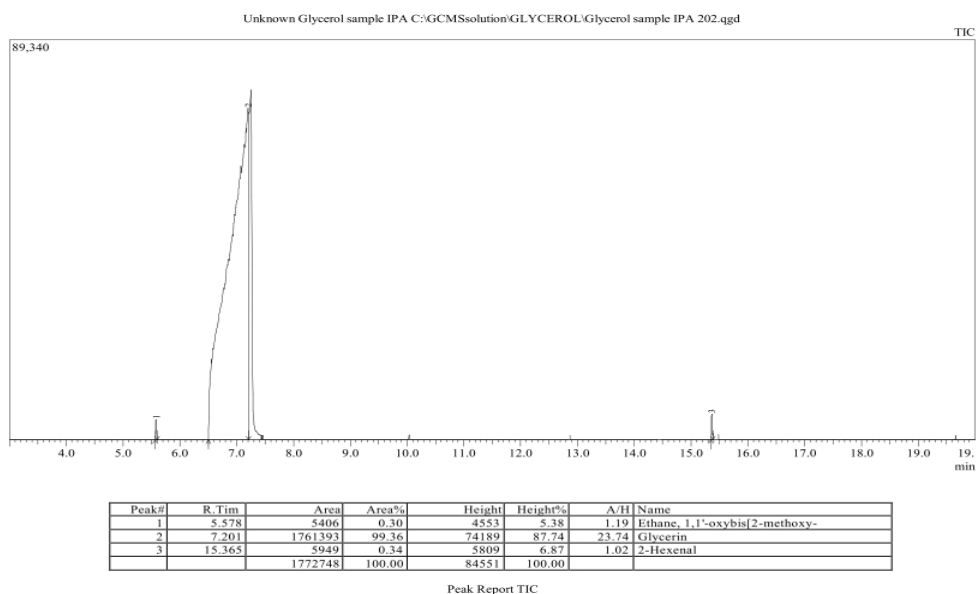


Fig. 3. GCMS spectra for the refined glycerol

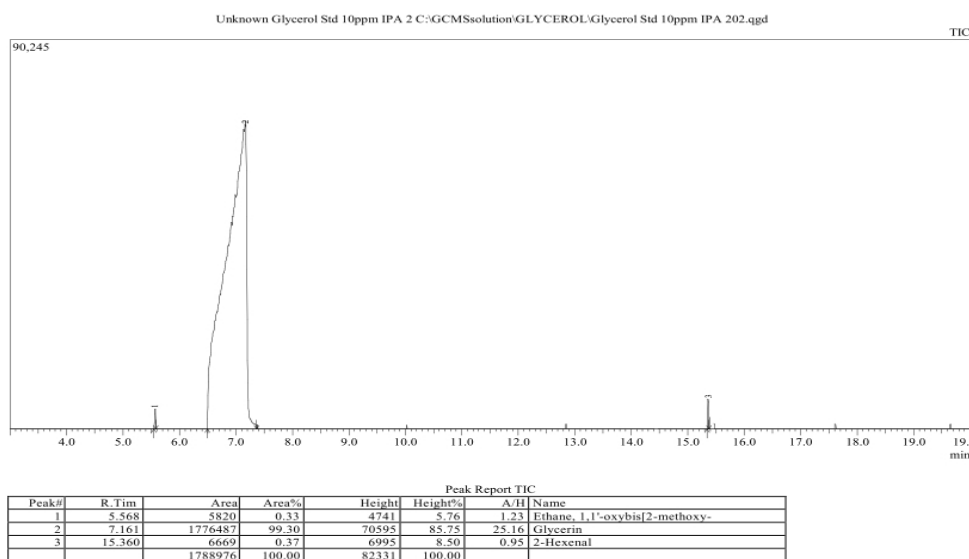


Fig. 4. GCMS spectra for the glycerol standard

Table 2. Comparison of properties of the glycerol refined in this work with commercial grade and work done by Manosak et al. [12]

Parameters	Commercial glycerol	Purified glycerol from this work		Manosak et al. [12]
		Neem	W.C.V.O.	
pH	6.97	6.30	6.42	7
Ash content (%)	0.000 2	1.30	1.10	2.08±0.06
Density at 20°C (g/cm ³)	1.2671	1.240	1.234	-
Purity (%)	99.98	97.84	97.37	96.2±0.03
Colour	Clear	Clear	Clear	Clear

The heavy metal and elemental analysis, phosphate and chloride tests were also carried out. The results obtained according to Table 3, shows they are all below 5.0 ppm as obtained in commercial analar grade glycerol.

Table 3. Elemental analysis of the refined glycerol

Element/ metal	Concentration (ppm)	
	Neem	W.C.V.O.
Zinc (Zn)	0.0463±0.0016	0.0848±0.0034
Iron (Fe)	0.0649±0.0015	0.1759±0.0022
Lead (Pb)	0.0946±0.0002	0.0541±0.0003
Cadmium(Cd)	0.0068±0.0002	0.01606±0.0004
Chromium(Cr)	0.0191±0.0001	0.0343±0.0005
Copper (Cu)	0.0139±0.0003	0.0343±0.0005
Sodium (Na)	0.1298±0.0006	0.1126±0.0004

4. CONCLUSION

High purity glycerol is a very important industrial feedstock. Its applications are found in foods, drugs, cosmetics, tobacco industries and a host of others. Refining the crude glycerol by-product of biodiesel production therefore, is of utmost importance in adding value to the overall biodiesel process thus increasing its profitability.

Purification of glycerol from a crude glycerol derived from a neem oil based biodiesel production and from waste cooking vegetable oil was achieved using combined methods of physical and chemical treatment. The acidification conditions used in this work are as follows: a reaction time of 120 min, a reaction temperature of 30°C, and a pH value of 6 and 6.5 for crude glycerol from waste cooking vegetable oil and neem biodiesel production respectively in the presence of dilute H₃PO₄. After that, the glycerol-rich layer obtained after neutralization was extracted with Isopropyl Alcohol (IPA) at an IPA:Glycerol ratio of 2:1 (v/v). Then, the samples were decolorized using activated carbon at a dose of about 35 g/l of the carbon to glycerol to give a clear solution. The

average purity of the refined glycerol was analyzed using the GCMS to give approximately 97% purity.

DISCLAIMER

This manuscript was presented in the conference “Vth International Symposium on “Fusion of Science & Technology” available link is <http://www.rdi.rmutsb.ac.th/2011/digipro/isft2016/content/papers/Paper%2032.pdf>”

Date: January 18-22, 2016, Place: New Delhi, India.

ACKNOWLEDGEMENT

The authors would like to acknowledge Federal Institute of Industrial Research, Oshodi (FIIRO) for funding this research.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Odeyemi O, Ogunseitan OA. Petroleum industry and its pollution potential in Nigeria. *Oil and Petrochemical Pollution*. 1985;223-229.
- Akande SO, Olorunfemi FB. Research and development potentials in biofuel production in Nigeria. *African Research Review*. 2009;3(3):34-45.
- Galadima A, Ibrahim BM, Adam IK, Leke L, Almustapha MN, Garba ZN. Biofuels production in Nigeria: The policy and public opinions. *Journal of Sustainable Development*. 2011;4(4).
- Jaime F. Puna, Joao F. Gomes, Joao C. Bordado, Joana Neiva Correia, Ana Paula Soares Dias. Biodiesel production over lithium modified lime catalysts: Activity and

- deactivation. *Applied Catalysis*. 2014;470:451-457.
DOI: 10.1016/j.apcata.2013.11.022
5. Kongjao S, Damronglerd S, Hunsom M. Purification of crude glycerol derived from waste used-oil methyl ester plant. *Korean J. Chem. Eng.* 2010;27(3):944-949.
 6. Hájek M, Skopal F. Treatment of glycerol phase formed by biodiesel production. *Biores. Technol.* 2010;101:3242-3245.
 7. Martin Hájek, František Skopal. Purification of the glycerol phase after transesterification of vegetable oils. 44th International Petroleum Conference, Bratislava, Slovak Republic; 2009.
 8. Johnson DT, Taconi KA. The glycerin glut: Options for the value-added conversion of crude glycerol resulting from biodiesel production. *Eng. Prog.* 2007;26:338-346.
 9. Isahak WNRW, Ismail M, Yarmo MA, Jahim JM, Salimon J. Purification of crude glycerol from transesterification RBD palm oil over homogeneous and heterogeneous catalysts for the bio lubricant preparation. *Journal of Applied Sciences*. 2010;10:2590-2595.
 10. Nanda MR, Yuan Z, Qin W, Poirier MA, Chunbao X. Purification of crude glycerol using acidification: Effects of acid types and product characterization. *Austin Journal of Chemical Engineering*; 2014.
 11. Ooi TL, Yong KC, Dzulkefly K, Wanyunus WMZ, Hazimah AH. Crude glycerine recovery from glycerol residue waste from a palm kernel oil methyl ester plant. *J Oil Palm Res.* 2001;13:16-22.
 12. Rudemas Manosak, Siripong Limpattayanate, Mali Hunsom. Sequential-refining of crude glycerol derived from waste used-oil methyl ester plant via a combined process of chemical and adsorption. *Fuel Processing Technology*. 2011;92-99.
 13. Cai Tianfeng, Li Huipeng, Zhao Hua, Liao Kejian. Purification of crude glycerol from waste cooking oil based biodiesel production by orthogonal test method. *China Petroleum Processing and Petrochemical Technology*. 2013;15(1): 48-53.

© 2016 Muniru et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

*The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/15709>*