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RECYCLING USED VEGETABLE OILS TO FATTY ACID ETHYL ESTER FOR BIODIESEL PRODUCTION

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ABSTRACT

Recycling of used vegetable oils (UVOs) into fatty acid ethyl ester (FAEE) for biodiesel production is a two way approach to solving rapid depletion of crude oil reserves and a safe environment option to reduce greenhouse gas emission in Nigeria. The present study is targeted at deriving FAEE from UVOs that could potentially be used as biofuel or blend in diesel engines. Acid and alkali-catalyzed transesterification processes using ethanol were used to obtain FAEE from fresh and used peanut and palm oils tagged as FP_eO, FPO; UPeO, and UPO, respectively. Silica gel adsorption process as post-transesterification treatment was used to improve the qualities of the generated FAEE. The quality of FAEE obtained from FP_eO, FPO; UPeO, and UPO, were compared to one another and were within European (EN14124) and USA (D6751) standards for biodiesels. Analysis of variance (ANOVA) showed significant variation in the yield of obtained FAEE for ethanol to oil molar ratio but independent of vegetable oil source and freshness while its biofuel quality was vegetable oil freshness dependent. Therefore, the UVOs are recyclable into production of biodiesel with optimized condition of molar ratio, pre and post transesterification treatments.

KEYWORDS: Biodiesel; fatty acid ethyl ester; palm oil; peanut oil; used vegetable oil; transesterification

INTRODUCTION

Globally, the last two decades witnessed discovery and employment of natural and renewable resources for alternative production of fuels for energy use due to depleting oil reserves, high cost of refining and importing of crude oil, greenhouse gas emission and increasing environmental pollution [1]. Biofuels including biodiesel, biogas and bioethanol are fuels obtainable from plant or animal origin and their major use is as stand-alone biodiesel in diesel engines or as diesel-biodiesel blends in conventional diesel fuel.

Biodiesel is reported to possess higher viscosity and cetane number, comparable to conventional diesel fuel and thus has been rated as a strong alternative to conventional diesel fuel [2-3]. In addition, biodiesel is the only alternative fuel that runs in any conventional, unmodified diesel engine and needs no change in refueling infrastructures and spare part inventories [4]. Also, lubricity is much more improved with higher flash point compared to that of conventional diesel [2]. Other advantages of biodiesel over conventional diesel include its environmental friendliness due to generation of lesser total unburned hydrocarbons, aromatic hydrocarbons, particulates and carbon dioxide [5]. Furthermore, pure biodiesel is non-toxic and biodegradable based on mutagenicity tests, and therefore cause reduction in cancer risk [6].

Biodiesel refers to methyl ester by EU norms and or ethyl esters by other standards and hence, the alternative names: fatty acid methyl ester (FAME) and fatty acid ethyl ester (FAEE). Pure biodiesel is known as B100 and mixtures of biodiesel with petroleum diesel are named as BXX, where XX is the percentage of biodiesel in the blend [7]. Biodiesel is obtained by esterification, transesterification or pre-esterification followed by transesterification of edible and non-edible vegetable oils, using mono, complex and heterocatalysts. Transesterification is a catalytic chemical process of exchanging an alkoxyl group of an ester compound with an alcohol using alkaline or acid catalysis and has been widely employed for biodiesel generation [8-11].

Most common feedstock for biodiesel are rapeseed and sunflower oil in Europe, soybean and waste vegetable oil in the USA and Canada; palm, jatropha and coconut oil in Asia, and are regulated with regional standards with technical specifications related to feedstock and characteristics of local markets [12]. Peanut (*Arachis hypogaea)* is also known as the groundnut and is a legume grown mainly for its edible seeds. It is native to South America and widely grown in the tropics and subtropics and is classified as both a grain legume and an oil crop because of its high oil content. Peanut is less prone to oxidation than other vegetable oils in frying applications. Peanut is one of the top ten oils listed in global oil market and the quality of its biodiesel is of international standards [13].

Another rich source of biodiesel is palm oil obtained from African oil palm (*Elaeis guineensis)*, native to West Africa. Oil palm plays dual role as a food and cash crop due to many products with various end uses that are obtained from it. In Nigeria, palm oil is use for frying, making stew and soup. It is also used as an antidote in case of food or drink poisoning and for wound dressing and boils softening in local setting. Palm oil is also a common cooking ingredient in other tropical belt of Africa, Southeast Asia and parts of Brazil and its commercial use is widespread in other parts of the world due to its lower cost and high oxidative stability of

its refined products [14]. Palm oil has gained popularity for production of biodiesel in Asia and Australia and a major producer is Madagascar and Malaysia. Main advantages of palm oil biodiesel are high yielding and high viscosity [15].

Use of VOs in diesel engine referred to as straight vegetable oil (SVOs) has been reviewed with several reported issues due to their high flash point, viscosity and cetane value [15-16]. In addition, edible vegetable oil for biodiesel competes with food sustenance and land use for food production [17]. Furthermore, the cost and availability are among the main disadvantages of edible vegetable oils for production of biodiesel. Consequently, used or waste vegetable oil (WVO) is found more attractive as a cost effective resource for biodiesel production [18-19].

Recycling of UVOs into production of biofuel is considered as both economic and safe environment approach for Nigeria [20]. Waste vegetable oils are abundant and available at little or no cost and some fractions are used for soap making and animal feeds while a large proportion are disposed into the environment [12]. There is global efforts directed at gathering WVOs for biodiesel production and lots of research efforts are geared towards getting optimal conditions for production and purification of its biodiesel [2, 5, 21-22]. Pre, post and two steps transesterification treatments of WVOs to biodiesel have been reported and the most important lesson learnt is “single step transesterification process is not efficient for production of neat biodiesel from WVOs” [2, 20, 23-24].

The most often used biodiesel are FAME or FAEE of vegetable oils produced by transesterification using methanolyisis or ethanolysis, respectively [25]. Fatty acid methyl ester is most common and extensively researched biodiesel from vegetable oils with little or no attention on FAEE. Methanol is the most commonly employed alcohol in transesetrification of vegetable oils to biodiesels due to its low price, high reactivity and minimization of hydrolysis and soap formation, making FAME widely produced, globally. However, methanol is toxic and hygroscopic resulting into contaminants such as moisture, which can decrease the effectiveness of the catalyst, creating the potential for yield loss and foaming in biodiesel production [16].

The prospects of using ethanol for transesterification are rather attractive due to its environmentally friendliness with low toxicity and in addition, ethanol can be of renewable origin as bioethanol and therefore, the final product would be produced from 100% renewable sources. Furthermore, the use of ethanol in transesterification process enhances the possibility of simultaneously extraction ofthe potential oil from the seeds and its transesterification reaction [18, 26]. Ethyl-esterified biodiesel, FAEE, has lower cloud and pour point, reduced ignition

delay, and higher cetane number compared to FAME and conventional diesel. However, FAEE requires post-transesterification purification steps to dry out ethyl alcohol, remove moisture and separate glycerol [27-28].

Nonetheless, production of FAEE is limited globally, and only, Brazil practiced ethanolysis of vegetable oils for use as blends in diesel engines. Also, industrial-scale production and research studies of FAEE with vegetable oils are equally limited compared to FAME [15, 27-31]. Therefore, the present study is designed to assess the potential of recycling common Nigerian UVOs into FAEE. This will complement petrodiesel use, thereby conserving crude oil reserves, while it is a safe environment option in Nigeria.

MATERIALS AND METHODS

Vegetable oils sampling and preparation

Fresh edible peanut and palm oils were purchased in Bodija market, Ibadan, Nigeria. Used vegetable oils were obtained from traditional bean cake sellers and restaurants after a number of reuse for frying. Both the fresh vegetable oil (FVO) and UVO samples were heated at 100 ^{o}C for 1 hr to remove moisture and volatiles. The fried UVO samples were further filtered, washed with hot water and allowed to stand for 24hr. It was separated using separating funnel to remove residues, before ethanolysis reaction while the preheated FVOs were used directly without further preparation. Two replicates were analyzed per sample, fresh palm oil (FPO), fresh peanut oil (FPeO), used palm oil (UPO) and used peanut oil (UPeO).

Pre-transesterification using Acid-esterification

A pre-transesterification treatment of the oil samples was carried out at a ratio of 1:5 v/v ethanol to oil using 1% oil vol. H_2SO_4at 60^{o}C for a reaction time of 3hr to reduce free fatty acid (FFA) content by conversion to corresponding esters. The resulting mixture was left in the reaction conical flask for 24hr to separate and the lower layer was run off while the top layer was washed with hot water till neutral and transparent. The final supernant containing esterified FFAs and glycerides was collected in a clean 250 mL beaker.

Alkali-transesterification

The triglycerides of the esterified oil samples were subjected to transesterification in stepwise procedure using 1% wt. potassium hydroxide in a varying molar ratio of ethanol to oil of 3:1, 6:1 and 9:1. The ethoxide intermediate was first produced for efficiency by addition of corresponding volume of ethanol into a beaker containing 1.0 g potassium hydroxide (0.025M

KOH) pellet as catalyst. Afterwards, esterified 5 mL FPO, FP_eO, UPO and UP_eO at 60 ^oC was separately transferred into the conical beaker containing an alkalized-ethanol solution and closed the lid with a cork. The mixture was fitted into a water bath shaker at 60^oC and 150 rpm for 1 hr. The resulting mixture was then transferred into a separating funnel, allowed to settle overnight and the lower dark coloured glycerol was run off into a clean beaker while the transparent colored FAEE at the upper layer was collected in a clean beaker and washed consecutively with hot water at 60 ^oC until neutral to remove the residual by-products such as excess alcohol, catalysts, soap and glycerin.

Post-transesterification

The FAEEs produced were passed through a bed of silica gel top-layered with anhydrous sodium sulphate to remove remnant FFAs, ethanol, glycerol, salts and water and collected in a clean 250 mL beaker.

Characterization of FAEEs

Viscosity, specific gravity (SG), carbon residue (CC), acid value (AV) and ash content as common physicochemical characteristics for standardization of biodiesel for different purposes by standard norms were evaluated using standard methods considering cost, and availability of materials and tools. Specific gravity as an alternative to density was measured using gravimetric density bottle method. The viscosity at 40^oC (mm^2/s) was by Ferranti portable viscometer measurement using EN ISO 3104 andsulphated ash content by combustion method using a furnace. Residual carbon is estimated as Conradson carbon residue according to D 189, 100% distribution was estimated for crude feedstock and 10% for distilled sample for FAEEs. Total acid value (mg KOH/g) of the FAEE is estimated using macro method of titration after Pr EN 14104[32-34].

Data analysis

All data analyses for descriptive, ANOVA, and correlation were carried out using SAS University Edition 3.

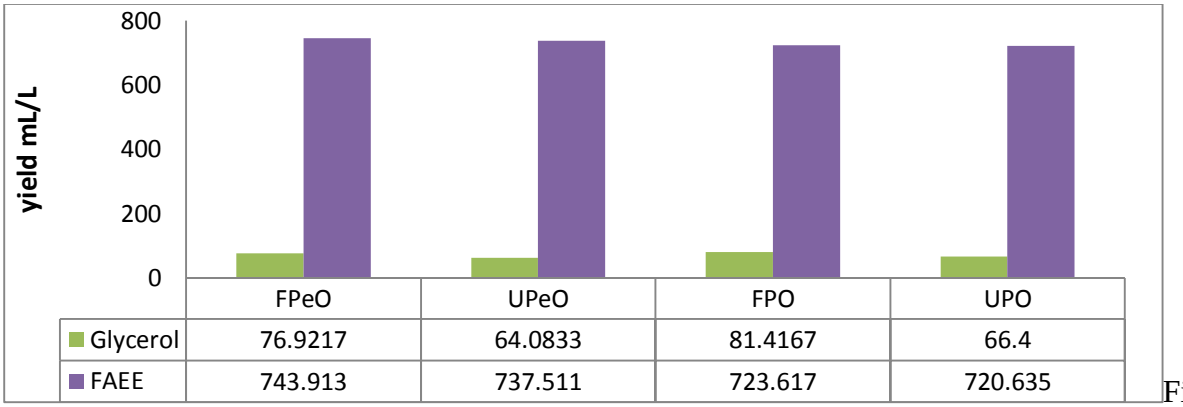
RESULTS AND DISCUSSION

Yield of FAEE and glycerol obtained from FP_eO, FPO, UP_eO and UPO

Figure 1 shows comparative mean yield of glycerol and FAEE obtained from FPeO, FPO, UPeO and UPO and it presents higher FAEE yield for FVOs when compared to corresponding UVOs and also higher PeOs over POs. The higher yield of FAEE in FVOs over UVOs could be due to

the presence of polymerization and oxidative degradation products contributing higher FFA content in UVOs. High yields of FAEE by PeOs could be attributed to its lower content of FFA compared to POs. Mean yield of glycerol was higher for FVOs than UVOs.This could be explained for by higher conversion of triglycerides in FVOs to FAEE and lower FFA content in FVOs [16, 20, 35-37].

Table 1 shows detailed precision measures of the collected data on the obtained yield of FAEE and glycerol. The presented ranges of FAEE yield is within ranges reported in previous similar studies [8, 11, 38-40]. Differences in the ranges of diverse studies could be accounted for by factors such as divergence in feedstock nature, volume of oil used, reaction time, reaction temperature, the ratio of alcohol to the vegetable oil, concentration of the catalyst used, incomplete transesterification due to high FFA and water content[38, 40-42].. Higher yields were obtained with low FFA oils, higher temperature and catalysts loading, controlled transesterification, drying and washing processes in some previous reports [40-41, 43]. In addition, losses during esterification process have been previously reported and were due to some unreacted alcohol, residual catalyst and emulsion removed during the washing stage of the production [8, 44].



	FPeO	UPeO	FPO	UPO
Glycerol	76.9217	64.0833	81.4167	66.4
FAEE	743.913	737.511	723.617	720.635

Figure 1: Overall mean yield of FAEE and glycerol obtained from FPeO, FPO, UPeO and UPO

Table 1: Descriptive statistics for yield of biodiesel and glycerol obtained from assessed fresh and used vegetable oils from peanut and palm oil

Oil/biofuel	Yield	SD	SE±	CV	Range	Min	Max	N
FP_eO								
FAEE (% v/v)	74.63	6.77	2.76	9.07	18.6	61.5	80.1	6
FAEE (ml/L) †	743.91	66.99	27.35	9	186.45	615	801.45	6
Glycerol (ml)	14.59	5.22	2.13	35.79	12.15	9	21.15	6
Glycerol (% v/v)	7.72	1.43	0.58	18.53	3.5	6.5	10	6
Glycerol (ml/L)	76.92	14.44	5.9	18.78	35	65	100	6
FPO								
FAEE % v/v)	72.6	8.2	3.35	11.3	22.5	61	83.5	6
FAEE (ml/L)	723.62	81.2	33.15	11.22	225	610	835	6
Glycerol (ml)	16	6.35	2.59	39.68	15	7.5	22.5	6
Glycerol (% v/v)	8.18	0.84	0.34	10.27	2	7.5	9.5	6
Glycerol (ml/L)	81.42	8.56	3.5	10.52	20.75	74.25	95	6
UPO								
FAEE (% v/v)	72.28	4.66	1.9	6.45	13.6	65	78.6	6
FAEE (ml/L)	720.63	47.42	19.36	6.58	136.15	650	786.15	6
Glycerol (% v/v)	6.65	1.03	0.42	15.47	2.7	5.5	8.2	6
Glycerol (ml/L)	66.4	10.33	4.22	15.56	27	55	82	6
UPeO								
FAEE (% v/v)	73.75	4.32	1.76	5.85	12.17	67.5	79.67	6
FAEE (ml/L)	737.51	43.16	17.62	5.85	121.65	675	796.65	6
Glycerol (% v/v)	6.41	1.01	0.41	15.69	2.55	5.35	7.9	6
Glycerol (ml/L)	64.08	10.05	4.1	15.69	25.5	53.5	79	6
Overall								
FAEE (% v/v)	73.32	5.86	1.2	7.99	22.5	61	83.5	24
FAEE (ml/L)	731.42	58.31	11.9	7.97	225	610	835	24
Glycerol (% v/v)	7.24	1.27	0.26	17.53	4.65	5.35	10	24
Glycerol (ml/L)	72.21	12.67	2.59	17.54	46.5	53.5	100	24

†yield in ml/L; FPeO, fresh peanut oil; FPO, fresh palm oil; UPeO, used peanut oil; UPO, used palm oil,

Molar ratio of ethanol to oil and yield of biodiesel and glycerol

Figure 2 shows comparison of FAEE yield with respect to the fresh or used VO at same molar ratio of ethanol to oil in the alkali-transesterification step. At 3:1 molar ratio of ethanol to oil, UVOs generated higher yield of FAEE than FVOs while at 6:1 and 9:1 molar ratios, FVOs produced higher yield of FAEE than UVOs. In addition, irrespective of freshness, PeOs produced higher FAEE than POs across the three assessed molar ratios as previously observed. Nonetheless, all the oils produced FAEE at a yield above 60.0% across the three assessed molar ratios (Table 1). Conversely, FVOs had higher yield of glycerol than the corresponding UVOs, of which FPeO had the highest yield. The differences in the yield of the assessed oils at same ethanol to oil molar ratio could be due to feedstock type which is largely due to their FA composition [12, 18, 44-45]. In addition, an undertone of the physical properties of the VOs with

respect to freshness when structurally deformed with formation of heterogenous mixture under frying process could be a factor [2, 16, 22, 36-37].

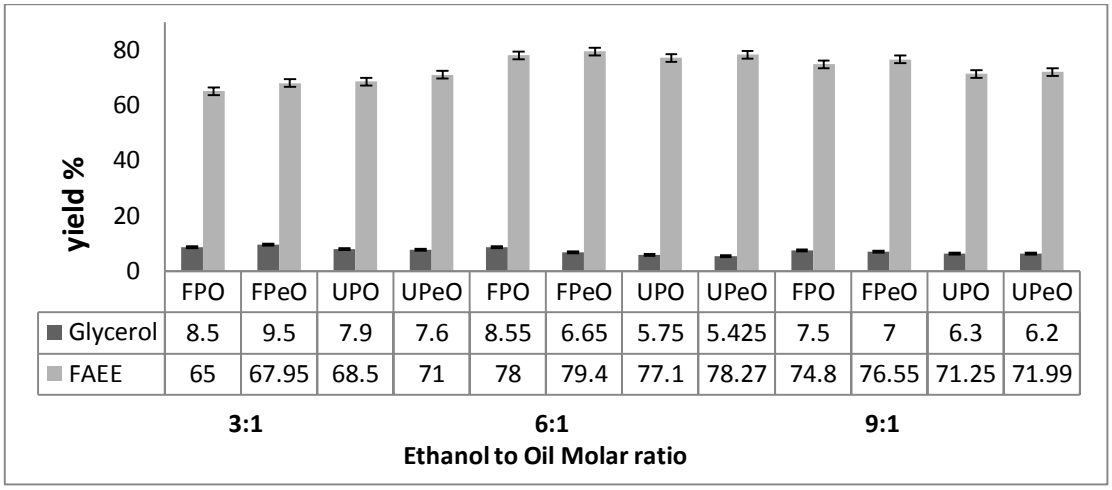


Figure 2: Yield of biodiesel and glycerol generated from FP_eO, FPO, UP_eO and UPO at same ethanol to oil molar ratio of 3:1, 6:1 and 9:1. FP_eO, fresh peanut oil; FPO, fresh palm oil; UP_eO, used peanut oil and UPO, used palm oil.

Figure 3 shows increasing ethanol to oil molar ratio from 3:1 to 6:1caused a co- increase in the yield of FAEE but with a fall at the highest ethanol to oil molar ratio of 9:1. However, a reversed trend is observed in the mean yield of glycerol which showed a large fall from 3:1 to 6:1 molar ratio but with a slight increase at 9:1 molar ratio. The present obtained highest FAEE yield at 6:1 ethanol to oil ratio as optimum corroborates previous reports on FAEE yield at diverse assessed ethanol to oil molar ratios [19, 40]. Though, stoichiometric equation of transesterification is a 3:1 ethanol to oil molar ratio. However, higher molar ratios are reported to drive the reaction to equilibrium and obtain good yield of esters as presently observed and 6:1 molar ratio of ethanol to oil is commonly reported as optimum for FAEE.

The fall in yield of FAEE observed at 9:1 ethanol to oil molar ratio could be largely due to insufficient amount of alcohol and catalyst employed at present for high triglycerides content of the assessed UVOs causing high level of unreacted oil residues washed off. Also, the lowest yield observed at 3:1 molar ratio, perhaps, emanated from excess residual catalyst and unreacted alcohol washed off [2, 12, 16, 18, 22, 36-37, 44-45]. Nonetheless, more yield of biodiesel could be produced if factors affecting transesterification as reported by Allawzi and Kandah [38] are

optimized, and also, use of automated reactors and employment of pre and post-transesterification treatments [20, 46] were considered.

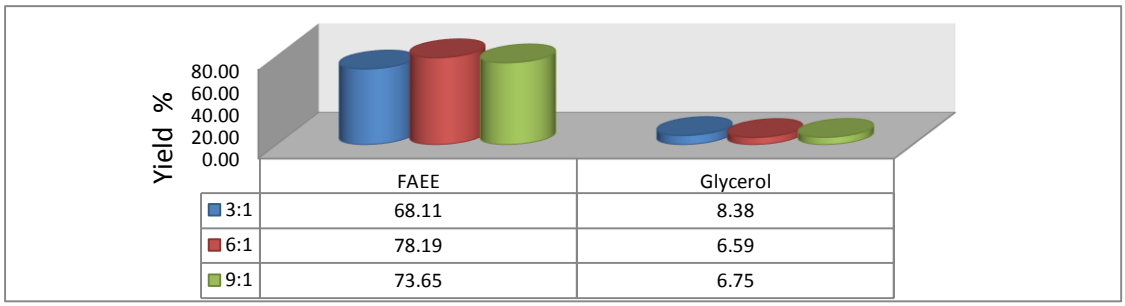


Figure 3: Overall yield of FAEE and glycerol obtained across ethanol to oil molar ratio of 3:1, 6:1, and 9:1

Qualitative characterization of FAEE generated from FP_eO, FPO, $UPeO$ and UPO

Five common characteristics of biodiesel, namely, viscosity, SG, ash content, carbon residue and acid value were used to evaluate quality of the FAEE from the assessed VOs. Figure 4 shows the comparable SG, viscosity, ash content, carbon residue and acid values for the ethyl ester generated from the FP_eO (P_eEE), FPO (PEE), UP_eO (UP_eEE) and UPO (UPEE) and reveals UPeEE and UPEE are of good qualities as P_eEE and PEE and all have the assessed five qualities within ASTM for alkyl esters (ASTM D 6751) [12, 47] except UPeEE and UPEE for CC. Nevertheless, they could be used as commercial neat or blend biodiesel. According to Table 2, mean viscosity ranged from 4.07mm^2/s for PeEE to 4.48 mm^2/s for UPeEE, indicating higher viscosity of PEE over P_eEE, and also higher viscosity for UPeEE and UPEE when compared to corresponding PeEE and PEE. This is because FPeO has more of unsaturated fatty acid than FPO and hence lower viscosity of FPeEE due to carryover from parent feedstock as earlier explained. According to Allen *et al* [48], the viscosity of biodiesel fuels reduced considerably with increasing unsaturation and contamination with small amounts of glycerides significantly affects the viscosity of biodiesel fuels. Also, UVOs had undergone processing that resulted into dis-conformation of primary and secondary native structures leading to elevated FFA, and formation of polymerization and oxidative degradation products contributing higher total polar materials (TPM) and hence, increased viscosity [16, 35-37]. Noteworthy, the presence of these polar organic substances in UVOs results into loss of their nutritional properties and perhaps, recast for further cooking because they could be detrimental to health [49].

The ash content of UPeEE and UPEE doubled the content found in FPeEE and FPEE, specifying possible higher content of metals in the UVOs compared to FVOs. In addition, the

carbon residue and acid number of UPeEE and UPEE are higher than those of FPeEE and FPEE, indicating possible presence of high contaminated organic compounds, inorganic acids and salts as carry over from UVOs. Therefore, the presently obtained UPeEE and UPEE are not biodiesel by EN and US norms [12]. Consequently, the UPeEE and UPEE were made to undergo second adsorption process using silica gel, which reduced the AV (0.37, 0.41 mg/KOH/g, respectively) and CC (0.2, 0.18 % mass, respectively) to acceptable level within biodiesel norms. Therefore, recycling UPO and UPeO into biodiesel production is a promising economic and safe environment driving routes. Also, it avoids health complications that could emanate from reuse of UVOs for cooking processes. Diverse adsorption techniques and processes other than silica gel such as printing paper paste are also promising tools for a cleaner and purer biodiesel from UVOs [46].

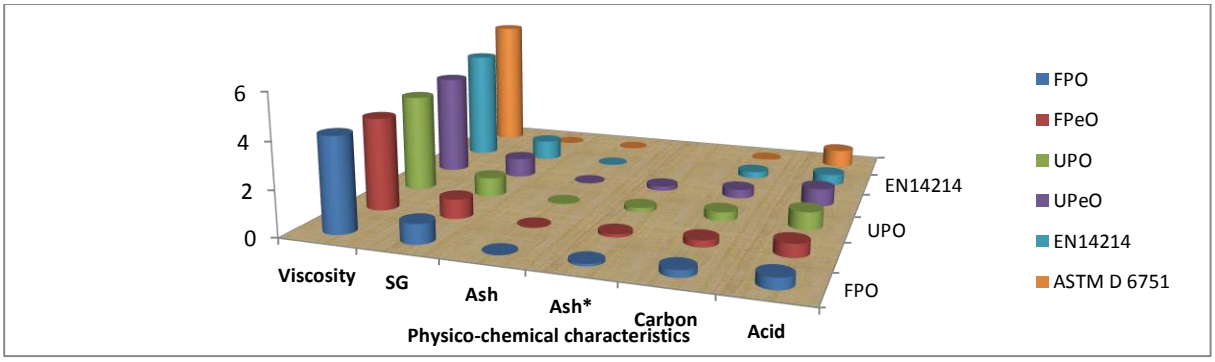


Figure 4: Physicochemical characteristics of FAME from FGO, FPO, UPeO and UPO.
SG, specific gravity; ash*, ash contentment multiplied by 10.

Table 2: Descriptive statistics for physicochemical characteristics of biodiesel obtained from FGO, FPO and UPO

Biodiesel	Mean	SD	SE	CV	Range	Min	Max	N
FPeEE								
Viscosity mm^2/sec	4.07	0.35	0.14	8.56	0.81	3.63	4.44	6
SG	0.86	0.01	0	1.21	0.03	0.84	0.87	6
Ash (% mass)	0.01	0	0	35.39	0.01	0.01	0.02	6
Carbon (% mass)	0.29	0.03	0.01	8.72	0.07	0.26	0.33	6
Acid **no. (**mg KOH g^{-1})	0.58	0.04	0.02	7.28	0.11	0.52	0.63	6
FPEE								
Viscosity (mm^2/sec)	4.14	0.25	0.1	6.05	0.67	3.85	4.52	6
SG	0.87	0.01	0.01	1.45	0.03	0.85	0.88	6
Ash (% mass)	0.01	0	0	20.02	0.01	0.01	0.01	6
Carbon (%mass)	0.3	0.04	0.02	13.46	0.12	0.24	0.36	6
Acid no. (mg KOH g^{-1})	0.47	0.02	0.01	4.66	0.06	0.44	0.5	6
UPEE								
Viscosity (mm^2/sec)	4.29	0.45	0.18	10.38	1.18	3.65	4.83	6
SG	0.85	0.02	0.01	2.88	0.07	0.81	0.88	6
Ash (% mass)	0.02	0	0	0	0	0.02	0.02	6

Carbon (% mass)	0.39	0.03	0.01	7.54	0.08	0.34	0.42	6
Acid no. (mg KOH g^{-1})	0.78	0.04	0.02	4.9	0.1	0.72	0.82	6
UPeEE								
Viscosity (mm^2/sec)	4.48	0.23	0.1	5.2	0.63	4.17	4.8	6
SG	0.86	0.01	0.01	1.58	0.04	0.84	0.88	6
Ash (% mass)	0.02	0	0	0	0	0.02	0.02	6
Carbon (% mass)	0.4	0.04	0.01	9.16	0.09	0.35	0.44	6
Acid no. (mg KOH g^{-1})	0.78	0.03	0.01	3.24	0.07	0.74	0.81	6

Variation of glycerol, yield and fuel characteristics of obtained FAEE among feedstock, feedstock source, and ethanol to oil molar ratios

Table 3 reveals general non-significant difference in the yield of obtained FAEE indicating FAEE yield at present study is not influenced by feedstock, VO source or freshness. Therefore, FAEE yield from any VO, either fresh or used is considered the same and perhaps not a parameter to consider for FAEE optimization. Noteworthy, is the low number of assessed VOs at present for the generated result to be considered as a liming factor for conclusion. Conversely, molar ratio of ethanol to oil significantly affected yield of FAEE and perhaps, might be an important parameter to optimize for good yield and has been an emphasized parameter for generating FAEE from VOs [25]. Furthermore, the obtained results show glycerol is significant for feedstock, VO freshness and ethanol to oil molar ratio and these are parameters to consider when glycerol is the main focus of synthesis, of which transesterification process is not an option for its synthesis due to its availability, abundance and uses. There is high variation among the assessed VO feedstock for levels of acid value, ash and carbon residue of the obtained FAEE. Also, there was high impact of VO freshness on all biofuel characteristics assessed and molar ratio of ethanol to oil only affected viscosity while VO source had no significant effect on any biofuel characteristic. Therefore, the quality of the generated FAEE is affected by VO freshness, and this could be taken care of at both pre and post transeterification processes as previously mentioned and carried out in the present study. Similar significant variations in yield and quality of biodiesel among different VOs feedstock have been observed using ANOVA and other similar chemometrics methods [20, 40].

Table 3: Analysis of variance of Glycerol, FAEE and its characteristics among VO feedstock, Feedstock source, VO freshness and ethanol to oil molar ratio.

Model Source	**DF**	**SS III**	**MS**	**F**	**Pr > F**	**Model Source**	**SS III**	**MS**	**F**	**P.r > F**
Glycerol yield						**FAEE yield**				
VO Feedstock	3	12.47	4.16	3.49	*	Feedstock	18.62	6.21	0.15	Ns
Feedstock Source	1	0.98	0.98	0.60	Ns	Feedstock Source	16.69	16.69	0.46	Ns
VO Freshness	1	11.39	11.39	10.1	**	VO Freshness	1.58	1.58	0.04	Ns
E:VO	2	14.50	7.25	7.04	**	E:VO	423.5	211.7	11.82	***
Viscosity						**Carbon**				
VO Feedstock	3	0.62	0.21	1.86	ns	VO Feedstock	0.05	0.02	15.34	***
Feedstock Source	1	0.02	0.02	0.14	ns	Feedstock Source	0.00	0.00	0.01	Ns
VO Freshness	1	0.50	0.50	4.63	*	VO Freshness	0.05	0.05	48.88	***

E:VO	2	1.00	0.50	5.76	*	E:VO	0.00	0.00	0.19	Ns
Ash						**Acid Value**				
VO Feedstock	3	0.00	0.00	21.5	***	VO Feedstock	0.43	0.14	127.5	***
Feedstock	1	0.00	0.00	0.69	ns	Feedstock	0.02	0.02	0.85	Ns
Source						Source				
VO Freshness	1	0.00	0.00	51.9	***	VO Freshness	0.40	0.40	156.9	***
E:VO	2	0.00	0.00	0.58	ns	E:VO	0.00	0.00	0.11	Ns

VO feedstock, FPeO, FPO, UPeO and UPO; feedstock source, PO and P_eO; VO freshness, fresh and used; E:VO, ethanol to oil molar ration; SS III, type 3 sum of square; MS, mean square; *, p <0.05; **, p <0.05; ***, p <0.0005; ns, not significant at P≤0.05.

Table 4 shows no significant relationship for FAEE yield and other parameters assessed, not even for ethanol to oil molar ratio and might be due to a fall at 9:1 molar ratio. There were strong relationships among ash content, carbon residue and acid value with each having a strong positive relationship with VO freshness supporting increased degradation and oxidative products with reduced VO freshness. The present relationships are useful for making predictions among biodiesel properties for quality evaluation studies. However, yield of glycerol had inverse relationships with VO freshness, ash, carbon residue and acid value, which indicated increasing yield of glycerol, is associated with reduced ash content, acid value and carbon residue. Consequently, reduced level of inorganic composition and heterogeneous mixture in VOs favored production of glycerol and enhanced biofuel characteristics.

Table 4: Pearson correlation among VO, glycerol, FAEE and biofuel characteristics

	VO Source	**Molar ratio**	**Glycerol yield**	**FAEE yield**	**Viscosity**	**SG**	**Ash**	**Carbon**	**Acid**
VO Freshness	ns	ns	-0.57^{**}	ns	0.41^{*}	-ns	0.85^{***}	0.84^{***}	0.94^{***}
VO Source		ns	ns	ns	ns	ns	ns	ns	ns
Molar ratio		1.00	-0.53^{*}	ns	-0.43^{*}	ns	ns	ns	ns
Glycerol yield			1.00	ns	ns	ns	-0.61^{**}	-0.48^{*}	-0.61^{**}
FAEE yield				1.00	ns	ns	ns	ns	ns
Viscosity					1.00	ns	ns	ns	ns
SG						1.00	ns	ns	ns
Ash							1.00	0.76^{***}	0.88^{***}
Carbon								1.00	0.83^{***}

*, p <0.05, **, p <0.05, ***, p <0.0005, ns, not significant at P≤0.05

CONCLUSIONS

The study reveals used peanut and palm oil as potential feedstock for production of FAEE using transesterification method with pre- and post-transesterification treatments. The study also shows

that the yield and quality of obtained FAEE is ethanol to oil molar ratio and VOs freshness dependent, respectively, but independent of VO feedstock source. Therefore, recycling UPO and UPeO into biodiesel production is a promising economic and safe environment driving routes, though, require optimization for high and good quality yield. The content of the present study adds to the scanty information available on FAEE production from UVOs.

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