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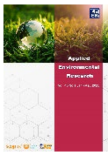

Research Article

Determinants of Physicochemical Composition of Palm Oil Mill Effluent - Implications on Environment and Bio-digester Treatment Design

Tambe, E.B.[1,*], Okonkwo, A.U.[2], Mbuka-Nwosu, I.E.[3], Cookey, C.O.[4], Agbe, E.[5], Onwusa, S.C.[6], Ekpe, I.N.[7], Evuen, U.F.[8], Okpoghono, J.[8]

[1] *Department of Environmental Management & Toxicology, Delta State University of Science and Technology, Ozoro, Nigeria*
[2] *Department of Environmental Management, Chukwuemeka Odumegwu Ojukwu University, Uli, Nigeria*
[3] *Department of Environmental Management, Federal University of Technology, Owerri, Nigeria*
[4] *Department of Crop Science and Technology, Federal University of Technology, Owerri, Nigeria*
[5] *Department of Environmental Management, Delta State University of Science and Technology, Ozoro, Nigeria*
[6] *Department of Mechanical Engineering, Delta State University of Science and Technology, Ozoro, Nigeria*
[7] *Department of Civil and Water Resources Engineering, Delta State University of Science and Technology, Ozoro, Nigeria*
[8] *Department of Biochemistry, Delta State University of Science and Technology, Ozoro, Nigeria*

*Correspondence Email: tambe_besong2001@yahoo.com

Abstract

Growing need for renewable energy and addressing challenges associated with indiscriminate wastes disposal has necessitated harnessing wastes to wealth. The study investigated parameters determining the physicochemical composition of palm oil mill effluent (POME) generated at Agricultural Development Authority Palm (ADAPALM) and palm oil mills in its catchment communities, located at Ohaji/Egbema Local Government Area of Imo State, Nigeria and their implications on environmental health and treatment approaches required. Survey research design was used. From a randomly sampled small-scaled mill in each community, and for the lone medium and large-scaled mills, four homogenous samples of POME were collected from sampled small, medium and large-scaled mills for laboratory analysis of potential of hydrogen (pH), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total carbon (TC), total solid (TS), total suspended solid (TSS), total organic carbon (TOC), total nitrogen (TN), total kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N), Manganese (Mn), Nickel (Ni), Iron (Fe), Copper (Cu), Chromium (Cr), Cadmium (Cd), Potassium (K), total phosphorus (TP), Calcium (Ca), and Magnesium (Mg) using standard methods for wastewater analysis as described in American Public Health Association. Data was analysed using multivariate analysis of variance, and showed that the physicochemical composition of POME was significantly different ($p<0.01$) across milling-scales, types of FFBs and seasons. The pH=11.728±0.467 and 4.10563±0.030, BOD=52.042±1.669 and 233.125±10.674; TSS=14421.748±2431.870 and 974.344±29.764; TN=347.918±7.371 and 468.92500±31.315; TP=127.890±1.478 and 26.476±6.339 for dry and wet seasons respectively, and COD=3731.250±154.574 for dry season only were not within the acceptable wastewater discharge limits. The pH, Cd, Ni, Cu, K and organic content across seasons highlight specific concerns in the wastewater treatment. The study has simultaneously addressed a wider scope of independent variables that define the composition of POME, and required approaches necessary to revert environmental degradation and promote green energy access in the area.

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Introduction

Waste generation is an inextricable part of human existence. In the course of processing oil palm (Elaeis guineensis) to palm oil so as to serve society, copious volumes of wastewater termed palm oil mill effluent (POME) are being generated [1-2]. When agricultural wastewater is indiscriminately disposed, it distorts the efficient functioning of aquatic and terrestrial ecosystems, alters atmospheric chemistry and weakens human sustenance network [3]. Fortunately, these deteriorating effects of POME could be reduced by transforming its composition to biogas, thus enhancing energy security in some regions of the world [4-5].

This approach of transforming wastes to wealth are frontiers of opportunities that are being exploited to achieve triple win of climate-smart agriculture which is premised on increase food production, enhance resilience and reduce emissions. These are well captured in sustainable development goals number 7 on affordable and clean energy, goal number 11 on sustainable cities and communities; and goal number 12 on responsible consumption and production [6]. In addition, it is also in conformity with global policy and Nigeria efforts to enhancing renewable energy in energy mix and curbing greenhouse gas emissions [7-9]. Following the interconnectedness of all the sustainable development goals [10-11], relegating the pathways of achieving sustainable energy development weakens their contributions to the attainment of these goals and impedes the progress of society [12-13, 6].

However, POME composition - a measure of the amount of the various constituents of the wastewater, depend mainly on the season of the year, the type of technology used in the production process, and the quality of the raw materials being processed [14-15]. These determinants of wastewater composition – location-specific variables, do influence its reactivity and interaction (properties), hence treatment approach and biogas generation. In this regard, physicochemical characterisation - a list of the various physicochemical constituents of POME, and the composition of these constituents are necessary in assessing its potentials, project feasibility, choosing suitable POME effluent treatment method, monitoring the treatment plant and prediction of biomethane potential [15-16].

Several studies on POME characterisation and physicochemical composition have revealed the implications of these contents and their dynamic, and the necessary treatment approaches required in an anaerobic bio-digester [15, 17]. For example, oil and grease are obstacles for biological digestion while removal of gross solids and unexpected mass protect downstream equipment from damage. To sustain microbial consortia in a bio-digester and ensure effective system function, the pH is required to be within the range of 6.8 to 7.2 and C/N ratio of range 10-45 is preferred.

The biodegradability index (BI) of POME, a measure of its possibility of being biologically degradable, and defined mathematically as ratio of BOD to COD (BOD/COD) or measured in terms of proportion of total organic carbon (TOC) is also essential in articulating wastewater treatability [18-19]. When BOD/COD is used and the ratio is greater than 0.5, the wastewater is considered highly biodegradable and if it is less than 0.3, the wastewater is considered to be slowly biodegradable [20]. Toxicity, the degree to which a substance will damage an exposed organism contributes to inhibiting respiration of microbial consortia in wastewater, thus limiting the ability of microbes to breakdown organic matter [21–22]. As toxicity concentration increases (increase inhibition), the rate of respiration falls and this threatens the efficiency of wastewater treatment. Numerous substances are toxic to anaerobic digesters, however, ammonia, hydrogen sulphide and heavy metals are the three most commonly reviewed types of toxicity [23].

Therefore, understanding POME characteristics and composition is necessary to assist in setting standards for effluent discharge and employing efficient technologies in harnessing the resource to valuable materials [17]. Thus, relegating POME characterisation studies and/or importing foreign data to another palm oil mill in order to manage its POME could lead to system failure and huge financial loses in the biogas plant. Furthermore, specific studies that have simultaneously defined the composition of POME across different milling scales, seasons, types of FFBs in order to provide a wider scope of parameters that influence POME composition for treatment still remain at infancy.

To reduce the data gap and promote sustainability in the oil palm industry, [2] and [24] conducted studies at Ohaji/Egbema Local Government Area (LGA), Imo State, Nigeria, on the determinants of volume of POME and the cumulative volume of POME generated, estimated to exceed 15 m^3 per day. The current research investigated the physicochemical composition of POME across milling scales, types of FFBs and seasons, a location-specific data for the oil palm communities, and capturing a wider scope of independent variables that influence POME composition. These variables have rarely been simultaneously addressed in POME studies. This was necessary for setting a palm oil industry agenda for the strategic treatment and use of POME resources for green energy generation at Ohaji/Egbema LGA. This will avert the existing environmental degradation effect of POME in the area and improve sustainable energy needs for the communities.

Materials and methods

1) Research design and sampling techniques

The study employed non-experimental research design. For each of the sampled mills in a milling scale, triplicate samples were collected [16, 25-26] for each batch of milling to yield a composite sample before laboratory analysis. The collected POME samples were being kept in closely tight containers, transported to the laboratory under preserved condition at 4°C in order to prevent the wastewater from undergoing biodegradation [25, 27].

2) Laboratory analysis of POME

Determination of POME physicochemical composition employed standard laboratory methods for wastewater analysis as described in the previous studies [20, 25, 28] to determine potential of hydrogen (pH), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total carbon (TC), total solid (TS), total suspended solid (TSS), total organic carbon (TOC), total nitrogen (TN), total kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N), Manganese (Mn), Nickel (Ni), Iron (Fe), Copper (Cu), Chromium (Cr), Cadmium (Cd), Potassium (K), total phosphorus (TP), Calcium (Ca), and Magnesium (Mg) (Table 1). These physicochemical parameters of POME were determined for four batches for each milling scale in each crop season (low and high crop seasons).

3) Statistical analysis

The variation of the dependent variables (physicochemical composition of POME) across the independent variables (milling scales, types of FFBs and seasons) were analysed using multivariate analysis of variance (MANOVA) and reported using Wilks' Lambda [29–30]. The statistic assesses the proportion of variance in the dependent variables that is not accounted for by the intergroup variation. This multivariate analysis of General Linear Model (GLM) is capable of revealing that differences exist among the groups (independent variables) on the dependent variables taken together (all the physicochemical compositions). If the proportion is small, Wilks' Lambda suggests that the dependent variables vary greatly among groups, and these groups might have different mean values for the dependent variables.

Results and discussion

1) Physicochemical composition of POME

1.1) Variation of POME composition across milling scales, types of FFBs and seasons

The overall test effect of the multivariate analysis revealed that there was a significant difference ($p<0.01$) in the physicochemical composition of POME across milling scales: Wilks' Lambda=0.000, $F(52,12)= 14.766$, $p=0.000$; types of FFBs: Wilks' Lambda=0.002, $F(52,12)= 4.751$, $p=0.003$; and seasons: Wilks' Lambda=0.000, $F(26,6)= 4482.803$, $p=0.000$ (Table 2).

Similarly, even within small-scaled mills (similar milling scales), the physicochemical composition of POME was found to be significantly different ($p<0.05$) across the various small-scaled mills: Wilks' Lambda=0.000, $F(40,2)= 333.585$, $p=0.003$; types of FFBs: Wilks' Lambda=0.000, $F(20,2)=23.284$, $p=0.042$; and seasons: Wilks' Lambda=0.000, $F(20,1)=557351.522$, $p=0.001$ (Table 3). This explains the location-specific (mill-specific) nature of POME composition and its importance for consideration prior to its treatment for bio-methane development.

Table 1 Methods employed to determine POME composition

Parameters	Method
pH	APHA 4500H+B
[b]DS	
DO/BOD_5	5 days BOD dark incubator test at 20 °C
COD	Open reflux method
TS	APHA 2540 B
TSS	HACH method 8006 (Photometric)
TN	HACH method 10072
TKN	HACH Nessler's method 8075
NH_3-N	HACH Nessler's method 8038
TP	HACH total phosphorus method 10127
TC/TOC	High temperature combustion method
Heavy metals and metals	Flame atomic absorption spectrometry

Note: [b]DS is calculated on the basis of the following formula: DS (mg L^{-1}) TS -TSS.
Source: [20, 25, 28]

Table 2 Variation of POME composition across milling scales, types of FFBs and seasons

Effect	Wilks' Lambda	F	Hypothesis df	Error df	P-value
Intercept	0.000	6174.513	26.000	6.000	0.000
Milling scales	0.000	14.766	52.000	12.000	0.000
Types of FFBs	0.002	4.751	52.000	12.000	0.003
Seasons	0.000	4482.803	26.000	6.000	0.000

Table 3 Variation of POME composition across small-scaled mills, type of FFBs and seasons

Effect	Wilks' Lambda	F	Hypothesis df	Error df	P-value
Intercept	0.000	19915.583	20.000	1.000	0.006
Small-scaled mills	0.000	333.585	40.000	2.000	0.003
Types of FFBs	0.000	23.284	40.000	2.000	0.042
Seasons	0.000	557351.522	20.000	1.000	0.001

The variation of the various physicochemical composition of POME across these milling scales (Table 2) could be associated with the different practices carried out in these mills. For example, while the small-scaled mills slice the FFBs and keep them for some days for fermentation and to facilitate removal of fresh fruits from the bunches, the large-scaled mill could process these whole FFBs barely few hours after harvest, even on the day it is harvested. Like the large-scaled mill, the medium-scaled mill uses steaming within few minutes prior to digestion of the fresh fruits. In the small-scaled mills, the fresh fruits are boiled for several hours before digestion. The variation of the physicochemical composition of POME across types of FFBs could result from the high oil content of the Tenera variety and its related low moisture content, compared to the low oil content of the Dura variety and its related high moisture content. In the course of milling, millers tended to use more water to extract the available oil in the low oil content Dura variety, hence increasing the volume of its wastewater. This variation in the oil and water content of the various types of FFBs and its subsequent volume of POME generated [2] influence the concentration of the various physicochemical composition of the wastewater. Similarly, seasonal variations influence the moisture content of fresh fruits. This moisture content influences the volume of the wastewater and the composition of its constituents. The variation of the physicochemical composition of POME across seasons agrees with study by [28] who showed that the physicochemical composition of POME during high crop season for Golconda palm oil mill deviated at approximately ±20-50% from the values recorded during low crop season.

1.2) Mean values of physicochemical composition of POME

The multivariate analysis of GLM computes MANOVA in order to define the significance of the mean difference and which means of POME composition differ. Post Hoc Analysis using Duncan Multiple Range Test (DMRT) was employed for pairwise comparison of the parameters of POME across milling scales and types of FFBs (Table 4). These mean values of POME composition for each milling scale and types of FFBs could assist to inform decision making where regulation interventions are necessary (identifying the source of certain pollutants) for pollution abatement and treatment approaches of the wastewater [31, 28].

2) Seasonal variation of POME composition and environmental health

Similarly, the difference in the mean values of these parameters across seasons were computed using an independent sample T-test. Except for Fe, the mean values for all other parameters of POME were statistically highly significant ($p<0.01$) across seasons (Table 5). This could be associated with varying moisture content across seasons, increasing organic matter production in the wet season and other biochemical reactions that are related to seasonal variations. The difference in the mean values across seasons could assist to regulate disposal practices when compared with standard for effluent discharge, compute greenhouse gas emission threats, define appropriate treatment measures for the wastewater-to-energy and predict the biogas potential of the wastewater [16, 28, 31-32].

The composition of some parameters of POME generated in ADAPALM and palm oil mills in its catchment communities do not fall within the acceptable national and international guideline values for wastewater disposal; these compositions cannot guarantee environmental safety (Supplementary Material (SM) 1). Most of these parameters were significantly influenced by seasons, types of FFBs, and milling scales (Tables 4 and 5), hence making the composition beyond the ambits of the acceptable guideline values for wastewater disposal. Seasonal variations of POME composition with reference to the discharge limits by the [33] showed that the pH (dry season), BOD, COD (dry season), TSS, TN, and TP were not within the acceptable discharge limits for wastewater disposal during vegetable oil pro-cessing (SM 1). With reference to the previous studies [34-35] standards, pH, TSS (except for dry the season), BOD, and COD (indicated for World Bank Group and NESREA only) were not within environmental safety limits. The DO for POME generated in the dry season was not within the acceptable level for WHO and NESREA standard.

Table 4 Variation of POME composition across milling scales and types of FFB

POME parameters	Milling scales			Types of FFB		
	Small-scaled mill	Medium-scaled mill	Large-scaled mill	Dura variety (local type)	Tenera variety ('Agric type')	Mixed variety (Dura and Tenera)
pH	8.860^{a}	11.310^{b}	5.928^{c}	8.550^{xy}	7.727^{yz}	9.254^{xz}
DO	10.863^{ab}	4.923^{bc}	7.530^{ac}	5.200^{xy}	9.331^{yz}	10.614^{xz}
BOD	143.610^{a}	55.807^{b}	114.915^{ac}	145.105^{xy}	132.897^{yz}	125.477^{xz}
COD	$1{,}921.917^{a}$	152.547^{b}	$1{,}894.605^{ac}$	$1{,}933.060^{xy}$	$2{,}047.816^{y}$	$1{,}425.605^{xz}$
Total carbon	$8{,}818.288^{ab}$	$3{,}347.000^{bc}$	$2{,}630.064^{ac}$	$3{,}603.115^{xy}$	$8{,}207.831^{yz}$	$6{,}075.124^{xz}$
TS	$134{,}830.123^{a}$	$11{,}616.733^{bc}$	$99{,}890.763^{ac}$	$71{,}474.300^{xy}$	$142{,}219.616^{yz}$	$88{,}652.388^{xz}$
TDS	$126{,}147.896^{a}$	$4{,}654.067^{bc}$	$62{,}665.175^{ac}$	$62{,}552.900^{xy}$	$123{,}880.779^{yz}$	$82{,}268.019^{xz}$
Total suspended solids	$8{,}368.370^{ab}$	$6{,}962.700^{bc}$	$9{,}997.563^{ac}$	$8{,}921.750^{xy}$	$10{,}874.405^{yx}$	$5{,}874.313^{xz}$
TOC	534.579^{ab}	178.333^{bc}	114.783^{ac}	246.885^{xy}	498.656^{yz}	336.508^{xz}
TN	413.992^{ab}	321.433^{bc}	385.121^{ac}	327.350^{xy}	428.467^{yz}	375.844^{xz}
TKN	249.448^{ab}	199.900^{bc}	209.163^{ac}	196.750^{xy}	255.977^{yz}	218.850^{xz}
NH3-N	197.744^{ab}	136.663^{bc}	172.911^{ac}	156.327^{xy}	215.477^{yz}	157.993^{xz}
Organic nitrogen	51.705^{ab}	63.237^{bc}	36.251^{ac}	40.424^{xy}	40.499^{yz}	60.857^{xz}
C/N	18.035^{ab}	10.414^{bc}	6.767^{c}	10.967^{xy}	15.531^{yz}	14.829^{xz}
Biodegradability index (BI)	0.175^{a}	0.366^{b}	0.063^{c}	0.127^{a}	0.120^{ab}	0.226^{c}
Mn	3.784^{a}	0.135^{bc}	1.124^{ac}	1.634^{xy}	3.435^{yz}	2.452^{xz}
Ni	0.501^{ab}	0.710^{bc}	0.666^{ac}	0.326^{ab}	0.600^{yz}	0.525^{xz}
Fe	3.293^{a}	1.300^{bc}	1.320^{c}	1.321^{xy}	2.872^{yz}	2.732^{xz}
Cu	5.475^{ab}	0.206^{bc}	0.991^{ac}	2.071^{xy}	5.510^{yz}	2.629^{xz}
Cr	0.550^{a}	0.018^{b}	0.351^{ac}	0.455^{xy}	0.514^{yz}	0.405^{xz}
Cd	0.051^{ab}	0.055^{bc}	0.048^{ac}	0.041^{xy}	0.047^{yz}	0.056^{xz}
K	221.178^{a}	3.123^{b}	26.252^{ac}	79.260^{xy}	205.674^{yz}	118.981^{xz}
TP	83.467^{a}	129.693^{b}	68.760^{ac}	67.110^{xy}	83.826^{yz}	86.399^{xz}
Ca	92.705^{ab}	135.750^{b}	66.964^{ac}	79.100^{xy}	90.615^{yz}	92.088^{xz}
Mg	64.800^{a}	125.867^{b}	103.988^{bc}	89.250^{xy}	82.731^{yz}	71.487^{xz}

Note: a, b, c: Means with similar or overlapping subscripts indicate no significant difference across milling scales.
x, y, z: Means with similar or overlapping subscripts indicate no significant difference across types of FFBs. Mean value of POME composition is statistically significant at p=0.05 using DMRT for pairwise comparison.

Table 5 Variation of POME composition across seasons

Parameters	Season of milling		P-value
	Wet season (low crop production season)	Dry season (High crop production season)	
	Mean±SE		0.000
pH	11.728±.467	4.106±0.030	0.000
DO	14.868±2.028	2.830±.045	0.000
BOD	52.042±1.669	233.125±10.674	0.000
COD	280.205±38.059	3,731.250±154.574	0.000
Total carbon	3,303.010±59.112	11,937.113±2,581.601	0.000
TS	29,699.329±10,900.491	232,242.100±30,482.750	0.000
TDS	4,905.048±163.375	230,757.681±30,395.805	0.000
Total suspended solids	14,421.748±2,431.870	974.344±29.764	0.000
TOC	224.724±14.189	664.569±171.439	0.002
TN	347.918±7.371	468.925±31.315	0.000
TKN	157.412±5.460	340.812±24.770	0.000
NH_3-N	122.800±4.900	272.239±25.754	0.000
Organic itrogen	34.613±5.825	68.573±12.133	0.004
C/N ratio	9.548±0.221	22.111±3.783	0.000
Biodegradability index (BI)	0.245±0.023	0.063±0.003	0.000
Mn	0.436±0.051	6.164±1.041	0.000
Ni	0.898±0.066	0.099±0.019	0.000

Table 5 Variation of POME composition across seasons (*continued*)

Parameters	Season of milling		P-value
	Wet season (low crop production season)	Dry season (High crop production season)	
	Mean±SE		0.000
Fe	2.760±0.362	2.633±0.467	0.558
Cu	0.349±0.038	8.973±2.040	0.000
Cr	0.047±0.009	1.010±.087	0.000
Cd	0.071±0.008	0.023±0.002	0.000
K	4.143±0.321	367.689±78.585	0.000
TP	127.890±1.478	26.476±6.339	0.000
Ca	159.680±11.199	0.000±.000	0.000
Mg	137.818±10.348	0.001±0.001	0.000

When POME with these unacceptable parameter range is indiscriminately disposed into any of the environmental compartments (soil, water and air), the chemistry and the biological species of the compartment is altered. This degenerates to interconnected impacts which affects the quality of our environment and human wellbeing. For example, when POME is kept in the pond of ADAPALM or disposed at the vicinity of small-scaled mills, anaerobic decomposition of the wastewater adds to the emission of methane and other greenhouse gases into the atmosphere. This leads to enhanced greenhouse effect and alters the temperature of our planet.

Considering the COD content of POME, for example, baseline methodologies have been employed to compute the carbon emission reduction if POME had been confined for treatment [36-37]. When POME in the current study undergoes anaerobic degradation with subsequent emission of methane, carbon dioxide equivalence can be computed (Eq. 1).

From the baseline methodology formula, CO_2 equivalence of methane emission occurring in ADAPALM and palm oil mills in its catchment communities can be computed for each season, with data on cumulative daily generation of POME of at least 15 m^3 [24].

In the wet season, annual baseline emission = (147.72 kgCOD per month) × 12 months × 0.057kg CH_4 per kg COD × 0.65×21/1000kg per t = 1.379 tCO_2 per year.

In the dry season, annual baseline emission = (1736.01 kgCOD per month) × 12 months × 0.014 kg CH_4 per kg COD × 0.65 × 21/1000kg per t = 3.981 tCO_2 per year.

These emissions across seasons in the study area emanating from the agricultural sector are contributing to the one-third of total global anthropogenic greenhouse gas emissions from agriculture [38-39]. The interconnected impacts associated with methane emissions and climate change undermines all the sustainable development goals [10-11]. Recurrent undermining of this sustenance network (sustainable development goals) widens access to human gateway of extinction. Several authors have reported POME compositions that exceed guideline values for wastewater disposal and their subsequent impact on the environment [32, 31]. Consequently, the indiscriminate disposal and absence of treatment of POME generated by these mills cannot be relagated by the State and Federal government in their quest to achieve sustainable development. It is therefore imperative to confine the POME for treatment and subsequent recovery of bio-methane.

The approach to confine and treat POME is aligned to averting its environmental impacts, attaining the triple win of climate-smart agriculture, and is also within the ambits of the concept of decoupling and sustainable energy development. Impact decoupling is strengthened through carbon capture which ensures that there is reduction in methane emission into the atmosphere. As the palm oil mills advance in their activities and subsequent carbon capture for domestic fuel (methane), economic output is strengthened, hence subsequent improvement on the wellbeing of the people. This is interconnected in extending the lifespan of non-renewable resource base (resource decoupling) e.g fossil fuel and reduction of greenhouse gas emissions. However, the treatment approaches of the generated POME by ADAPALM and palm oil mills within its catchment communities are also dependent on the composition of the wastewater treatment parameters such as pH, BI, C/N ratio, toxicity among others. Hence, an in-depth analysis of these parameters will assist in pre-treatment in the primary pond prior to injection into the digester.

$$\text{Annual baseline emission} = \text{COD generated} \times \text{Bo kgCH4/kg COD}) \times \text{MCFbaseline} \times \text{GWP}/1000\text{kg/t} \qquad \text{(Eq. 1)}$$

Where: $MCF_{baseline}$= Monthly methane conversion factor, GWP= Global warming potential=21 times that of CO_2 and B_o= Methane production capacity.

3) POME composition, treatment and monitoring for biogas production

Following unacceptable composition of some POME parameters by national and international guideline values such as those of pH (dry season), BOD, COD (dry season), TSS, TN, and TP were not within the acceptable discharge limits for wastewater disposal during vegetable oil processing (SM 1) and their possible impacts on the quality of our environment, the wastewater can be confined, treated and transformed to biogas and subsequent recovery of bio-fertilizers. From the variation of POME composition, the independent variables that influence the composition of wastewater could be regulated where necessary to achieve workable composition for wastewater treatment. However, where these independent variables do not significantly influence the parameter for wastewater treatment and monitoring, chemical approaches could be induced.

The pH of POME was found to be significantly different across milling scales and seasons (Table 4 and 5). As the wet season makes the pH of POME more alkaline (11.728±0.467), small-scaled mills tended to contribute significantly to this increasing alkaline nature of POME. Within this season, there was none of the analysed independent variables that could reduce the pH within the workable level for wastewater treatment. It is necessary to maintain the pH between 6.8-7.2 for effective function of the biogas plant [23, 40-41]. Gerardi [23] argued that although the pH in anaerobic digester is satisfactory within 6.8 to 7.2, the best range is within 7.0 to 7.2. Below or beyond the pH range experimented by several authors as suitable for anaerobic digestion, the medium become toxic to methane-forming bacteria, impedes degradation of organic matter and subsequent collapse of the wastewater treatment for biogas recovery. Consequently, in the dry season (Table 5), the pH of POME was below the workable level for wastewater treatment. However, from the pH analysis, adding more POME coming from small-scaled mills can significanly increase the pH (Table 4). This means that more POME coming from these mills within this period could assist to achieve a desired pH for POME treatment. However, when the pH of POME in wastewater treatment plant is still below the workable level for proper functioning of the system, caustic soda could be used [40-41] and ferric chloride or citrate can be used to neutralise or destroy excessive alkalinity in a biodigester [23] .

C/N ratio of POME generated at Ohaji/Egbema was found to be significantly related to milling scales and seasons. Seasonal variations indicated that C/N ratio was 9.548±0.221 in the wet season and 22.111±3.783 in the dry season. C/N ratio of 10.58±0.51 is generally a good substrate for microbial proliferation and biogas production [40]. According to [42], methanogenic bacteria in anaerobic digestion require optimum C/N ratio of 8-20. Similarly, [43] posit that that appropriate C/N ratio of POME (with optimum value of 30) is significantly related to biogas production. [41] maintained that for effective anaerobic digestion and system function of the biogas plant, C/N ratio should be within the range of 10-45 for hydrolysis and acidogenesis and 20-30 for methanogenesis. However, when all steps of the anaerobic process take place in a single reactor, methanogenic requirement must be given the priority. In this regard, considering total carbon content of the wastewater, the C/N ratio for POME in the wet and dry season tended to be within the workable range for wastewater treatment. However, considering methanogenic requirements, C/N ratio can be stregthened by increasing on the organic content of the wastewater prior to treatment.

A higher C/N ratio above the workable range for wastewater treatment causes slower microorganism multiplication due to low protein formation (Nitrogen is an essential structural component of protein) and thus low energy and structural material metabolism of micro-organisms. This leads to lower substrate degradation efficiency in the biogas plant. On the contrary, low C/N ratio associated with Nitrogen-rich substrate leads to a possible ammonium inhibition of the micro-organisms and a subsequent collapse of the treatment process of biogas production. [28] showed that supplements of nitrogenous compounds could be added to regulate nitrogenous needs and balance the C/N or related ratio. Therefore, the independent variables of POME that influence the C/N ratio could be regulated where necessary to meet the workable range in wastewater treatment for biogas recovery.

The biodegradability index of POME was also found to be significantly varied with milling scales and seasons (Tables 4 and 5). Seasonal observations of biodegradability index revealed that POME generated in the study area showed a BI of 0.245±0.023 in the wet season and 0.063±0.003 in the dry season (Table 5). Despite the significant difference ($p<0.01$) in the BI of POME generated across seasons, the value of BI in each season was less than 0.3. POME is considered highly biodegradable when its biodegradability index is greater than 0.5, and when the BI is less than 0.3, the wastewater is considered to be slowly biodegradable and it is imperative to employ chemical treatment prior to biological treatment [20]. The BI of POME reported in this study was quite low when compared to that in a study by [28] who reported an average BI of 0.5 for POME samples collected from three different palm oil mills in Selangor, Malaysia. However, the value of BI in the current study is similar to that of [28] who reported BI as low as 0.2 in POME samples drawn from five palm oil mills Amohuru village, Aboh Mbaise LGA of Imo State, Nigeria.

The low BI of POME in the study area confirms with its low organic nitrogen content. Organic nitrogen and ammonia nitrogen sum up to the TKN in any wastewater. For the wastewater to be highly biodegradable, the proportion of organic nitrogen should be higher than the proportion of ammonia nitrogen in the wastewater. Where this becomes the contrary like in the current study, the wastewater is considered slowly biodegradable and is deemed for chemical treatment before biological treatment. [28] reported a BI of POME samples exceeding 0.5, and the proportion of organic nitrogen in TKN was higher than the proportion of ammonia nitrogen. The necessity for higher organic nitrogen compared to ammonia nitrogen in TKN in wastewater is on the basis that natural biochemical processes slowly convert organic nitrogen into ammonia, the form of nitrogen readily to be utilised as a nutrient by microorganisms in the treatment process of POME.

The BI, organic nitrogen and total organic carbon (TOC) are related in terms of measuring the biodegradability of the wastewater. POME composition with a higher proportion of organic carbon content in the total carbon (TC) content of POME is said to be highly biodegradable. TOC of POME in the study area was significantly varied ($p<0.05$) across all the independent variables outlined to be influencing the composition of POME (Table 4 and 5). In the wet season, TOC of POME was 224.724±14.189 mg L^{-1} compared to a total carbon content of 3,303.010±59.112 mg L^{-1}. In the dry season, TOC of POME was 664.569± 171.439 mg L^{-1} compared to its total carbon content of 11,937.113± 2581.601 (Table 5). The proportion of TOC is quite low compared to the inorganic carbon content in the total carbon content of POME. Consequently, this is aligned to the low biodegradability of the wastewater. TOC of 24,100 mg L^{-1} from POME samples had been reported in Malaysia and the high TOC was positively related to its high BI and organic nitrogen, thus making the wastewater highly biodegradable [28]. Therefore, for POME generated at Ohaji/Egbema and its associated low BI, organic nitrogen content and TOC, chemical treatment of the wastewater is required before biological treatment.

The toxicity of POME associated with heavy metal is another very important issue of concern in wastewater treatment. Presence of these heavy metals and inorganic components in POME could be associated to leaching of the metallic components from the milling machines during the milling process. Some of these metallic ions like Mn, Cu and Cr were found to increase significantly with increasing acidity of the wastewater across seasons. That is, they were significantly ($p<0.01$) negatively correlated with the pH of POME as more of the metal tended to be leached into the wastewater with increasing acidity, that is decreasing pH (SM 2). Therefore, besides the challenges associated to acidity and undermining of the microbial consortia, acidity increases leaching of some heavy metals and inorganic substances which could weaken the functioning of methane-forming bacteria.

Examining the seasonal variation of some heavy metals analysed in the study that influence toxicity revealed that some of these heavy metals in POME were not within acceptable level for influent wastewater into a biodigester (SM 3). With reference to [23], the level of concentration of Fe and Cr in both seasons, and Cu in the wet season were within acceptable range of influent wastewater into a bio-digester. On the contrary, the level of concentration of copper in the dry season and the concentration of cadmium in both seasons was found to be toxic to the microbial conortia for wastewater treatment for biogas generation. These values exceeded the minimum acceptable influent composition of wastewater into the bio-digester. Ni and Ca concentrations in the POME generated at Ohaji/Egbema were within the acceptable level of efficient functioning of the biodigesters. [38] maintained that the limiting concentration for biomethanation to occur in anaerobic digester is 100-1,000 mg L^{-1} for Ni and 8,000 mg L^{-1} for Ca.

Above this maximum acceptable concentration, the toxicant inhibits respiration of the microbial consortia and limits the ability of microbes to breakdown the organic matter [22]. When toxicity of the heavy metal increases, the rate of respiration of the microbes is undermined and threatens the efficiency of wastewater treatment. During the treatment process and where these heavy metals exceed the maximum acceptable level, the heavy metals in their soluble forms are absorbed on the surface of bacteria cells and exert toxicity by inactivating enzymatic systems. Where heavy metal toxicity occurs in wastewater, such as POME, hydroxides are used to precipitate them in the primary sludge and sustain the treatment process.

The organic content of POME generated in ADAPALM and palm oil mills in its catchment communities was quite low, hence its anaerobic digestion process will mean a very low organic loading rate. This undermines the efficiency of the digester, hence methane production. A successful treatment of wastewater with low organic loading rate (OLR) requires increasing the substrate concentration through addition of high amount of external organic compounds [4, 44]. However, a desired

OLR for maximum biogas production will depend on the nature of the organic substrate to be added and type of wastewater to be treated [44-45]. [46] maintained that appropriate proportion of co-digesting substrates improves on biogas yield, hence strengthening the plant efficiency. Thus, as the organic strength of the POME exceeded guideline values and the necessity to treat it, organic substrate of the wastes generated in the study area such as pig and poultry wastes could be studied and added to the POME in order to facilitate treatment and generate greater volume of bio-methane.

Following the availability of microbes in POME for its degradation [31, 47] and the necessity of pretreatment of the substrate composition to improve on digester performance and enhance methane potential [48], these microbes need a suitable substrate composition for efficient functioning. Therefore, with a view of achieving sustainability in biogas programs, it is important to consider and define appropriate approaches of these physicochemical compositions and characteristics of POME in the study area prior to ingestion into the biodigester.

Conclusion

The composition of POME generated at Ohaji/Egbema LGA of Imo State, Nigeria, varies across milling scales, types of FFBs and seasons. Despite the low organic content of the wastewater, which showed TOC of 224.724±14.189 in the wet season and 664.569±171.439 in the dry season, and their associated BI of 0.245±0.023 and 0.063±0.003 in wet and dry seasons respectively, some parameters are not within safety guidelines. The pH=11.728±0.467 and 4.10563±0.030, BOD=52.042±1.669 and 233.125±10.674; TSS= 14,421.748±2431.870 and 974.344±29.764; TN= 347.918±7.371 and 468.92500±31.315; TP= 127.890± 1.478 and 26.476±6.339 for dry and wet seasons respectively, and COD= 3731.250±154.574 for dry season only were not within the acceptable discharge limits for wastewater disposal. These wastewater composition is altering the quality of the human environment, hence challenging the achievement of climate-smart agriculture and adding to our global environmental problems. In addition, the pH, Cd, Ni, Cu, K and organic content across seasons highlight specific concerns in the wastewater treatment. To curb this challenge, transforming POME to biomethane is required, while taking into cognisance the determinants of POME composition to inform efficient treatment in a bio-digester. The available data on POME composition informs the prospect of exploiting POME-to-energy in the area, with recommendation of co-digestion of the substrate with piggery and poultry wastes. This will enhance clean domestic energy access and strengthening achievement of sustainable development goals.

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