Journal of ENVIRONMENTAL Treatment Techniques

J. Environ. Treat. Tech.
ISSN: 2309-1185

Journal weblink: http://www.jett.dormaj.com

Estimation of Potential Biohydrogen from Palm Oil Mills' Effluent in Nigeria using Different Microorganisms under Light Independent Fermentation

Elijah Ige Ohimain and Sylvester Chibueze Izah*

Bioenergy and Environmental Biotechnology Research Unit, Department of Biological Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria.

Received: 15/12/2014 Accepted: 11/01/2015 Published: 30/06/2015

Abstract

Nigeria is the fifth largest oil palm producing nation with 930,000 metric tonnes in 2014 economic year. During oil palm processing, large volume of water are used and a significant amount end up as palm oil mill effluents (POME). POME has high pollution index due to high biological oxygen demand (BOD) and chemical oxygen demand (COD). This study estimates the potential biohydrogen yield from POME generated in Nigeria using different microorganisms (*Thermoanaerobacterium*, *Clostridium butyricum*, POME mixed culture) at nearly same condition of temperature (60ºC) and pH (5.5) under light independent fermentation. Projections of the production growth rate were made using secondary data. Results show that at anaerobic condition biohydrogen yield were in the order *Thermoanaerobacterium*> *Clostridium butyricum*> POME mixed culture. The potential hydrogen yield using *Thermoanaerobacterium* could have been 57 billion L in 2004, which could have reached 67 billion L in 2013. It was projected that hydrogen content could reach 101, 84, and 75 billion L at high, low and current growth rate scenario respectively by 2029. After considering the POME conversion potential challenges, about 45 – 55% of the theoretical yield estimated could be produced. Biohydrogen can be used as combined heat and power due to their high calorific value.

Keywords: Biohydrogen, Light Independent Fermentation, POME, Renewable Energy

1 Introduction

Toward the end of 19th century, there were intense search of high and efficient energy resources. This was attributed to the depletion and increase in prices of widely utilized fossil fuel. According to Foo and Hameed [1], exponential increase in population, civilization, affluent lifestyles, industrialization, expansion and modernization triggered the search for renewable energy resources. Additionally, the non-renewable energy resources has been contributing to climatic and environmental challenges especially the emission of carbon dioxide into the atmosphere. Carbon dioxide contributes about 50% of the greenhouse effects worldwide. Climate change has been combated with intensive policy and increased research into biomass energy [2]. However, several nations has begun to seek for efficient energy resources including Nigeria.

Nigeria is blessed with several biomass with potential energy sources as well as favorable climatic and soil conditions such as pH, relative humidity, temperature. Several plant resources are able to thrive in Nigeria. Most of these plant resources are potential sources of food. Some of the widely utilized plant resources in Nigeria are cassava and oil palm. However, Nigeria is the fifth largest oil palm producing country, accounting for 930,000 metric tonnes of palm oil from the fresh fruit bunch (FFB).

During oil palm processing, large wastes are generated in three phases including solid, liquid and gaseous emissions. Ohimain et al. [3] has estimated that smallholders palm oil processors account for about 80% of the Nigeria palm industry generating large solid waste streams during oil extraction including empty fruit bunch (23.7 – 32.4%), palm kernel shell (6.8 – 18.8%), chaff (0.8 – 2.4%) and palm press fiber (19.1 – 28.1%). Similarly, palm oil mill effluents (POME) is generated in voluminous quantity in palm oil mills [4]. According to Ahmad et al [5], Wu et al. [6], about 5.0 – 7.5 tonnes of water is used for the processing of 1 tonne of fresh fruit bunch. Of these, Ohimain and Izah [7], Singh et al. [8], Okwute and Isu [9], Chavalparit et al. [10] stated that 50 – 79% of the water end up as POME. The solid wastes are basically used as energy resources (i.e boilers fuel in smallholders and semi-mechanized palm oil mills).

The wastes (i.e. solid and liquid) have remained under-utilized in Nigeria despite their huge potentials in the energy sector. Energy carriers that be produced from POME include bioethanol [11, 12], biogas [13],

Corresponding author: Sylvester Chibueze Izah, Bioenergy and Environmental Biotechnology Research Unit, Department of Biological Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria, E-mail:sylvesterizah@yahoo.com; Tel: +234 703 0192 466.

biohydrogen [14 – 17]. Biohydrogen have recently been regarded as energy for the future, which is capable of replacing fossil fuel [18 – 21]. Hence, capturing energy from wastes water via treatment has gained importance globally [22]. Hydrogen produced from fossil fuels causes the coproduction of CO_2, which is assumed to be the main cause of greenhouse effect [23]. According to Oh et al. [24], hydrogen is the most abundant element on earth, and has been identified as one of the potential feasible and long term renewable resources capable of replacing the dwindling fuel. Like other biofuels, biohydrogen produced via fermentation is considered environmental friendly fuel when compared to hydrogen produced via thermochemical and electrochemical processes [25]. Also in the environmental sustainability perspectives, biohydrogen could be used to advert the attendant environmental pollution associated with conventional fuel. This is because biohydrogen burns in combustion engines to emit water [19] as against oxides of carbon emitted by fossil fuels. Biohydrogen can be produced from cellulose rich biomass [26] such as hemicellulose and lignocellulose [16, 18]. Lignocellulosic materials are products of photosynthesis, which form the structural constituent of plant cell wall [18]. Starch and cellulosic feedstock contain complex organic polymers which hydrolyze into glucose and then ferments to alcohols and low-molecular-weight organic acids, which undergo fermentation to form acetic acid and hydrogen by the activities of hydrogen-producing acetogenic bacteria [27, 28]. Pan et al. [21] reported that organic wastes are more appropriate and cost effective than pure substrates, such as sugars and starch for biohydrogen production. In Nigeria, POME is one of the largest organic wastes generated and they have remained underutilized.

Biohydrogen yield from POME is high compared to other agricultural residues such as swine manure, dairy manures, food wastes, rice slurry, apple and potato waste water [26]. Biohydrogen from POME can be harnessed using diverse technologies such as fermentation. Vijayaraghavan and Ahmad [15] have reported that biohydrogen can be harnessed using anaerobic treatment. Other biohydrogen production technologies include electrolysis of water, steam reformation of methane, thermocatalytic reformation [1, 14]. Biologically, biohydrogen have been produced by photosynthetic and chemosynthetic bacteria [1, 14]. Biohydrogen is produced via photo (light dependent) and dark (light independent) fermentation. The degradation of complex polymers of organic matter is critical during biohydrogen production. These processes is facilitated by solubilization and system performance. Ueno et al. [29] reported that phase-separation in anaerobic digestion are acidogenesis (conversion of monomers to intermediaries such as volatile fatty acids) and methanogenesis (conversion of volatile fatty acids to methane). During anaerobic digestion, excess electrons are recovered as hydrogen gas, through fermentation, hence solubilization and hydrogen production could be generated in a single bioreactor [29]. According to Hallenbeck and Gosh [30], photo fermenter have some draw back such as low light conversion efficiency and high energy demand. Similarly, Lam and Lee [26] have reported that dark fermenter is favorable due to non-sunlight requirement and utilization of acidogenic microorganisms such as *Bacillus, Enterobacter, Closridium* species. Light independent fermentor is more favorable because limited light penetration slows the conversion efficiency of light dependent microorganisms [26]. Like biogas, biohydrogen production via microbial processes requires some steps which are influenced by several factors such as microbial characteristics, pH, glucose and iron sulphate concentration, hydraulic retention time, substrate loading rate and has been comprehensively documented by Mohan [22], Waligórska [31], Chong et al. [32]. Guo et al. [19], Lam and Lee [26] have reported that pH, hydrogen partial pressure and temperature are the most vital factor that could affect biohydrogen production.

During biohydrogen production by fermentation, the microbial flora play a vital role. Several studies have been carried out with regard to the different microbial effectiveness for hydrogen production including POME mixed culture [4, 14, 15], *Clostridium butyricum* EB6 [16, 17], *Thermoanaerobacterium* species [33, 34], *Rhodopseudomonas palustris* [20]. POME contain a diverse group of microorganisms including acid formers, hydrocarbon degraders and methanogens [35].

Biohydrogen can be diversely applied in different sectors of the economy including power generation and transportation fuel. Therefore, this study estimates the potential biohydrogen from POME in Nigeria. This paper could be useful to the government, energy policy makers and biofuel experts searching for sustainable feedstock for biohydrogen production.

2 Methodology

Secondary data obtained from literature review were used for this study. Data on biohydrogen production from POME in Nigeria is deficient in literature. Therefore, information obtained from non-Nigerian environment on biohydrogen were used to estimate the Nigerian scenario. The data obtained were used to estimate the potential biohydrogen from highly under-utilized POME generated in Nigeria. The study period range from 2004 to 2013 and projections were made up to 2029 based on three categories i.e. high, low and current production status.

2.1 Estimation of quantity of POME generated for the period of study

Recent estimates on the quantity of POME produced for the past 10 economic years and projections made up to 2029 on three years interval and scenario is presented in Figure 1. A conversion factor of 1 tonne to 1000 liters were used assuming the density of the POME 1.

2.2 Estimation of total biohydrogen production

Biohydrogen is produced via different fermentation processes. It could be optimized to produce more at varying temperatures, type of fermentation, choice of microorganisms etc. Ismail et al. [4] has reported a biohydrogen yield of 1.72 with a composition of 48 - 51% at a temperature, pH and agitation of 55ºC, 5.5 and 200rpm respectively with a carbohydrate conversion efficiency of 58% using completely stirred tank reactor.

Vijayaraghavan and Ahmad [15] reported that the anaerobic microflora of POME produced a hydrogen yield of 102.6 ml from initial COD concentration of 59,300 mg/l in 7days. Singh et al. [36], studied biohydrogen production from POME using immobilized *Clostridium butyricum* EB6 and reported a yield of 5.35LH_2/L-POME. Atif et al. [14] studied hydrogen production from POME using its indigenous anaerobic microflora and reported a yield of 4.708 LH_2/L-POME at a temperature and pH of 60ºC and 5.5 respectively with a concentration of 66% in 38 hours using anaerobic digester at a maximum evolution time of 0.454 LH_2/L-POME-hour.

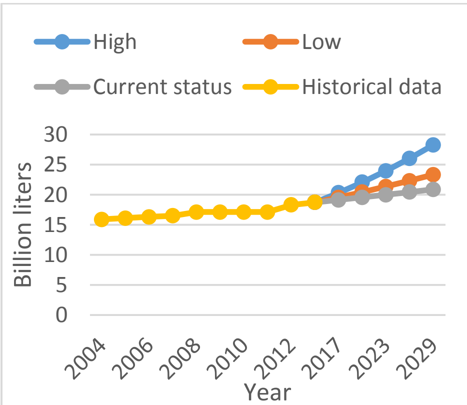

Figure 1: Estimated quantity of POME generated from Nigeria palm oil mills for the period (2004 – 2013 and projections up to 2029 [35]

The author also reported a yield of 2.4 L H_2/L-POME at evolution rate of 0.436 L H_2/L-POME in a reproducibility fed batch process. Jamil et al. [20] studied hydrogen production using phototrophic indigenous purple non-sulfur bacteria (*Rhodopseudomonas palustris* PBUM001) from POME with 100% (v/v) POME concentration, 10% (v/v) inoculum size, 4.0 klux light intensity, 250 rpm agitation time and at pH of 6 and reported maximum predicted (1.05 ml H_2/ml POME) and verification experiment (0.66 ml H_2/ml POME). O-Thong et al. [34] stated that POME sludge rich in *Thermoanaerobacterium* species under batch processing with conditions such as pH (5.5), temperature (60ºC) could produce 6.33 L H_2/L-POME. Chong et al. [17] studied biohydrogen production from POME using *Clostridium butyricum* EB6 isolated from the POME sludge and reported optimum hydrogen yield of 3.2 L H_2/L-POME at pH 5.5. O-Thong et al. [33] studied thermophilic fermentative hydrogen production from POME by *Thermoanaerobacterium*-rich sludge in a simultaneous process and reported a hydrogen yield of 3.8 – 6.7 L H_2/L-POME (mean 5.63 L H_2/L-POME) at a temperature of 60ºC and pH of 5.5. The authors reported that maximum yield of 6.7 L H_2/L-POME was obtained with the addition of iron, nitrogen and phosphate to the sludge prior to fermentation. In this study, the microorganisms that yielded hydrogen of more than 3.0 L H_2/L-POME were used for the computation. Based on this, it was observed that dark fermetation processes produces a superior yield when compared to photo-fermentation. The calculation were carried out considering different microorganisms used for hydrogen production from POME. The average hydrogen yield with the same microorganisms were computed together. Hence, a value of 4.3 L H_2/L-POME (*Clostridium butyricum*), 6.0 L H_2/L-POME (*Thermoanaerobacterium*) and 3.6 L H_2/L-POME (mixed culture) at optimum temperature of 60ºC and pH 5.5 which majority of authors have reported to be optimum for biohydrogen production from POME.

2.3 Estimation of hydrogen yield from biohydrogen gas

Like biogas, biohydrogen gas is a mixture of hydrogen and carbon dioxide. The concentration or proportion of these gases varies. For instance, hydrogen contents that has been reported from POME are 50.1 – 59.9% (mean 55.1%) [36], 58 – 60% (mean 59%) [33], 66% [14] and 57% [15]. The range of the reported hydrogen content is 55.1% to 66%. Yussof et al. [37] reported an optimum hydrogen content of 60% from biohydrogen gas. Hence, in this study the hydrogen content of 60% was used for the computation.

3 Results and Discussion

Table 1 presents the quantity of potential biohydrogen gas that would have been produced in Nigeria, if POME produced from palm oil mills for the period of study i.e. from 2004 to 2013 were collected and treated using various dark fermenter bioreactors at conditions such as pH and temperature of 5.5 and 60ºC respectively using different microorganisms. Also projections made in differentb production scenarios are presented in Table 2.

The result indicated that Nigeria could have produced 95 billion L in 2004 of biohydrogen gas which was estimated to have reached 112 billion L in 2013, if *Thermoanaerobacterium* in a dark fermentation were used. At high, low and current status projection scenario, 169, 140 and 125 billion L of biohydrogen respectively could be produced by 2029. Using *Clostridium butyricum* treatment system, Nigeria would have produced 68 billion L of biohydrogen gas in 2004 which could have reached 80 billion L in 2013, and it was projected to reach 121, 100 and 90 billion L at high, low and current status projection scenario respectively before 2030. The use of POME mixed culture showed that 57 billion L in 2004 of biohydrogen gas which could have reached 67 million L in 2013. High, low and current status projection scenario indicated that Nigeria could produce 101, 84 and 75 billion L of biohydrogen gas respectively up to 2030.

The production of biohydrogen from POME generates hydrogen and carbon dioxide. The hydrogen content about 50 - 66% by composition depending on the microorganism and other environmental conditions of the dark phase fermenter. Figure 2 presents the potential hydrogen yield from POME in Nigeria under different microorganisms in a dark fermentation in historical study period. Similarly, Table 3 shows the potential hydrogen yield in projected scenarios.

Table 1: POME to Biohydrogen generation palm oil mills in Nigeria for the period of 10 years

Year	*Thermoanaerobacterium*	*Clostridium butyricum*	POME Mixed culture
2013	112,471,875,000	80,604,843,750	67,483,125,000
2012	110,053,125,000	78,871,406,250	66,031,875,000
2011	102,796,875,000	73,671,093,750	61,678,125,000
2010	102,796,875,000	73,671,093,750	61,678,125,000
2009	102,796,875,000	73,671,093,750	61,678,125,000
2008	102,796,875,000	73,671,093,750	61,678,125,000
2007	99,168,750,000	71,070,937,500	59,501,250,000
2006	97,959,375,000	70,204,218,750	58,775,625,000
2005	96,750,000,000	69,337,500,000	58,050,000,000
2004	95,540,625,000	68,470,781,250	57,324,375,000

Table 2: Estimated potential of biohydrogen that could be produced from POME in Nigeria at projected scenarios (2017 – 2029).

Year	*Thermoanaerobacterium*	*Clostridium butyricum*	POME mixed culture
2017	[122,144,456,300]	[87,536,860,330]	[73,286,673,770]
	{117,521,865,800}	{84,224,003,810}	{70,513,119,470}
	(114,946,256,300)	(82,378,150,330)	(68,967,753,770)
2020	[132,648,879,500]	[95,065,030,290]	[79,589,327,690]
	{122,798,593,800}	{88,005,658,890}	{73,679,156,280}
	(117,475,073,900)	(84,190,469,610)	(70,485,044,330)
2023	[144,056,684,100]	[103,240,623,600]	[86,434,010,460]
	{128,330,250,700}	{91,970,013,020}	{76,998,150,430}
	(120,059,525,500)	(86,042,659,960)	(72,035,715,310)
2026	[156,445,558,900]	[112,119,317,200]	[93,867,335,320]
	{134,073,470,900}	{96,085,987,510}	{80,444,082,560}
	(122,700,835,000)	(87,935,598,430)	(73,620,501,010)
2029	[169,899,877,000]	[121,761,578,500]	[101,939,926,200]
	{140,093,365,100}	{100,400,248,400}	{84,056,021,890}
	(125,820,252,700)	(90,171,181,590)	(75,492,152,030)

[ ] = High; { } = Low; ( ) = Current status production rates projections.

The quantity of hydrogen that could be produce depends on the volume of POME in the year of study. Hence, for the past 10 years, the potential hydrogen from POME that have remained untapped ranged from 57 billion L in 2004 to 67 billion L in 2013. Based on the projections made, hydrogen content could reach 101 billion L (high scenario), 84 billion L (low scenario) and 75 billion L (current status scenario) before 2030 using *Thermoanaerobacterium*. Similarly, if the POME were converted to hydrogen using *Clostridium butyricum*, a yield of 41 billion L (2004) to 48 billion L (2013) could have been produced. On projections, hydrogen yield of 73, 60 and 54 billion L at high, low and current growth rate scenarios respectively could be produced before 2030. POME mixed culture could have produced biohydrogen gas with hydrogen yield of 34 billion in 2004, which could reach 40 billion in 2013. Projections indicates that it could reach 61, 50 and 45 billion L at high, low and current growth rate scenarios respectively by 2029.

In advanced oil palm producing nations like Malaysia, the industry can generate biogas to the tonnes of 1.55 GJ [38]. In this study, it was found that dark fermentation is the most suitable microbial approach for biohydrogen production. *Thermoanaerobacterium* can produce superior yield of hydrogen when compared to *Clostridium butyricum* and POME mixed culture under nearly the same environmental conditions.

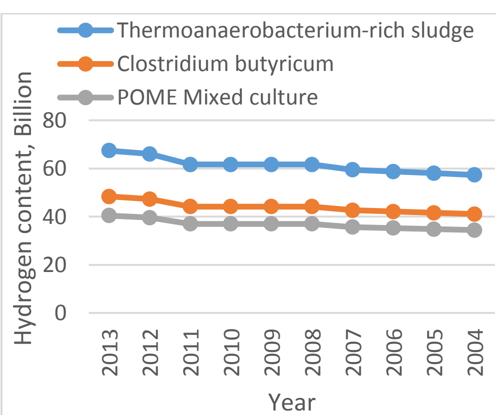

Figure 2: Potential hydrogen content from untapped POME in Nigeria for the period of 10 years

Table 3: Potential hydrogen yield from POME in Nigeria using various different microorganisms in anaerobic conditions in projected scenarios (2017 – 2029).

Year	Thermoanaerobacterium	Clostridium butyricum	POME mixed culture
2017	[73,286,673,770]	[52,522,116,200]	[43,972,004,260]
	{70,513,119,470}	{50,534,402,290}	{42,307,871,680}
	(68,967,753,770)	(49,426,890,200)	(41,380,652,260)
2020	[79,589,327,690]	[57,039,018,180]	[47,753,596,610]
	{73,679,156,280}	{52,803,395,330}	{44,207,493,770}
	(70,485,044,330)	(50,514,281,770)	(42,291,026,600)
2023	[86,434,010,460]	[61,944,374,160]	[51,860,406,280]
	{76,998,150,430}	{55,182,007,810}	{46,198,890,260}
	(72,035,715,310)	(51,625,595,970)	(43,221,429,190)
2026	[93,867,335,320]	[67,271,590,310]	[56,320,401,190]
	{80,444,082,560}	{57,651,592,500}	{48,266,449,540}
	(73,620,501,010)	(52,761,359,060)	(44,172,300,610)
2029	[101,939,926,200]	[73,056,947,120]	[61,163,955,730]
	{84,056,019,080}	{60,240,149,020}	{50,433,613,140}
	(75,492,151,630)	(54,102,708,950)	(45,295,291,220)

[ ] = High; { } = Low; ( ) = Current status production rates projections.

Biohydrogen can be produced using diverse anaerobic bioreactors and it is preceded by three major steps including hydrolysis, acidogensis and methanogensis. Hydrolysis break down the complex polymers of POME to their respective monomers; acidogenic microbes degrades the monomers to volatile fatty acids to produce hydrogen and carbon dioxide [26, 35]. Ohimain et al. [39, 40], Ugoji [41] have reported the variety of microbes that is found in POME. The POME microbes consists of hydrolytic, acidogenic, acetogenic and methanogenic metabolizers [13].

The physico-chemical constituents of POME have been reported in smallholder mills [42], semi-mechanized [39]. POME is rich in several nutrients, microbes with high pollution index. However, during biohydrogen production from POME, the complex constituents such as biological oxygen demand (BOD), chemical oxygen demand (COD) that determine the pollution index of POME is converted to less toxic or even harmless products, thereby preventing the attendant environmental impacts associated with POME discharge into the environment. Vijayaraghavan and Ahmad [15] reported that POME with initial COD concentration of 10,000 mg/l at a pH of 5 have 67% COD removal efficiency. Ismail et al. [4] studied hydrogen production from POME with carbohydrate constituent of 23%, have a conversion efficiency of 58%.

Biohydrogen can be utilized in several sectors due to its diverse uses. This is made possible due to its high calorific values. Pan et al. [21], Koutrouli et al. [25] have reported that hydrogen has energy content of 122 MJ/kg. Guo et al. [19], Das [43] reported a higher value of 142 MJ/kg as energy content of hydrogen. Hydrogen has the highest heating capacity as compared to other fuels [43]. The composition of energy value of hydrogen and other fuels such as gasoline, kerosene, methane, natural gas, coal, wood etc is presented in Figure 3.

Nigeria's total area is approximately 1 million square kilometer. Of these, agricultural land occupies 71.9 million hectares ranking Nigeria as one of the top bio-fuel potential countries in the world [1, 44]. Of the arable land, oil palm is suitable for cultivation in 24 million ha [45]. Though, oil palm can scantly grow in other soil and climatic conditions especially in the Northern region.

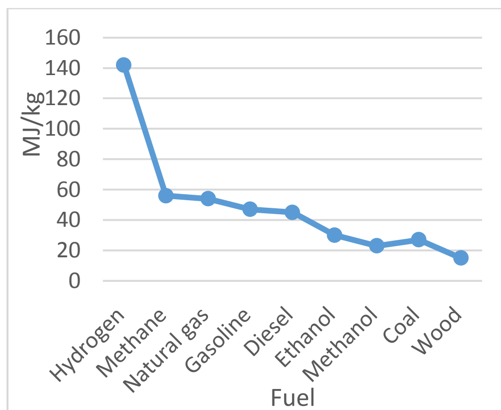

Figure 3: Modified from Lam and Lee [26]

Presently 3.0 million hectares are under cultivation. Ohimain and Izah [13], Business Day [45] estimated that about 1.4 – 1.8 million ha are found in the Niger Delta region. Basically, smallholder farmers covers an estimated land area of 97,000 – 360,000 ha [46]. Oil palm are found in Nigeria in both plantation and wild. The plantation ranged from 1- 5 ha (smallholder, which dominates the oil palm industry accounting for about 80%), 5 – 20 ha (semi-mechanized, covering about 16% of oil palm estates in Nigeria) and 20 and above (mechanized, accounting for about 4% of the Nigeria oil palm sector). On the projected scenarios, the potential biohydrogen production from POME could increase in future. Ugbah and Nwawe [47] stated that oil palm business could rise due to increased demand via different uses, which has motivated private sectors to invest in the expansion of previous ones and establishment of new oil palm estates.

Ohimain and Izah [48] have previously stated that palm oil mill is dominated by smallholders, hence, about 60 – 70% of the potential POME could be recovered. Also during conversion processes about 5 – 15% may be lost.

Therefore, in practice about 45 - 55% of biohydrogen could be generated unlike the estimated theoretical value.

The conversion of POME to biohydrogen in anaerobic dark fermenter which have proven to be a better technology than photo fermenters could be have microbial and technological challenges especially in developing countries like Nigeria. Some of the envisaged difficulties include operational conditions such as pH, temperature, nutrients and organic loading rate, microbes etc [35]. The microorganisms (*Thermoanaerobacterium* species and *Clostridium butyricum*) that could generate higher yield of biohydrogen may be challenged with identification and characterization. Nigeria as a nation may be reluctant to clinch biohydrogen production from POME due to high cost of production, hence, the economic feasibility of biohydrogen may be uncertain just as biogas [35]. Das [43] further stressed that use of efficient microbial strains which can utilize diverse carbonaceous organic matters found in the wastes is also a problem for commercializing biohydrogen.

4 Conclusion

Large volume of POME are generated in palm oil mills. In Nigeria, POME are discharged into the environment without treatment, thereby causing attendant environmental impacts. This study assessed the potential yield of biohydrogen that could be produced in Nigeria under dark fermentation using diverse microbes found in POME. The study found that *Thermoanaerobacterium* could produce superior hydrogen gas yield when compared with yield from *Clostridium butyricum* and POME mixed culture under nearly the same conditions such as pH and temperature. Like biogas, biohydrogen from POME can be used for heat and as transportation fuel due to its high energy content. The capture of biohydrogen from POME could reduce the environmental effects associated with POME discharge, while increasing the diversity of Nigerian energy mix.

References

1- Foo KY & Hameed BH (2010). Insight into the applications of palm oil mill effluent: A renewable utilization of the industrial agricultural waste. *Renewable and Sustainable Energy Reviews*, 14: 1445 – 1452.

2- Agboola OP, Agboola OM & Egelioglu F (2011). Bio-ethanol derivation from energy crop in Nigeria: a path to food scarcity or bio-fuel advancement. Proceedings of the World Congress on Engineering, July 6 - 8, 2011, London, U.K.

3- Ohimain EI, Izah SC & Obieze FAU (2013). Material-mass balance of smallholder oil palm processing in the Niger Delta, Nigeria. *Advance Journal of Food Science and Technology*, **5**(3): 289-294.

4- Ismali I, Hassan MA, Rahman NAA & Soon CS (2010). Thermophilic biohydrogen production from palm oil mill effluent (POME) using suspended mixed culture. *Biomass and Bioenergy*, 34: 42 – 47.

5- Ahmad AL, Ismail S & Bhatia S (2003). Water recycling from palm oil mill effluent (POME) using membrane technology. *Desalination*, 157: 87-95.

6- Wu TY, Mohammad AW, Jahim J, Anuar N (2009). A holistic approach to managing palm oil mill effluent (POME). Biotechnological advances in the sustainable reuse of POME. *Biotechnology Advances*, 27(1): 40-52.

7- Ohimain EI & Izah SC (2013). Water minimization and optimization by small-scale palm oil mill in Niger Delta, Nigeria. *Journal of Water Research*, 135**:** 190 – 198.

8- Singh RP, Ibrahim MH, Norizan E and Iliyana MS (2010). Composting of waste from palm oil mill: a sustainable waste management practice. *Reviews in Environmental Science and Biotechnology*, 9: 331-344.

9- Okwute LO & Isu NR (2007). The environmental impacts of palm oil mill effluent (POME) on some physico-chemical parameters and total aerobic bioload of soil at a dump site in Anyigba, Kogi State, Nigeria. *African Journal of Agricultural Research*, **2**(12): 656 – 662.

10- Chavalparit O, Rulkens WH, Mol APJ & Khaodhair S (2006). Options for environmental sustainability of the crude palm oil industry in Thailand through enhancement of industrial ecosystem, *Environmental, Development and Sustainability*, 8: 271-287.

11- Wakil SM, Fasiku, SA, Adelabu AB & Onilude AA (2013). Production of bioethanol from palm oil mill effluent using starter cultures. *New York Science Journal*, 6(3):77-85.

12- Wakil SM, Fasiku, SA, Adelabu AB & Onilude AA (2013). Production of bioethanol from spontaneous fermentation of palm oil mill effluent (POME). *Researcher*, 5 (2): 28-35.

13-Ohimain EI & Izah SC (2014). Potential of Biogas Production from Palm Oil Mills' Effluent in Nigeria. *Sky Journal of Soil Sciences and Environmental Management*, **3**(5): 50 – 58.

14- Atif AAY, Fakhru'l-Razi A, Ngan MA, Morimoto M, Iyuke SE & Veziroglu NT (2005). Fed batch production of hydrogen from palm oil mill effluent using anaerobic microflora. *International Journal of Hydrogen Energy*, 30:1393–1397.

15- Vijayaraghavan K & Ahmad D (2006). Biohydrogen generation from palm oil mill effluent using anaerobic contact filter. *International Journal of Hydrogen Energy*, 31:1284–91.

16- Chong ML, Abdul Rahman NA, Rahim RA, Aziz SA, Shirai Y, & Hassan MA (2009). Optimization of biohydrogen production by Clostridium butyricum EB6 from palm oil mill effluent using response surface methodology. *International Journal of Hydrogen Energy*, 34:7475–7482.

17-Chong ML, Rahim RA, Shirai Y & Hassan MA (2009). Biohydrogen production by *Clostridium butyricum* EB6 from palm oil mill effluent. *International Journal of Hydrogen Energy*, 34:764–771.

18- Chong M-L, Sabaratnam V, Shirai Y & Hassan ML (2009). Biohydrogen production from biomass and industrial wastes by dark fermentation. *International Journal of Hydrogen Energy*, 34: 3277 – 3287.

19- Guo XM, Trably E, Latrille E, Carrère H & Steyer JP (2010). Hydrogen production from agricultural waste by dark fermentation: a review. *International Journal of Hydrogen Energy*, 35:10660–10673.

20- Jamil Z, Annuar MSM, Ibrahim S & Vikineswary S (2009). Optimization of phototrophic hydrogen production by *Rhodopseudomonas palustris* PBUM001 via statistical experimental design. *International Journal of Hydrogen Energy,* 34:7502–7512.

21- Pan J, Zhang R, El-Mashad HM, Sun H & Ying Y (2008). Effect of food to microorganism ratio on biohydrogen production from food waste via anaerobic fermentation. *International Journal of Hydrogen Energy,* 33:6968–6975.

22- Mohan SV (2008). Fermentative hydrogen production with simultaneous wastewater treatment: influence of pretreatment and system operating conditions. *Journal of Scientific and Industrial Research,* 67: 950 – 961.

23- Balat H & Kırtay E (2010). Hydrogen from biomass e Present scenario and future prospects. *International Journal of Hydrogen Energy,* 35: 7416 – 7426.

24- Oh TH, Pang SY & Chua SC (2010). Energy policy and alternative energy in Malaysia: issues and challenges for sustainable growth. *Renewable Sustainable Energy Reviews,* 14:1241–1252.

25- Koutrouli EC, Kalfas H, Gavala HN, Skiadas IV, Stamatelatou K & Lyberatos G (2009). Hydrogen and methane production through two-stage mesophilic anaerobic digestion of olive pulp. *Bioresource Technology,* 100:3718–3723.

26- Lam MK & Lee KT (2011). Renewable and sustainable bioenergies production from palm oil mill effluent (POME): Win–win strategies toward better environmental protection. *Biotechnology Advances,* 29: 124–141.

27- Su H, Cheng J, Zhou J, Song W & Cen K (2009). Combination of dark- and photo-fermentation to enhance hydrogen production and energy conversion efficiency. *International Journal of Hydrogen Energy,* 34:8846–8853.

28- Xie BF, Cheng J, Zhou JH, Song WL, Liu JZ & Cen KF (2008). Cogeneration of hydrogen and methane from glucose to improve energy conversion efficiency. *International Journal of Hydrogen Energy*, 33(19):5006–5011.

29- Ueno Y, Tatara M, Fukui H, Makiuchi T, Goto M & Sode K (2007). Production of hydrogen and methane from organic solid wastes by phase-separation of anaerobic process *Bioresource Technology,* 98:1861–1865.

30- Hallenbeck PC & Ghosh D (2009). Advances in fermentative biohydrogen production: the way forward? *Trends Biotechnology,* 7:287–297.

31- Waligórska M (2012). Fermentative hydrogen production - process design and bioreactors. *Chemical and Process Engineering*, 33 (4): 585-594.

32- Chong ML, Abdul Rahman N, Yee PL, Aziz SA, Rahim RA, Shirai Y & Hassan MA (2009). Effects of pH, glucose and iron sulfate concentration on the yield of biohydrogen by *Clostridium butyricum* EB6. *International Journal of Hydrogen Energy,* 34:8859–8865.

33- O-Thong S, Prasertsan P, Intrasungkha N, Dhamwichukorn S & Birkeland NK (2008). Optimization of simultaneous thermophilic fermentative hydrogen production and COD reduction from palm oil mill effluent by Thermoanaerobacterium-rich sludge. *International Journal of Hydrogen Energy,* 33:1221–1231.

34- O-Thong S, Prasertsan P, Intrasungkha N, Dhamwichukorn S & Birkeland NK (2007). Improvement of biohydrogen production and treatment efficiency on palm oil mill effluent with nutrient supplementation at thermophilic condition using an anaerobic sequencing batch reactor. *Enzyme and Microbial Technology,* 41:583–590.

35- Ohimain EI & Izah SC (2014). Potential contributions of palm oil mill effluents to greenhouse gas emissions in Nigeria. *British Journal of Applied Science and Technology,* 4**(**33): 4705 – 4720.

36- Singh, L, Wahid ZA, Siddiqui MF & Ahmad A (2013). Biohydrogen production from palm oil mill effluent using immobilized Clostridium butyricum EB6 in polyethylene glycol. *Process Biochemistry,* 48: 294 – 298.

37- Yusoff MZM, Hassan MA, Abd-Aziz S and Rahman NAA (2009). Start-Up of biohydrogen production from palm oil mill effluent under non-sterile condition in 50 L continuous stirred tank reactor. *International Journal of Agricultural Research,* 4:163–168.

38- Yusoff, S. (2006). Renewable energy from palm oil innovation on effective utilization of waste. *Journal of Cleaner Production*, 14:87-95.

39- Ohimain EI, Izah SC & Jenakumo N (2013). Physicochemical and microbial screening of palm oil mill effluents for amylase production. *Greener Journal of Biological Sciences,* **3**(8): 314 – 325.

40- Ohimain EI, Daokoru-Olukole C, Izah SC, Eke RA & Okonkwo AC (2012). Microbiology of palm oil mill effluents. *Journal of Microbiology and Biotechnology Research,* 2(6):852 – 857.

41- Ugoji EO (1997). Anaerobic digestion of palm oil mill effluent and its utilization as fertilizer for environmental protection. *Renewable Energy*, 10(2-3): 291- 294.

42- Ohimain EI, Seiyaboh EI, Izah SC, Oghenegueke VE & Perewarebo TG. (2012). Some selected physico-chemical and heavy metal properties of palm oil mill effluents. *Greener Journal of Physical Sciences,* 2(4): 131 - 137.

43- Das D (2009). Advances in biohydrogen production processes: an approach towards commercialization. *International Journal of Hydrogen Energy,* 34:7349–7357.

44- Ohimain EI (2010). Emerging bio-ethanol projects in Nigeria: Their opportunities and challenges. *Energy Policy***,** 38: 7161-7168.

45- Business day (2013). Nigerian Oil Palm Industry 2013. http://businessdayonline.com/2013/08/reactivating-nigerias-oil-palm-industry-2/. Accessed February 7th, 2014.

46- Foundation for Partnership Initiatives in the Niger Delta (PIND) (2011) A report on Palm Oil Value Chain Analysis in the Niger Delta.

47- Ugbah, M.M. & Nwawe, C.N. (2008). Trends in oil palm production in Nigeria. *Journal of Food, Agriculture and Environment,* 6(1): 119-122.

48- Ohimain EI & Izah SC (2014). Estimation of potential electrical energy and currency equivalent from un-tapped palm oil mill effluents in Nigeria. *International Journal of Farming and Allied Science*, 3 (8): 855-862.