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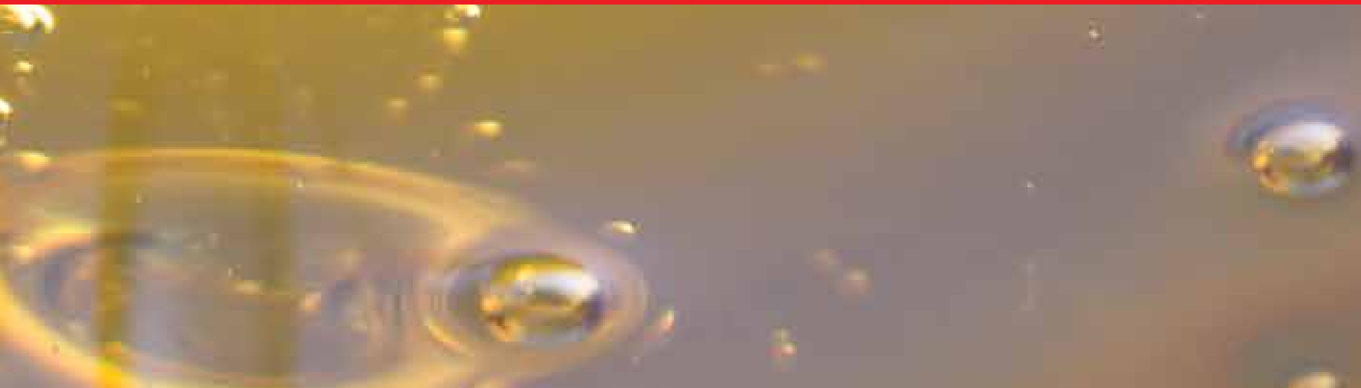
Palm Oil

Edited by Viduranga Waisundara



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Meet the editor

Dr. Viduranga Waisundara obtained her PhD degree in Food Science and Technology from the Department of Chemistry, National University of Singapore, in 2010. She was a lecturer at Temasek Polytechnic, Singapore, from July 2009 to March 2013. Following this, she relocated to her motherland of Sri Lanka and spearheaded the Functional Food Product Development Project at the National Institute of Fundamental Studies from April 2013 to October 2016. She is currently a senior lecturer on a temporary basis at the Department of Food Technology, Faculty of Technology, Rajarata University of Sri Lanka. She is a prolific writer with many research publications and articles in newspapers and magazines. She is also the current Global Harmonization Initiative (GHI) Ambassador to Sri Lanka.

Contents

Preface

Palm oil production is one of the most important industries in the world, where countries such as Malaysia, Indonesia, and Nigeria have invested heavily in its plantation and production. Indonesia is the world's largest producer of palm oil, contributing to approximately 44% of the global supply in the years 2006–2009, which is followed by Malaysia with 43%. When taking palm oil production as a whole, approximately 10% goes to oil palm produce, while the remaining 90% are considered as waste biomass. With these outcomes, there are several applications of the palm oil industry, which have led to commercialized by-products.

This book primarily focuses on four aspects: (1) Introduction (2) impact of the palm oil industry on the environment, (3) applications of palm oil and its industrial wastes, and (4) dietary applications of palm oil. Many food products and other types of resources are derived from palm oil, making it one of the most economically important agricultural crops. On the other hand, a declining supply of raw materials from natural resources has motivated scientists worldwide to find alternatives to produce new materials from sustainable resources such as palm oil. It is with these aspects in mind that this book project was launched, and contributions were gathered from renowned experts who have rendered their thoughts and views in putting the publication together.

I would like to extend my gratitude to the authors who have generously supported this book project by submitting their chapters; this publication would not have been a success without their hard work. Also, my heartfelt appreciation is extended to the InTech Publishing team with whom I have worked with for many book projects; this is my fourth publication with them. It has been a pleasure and heartening experience to see their growth as a leading open-access publisher. Last but not least, my appreciation goes to Mr. Julian Virag, the Publishing Process Manager assigned to this book, who has rendered his utmost support in putting the material together.

In conclusion, it is hoped that this book will be of value to all those who are interested and involved in the palm oil industry. It is without a doubt that the significance of this book and its contents will increase with the rising importance of the commercial value of palm oil and its by-products themselves.

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Section 1

Introduction

Introductory Chapter: Multifaceted Perspectives of Palm Oil

Viduranga Yashasvi Waisundara

Additional information is available at the end of the chapter

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1. Introduction

Palm oil is extracted from the ripened mesocarp of the fruits of the oil palm tree *Elaeis guineensis*. The oil palm can produce two types of oil: (1) palm oil from the fibrous mesocarp (which has a brilliant, deep red-orange pulp) and (2) palm kernel oil (which resembles coconut oil) from the kernel [1–3]. Crude palm oil (CPO) can be processed into various downstream products; however, most of the phytonutrients are partially removed during the processing steps involved. The major processed product of CPO is deodorised palm oil which involves refining and bleaching. It is during this refining process that the carotenes which give CPO its characteristic red-orange colour become decomposed, resulting in refined, bleached, and deodorised palm oil, which has a slight yellow colour [1].

The five leading producers of palm oil around the world are Indonesia, Malaysia, Thailand, Colombia and Nigeria [4]. According to Mba et al. [4], the oil palm tree gives the highest yield of oil per unit area of cultivated land, at an estimated 58.431 million metric tons per year. It is estimated that 1 ha of oil palm plantation is able to produce up to 10 times more oil than other types of leading oilseed crops [4]. The refining process of CPO through chemical and physical refining is shown in the schematics as per **Figures 1** and **2**.

Bearing these in mind, this book primarily focuses on various aspects of the palm oil industry, principally its impact on the current consumer market as a crop of agricultural and industrial value and effects on the environment. The sections which follow in this introductory chapter give brief overviews on other aspects which may or may not be covered in the rest of the content chapters, so that the voids and gaps are ideally filled. It is of importance to see the food technological and health aspects of palm oil as well, and thus, this chapter covers a certain amount of content on the food value of this product too.

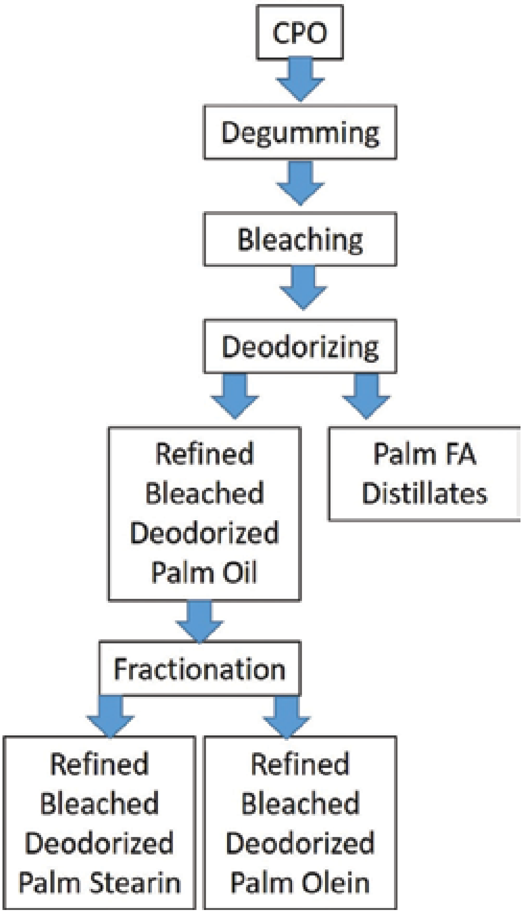

Figure 1. Refining process of CPO through physical processes.

2. Applications in the food industry

Palm oil has a very unique fatty acid (FA) and triacylglycerol (TAG) profile which makes it ideal for numerous food applications. It is the only vegetable oil presently available in the consumer market with an almost 1:1 composition of saturated and unsaturated FAs. CPO is primarily used in household and food retail outlets for cooking, frying and as a source of vitamins. Fractionation of CPO yields mainly palm olein as the liquid fraction and palm stearin as the solid fraction [4]. These fractions have distinct physico-chemical features. CPO, palm olein and palm stearin are important constituents of several food and industrial products such as shortenings and ice cream [4].

Palm oil is top prime among frying oils. Refined, bleached and deodorised palm oil is a versatile oil widely used in more than 150 countries worldwide [5]. In addition to its unique FA

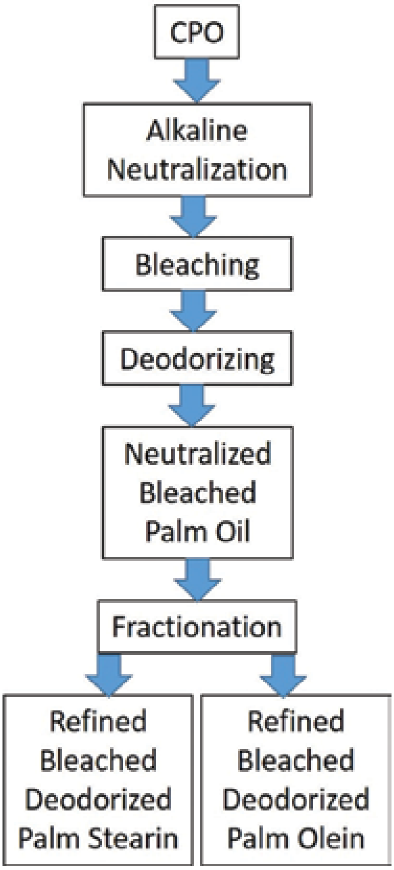

Figure 2. Refining processes of CPO through chemical processes.

composition, it has a high smoke point of about 230°C [4, 6]. The process of frying heats the food right through to the middle, cooking its interior and creating a 'crust' on the surface of the food plus a characteristic fried food flavour, which has resulted in the popularity of such food products among consumers in both household as well as fast-food applications [7]. The hot oil serves as a medium of heat and mass transfer, while some of the oil is absorbed by the product and moisture in the form of vapour is given off [4]. Thus, frying could be considered as a processing method which combines cooking and drying. Given the importance of frying, palm oil has become an essential component in many food preparations, resulting in a high placement of value in the modern consumer market.

3. Palm oil-based biodiesel

It is a well-known fact that there is a rapid depletion of crude oil reserves, increasing oil prices along with growing concerns about emission of greenhouse gases. This phenomenon has resulted in an increasing need for the adoption a global energy economy based on renewables. The usage of renewable energy technologies (RETs) are set to increase in future, directly influencing public opinion and the energy policies of governments around the world [8].

Biodiesel is an amber-yellow, liquid-based mono alkyl ester which is derived primarily from plant and animal oils [8]. The properties of biodiesel are nevertheless similar to petroleum-based diesel, although biodiesel is biodegradable, non-explosive and non-toxic which significantly reduces toxic emissions when burned [8–11]. Currently biodiesel is produced primarily from edible oils such as rapeseed oil, sunflower oil, soybean oil, tallow and palm oil [12, 13]. However, the fraction of palm oil which is being used for biodiesel production has increased from 3.2 to 8.3 million tonnes from 2009 to 2014, while Malaysia accounts for 40% of total global demand for strategically positioning the nation as a significant player in the global dynamics of biodiesel production [14]. CPO has the highest average oil yield of any oil-extracting crop, hence, its utilisation for biodiesel production offers many advantages over other crops used for the same purpose [15, 16].

4. Health benefits and safety of palm oil consumption

The current demand for functional foods is attracting a wide range of customers around the world. In response, supermarkets and producers are adapting their products and have identified the growth potential of products which bear a ‘free from’ claim in their packaging [17]. Despite various statements against the consumption of palm oil, up to now there is no substantiated indication that consumption of palm oil in a balanced diet is related to any specific health concern. In fact, it has been shown that replacing palm oil in food products or diets with fats higher in saturated FAs or with added sugar to compensate for the palatability and taste, will not provide a health benefit [17].

The safety of both CPO and refined, bleached and deodorised palm oil has been studied extensively in mutagenicity, nutritional and toxicological studies, with no adverse effects reported [1]. In general, fats are subjected to heat, thermal oxidation occurs and mutagens are formed; this is a common occurrence to all fats and oils, and heating can also lead to deterioration of the nutritional quality of the oil. Repeatedly, heated CPO and refined palm oil have been tested for mutagenicity to determine the safety of edibility, and no adverse effects have been identified to date [1].

Cardiovascular diseases (CVD) are responsible for 31% of global deaths [18]. This disease is a group of diseases of the heart and blood vessels including coronary heart disease (CHD), cerebrovascular disease, peripheral arterial disease, rheumatic heart disease, congenital heart disease, deep vein thrombosis and also pulmonary embolism [19]. The high proportion of saturated FAs, especially palmitic acid, in palm oil has been linked to the increased risk of atherosclerosis [20, 21]. However, findings of the systematic review by Ismail et al. [19] indicated that there is no evidence of a clear association between palm oil consumption and risk or mortality of CVD. Furthermore, Ismail et al. [19] observed that the effect seen between association of palm oil consumption and risk of coronary heart disease were not unique to only palm oil, especially since other food items were also included in the analysis, therefore rendering the association to be insignificant.

5. Impact of oil palm on forests and climate change

According to Shahputra and Zen [22], conversion of forests and peat lands for oil palm cultivation is considered by many to be the largest source of greenhouse gas emissions. According to Agus et al. [23], oil palm plantations are estimated to be responsible for substantial and increasing of total carbon emissions in Indonesia, Malaysia and Papua New Guinea. Recent statistics indicate that while some provinces with large expansions in oil palm plantations have had an increase in deforestation, others have not [24]. For where the instance of deforestation has not taken place, this indicates that plantation land previously used for food crops including rice, is being converted into oil palm plantations, since the previous crops may have become less attractive due to poor irrigation infrastructure and falling terms of trade.

Shahputra and Zen [22] recommend that given the environmental impacts of destroying intact forest and peat lands, a key development strategy which could be adopted to support rural communities is to implement sustainable land use planning, involving expanding oil palm into degraded land mostly covered by grass such as *Imperata cylindrica* which is commonly found in countries such as Indonesia. Additionally, Shahputra and Zen state that a large-scale oil palm expansion programme driven by estate companies needs to be accompanied by a well thought and effective smallholder development programme. Overall, if land issues could be resolved and local landowners included, oil palm acreage could be increased up to two-fold, without having to convert additional new forest land and peat lands, thus saving the environment from having to undergo negative effects.

6. Conclusions

The palm oil industry remains vital to many countries where it is grown in bulk, since its cultivation has led to socio-economic advancements and growth in gross domestic product. From the perspective of consumers, the palm oil is a good source of nutrients, functional bioactives, cooking media as well as a product to be consumed for health benefits. It has to be borne in mind though that there are environmental impacts in the mass cultivation of oil palm, and thus, the effects on farming practices resulting in deforestation and climate change need to be taken into account. Also, development of biofuel products and technologies based on the palm oil industry is heartening from the point of future sustainability. From this perspective, support should be rendered towards usage of different feedstocks and enhancing the efficiency of the production line to shift from petroleum to palm oil.

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Section 2

Impact of the Palm Oil Industry on the Environment

Chapter 2

Palm Oil Mill Effluent as an Environmental Pollutant

Hesam Kamyab, Shreeshivadasan Chelliapan,
Mohd Fadhil Md Din, Shahabaldin Rezania,
Tayebeh Khademi and Ashok Kumar

Additional information is available at the end of the chapter

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Abstract

In recent decades, Malaysia has been known as one of the world's leading producers and exporters of palm oil products. Every year, the number of palm oil mills increases rapidly, thus increasing the capacity of fresh fruit bunch waste or effluent discharge. Based on the data from the Malaysian Palm Oil Board in 2012, Malaysia produced 99.85 million tons of fresh fruit bunch (FFB) per year. However, about 5–5.7 tons of water was required in order to sterilize the palm fruit bunches and clarify the extracted oil to produce 1 ton of crude palm oil resulting in 50% of the water turning into palm oil mill effluent (POME). POME is one of the major environmental pollutants in Malaysia. The characteristics of POME and its behavior, if discharged directly, in water are described in this chapter. The suspended solid and nutrient content in POME could be able to support the growth of algae. This chapter aims to demonstrate that POME could be used as a main source for algae production, and this effluent is one of the main environmental problems in the tropical region especially in Malaysia.

Keywords: POME, Malaysia, wastewater, environmental pollution,industry

1. Introduction

These days, palm oil enterprise is developing quickly and turning into a noteworthy agriculture-based industry in Malaysia. The quantity of palm oil mills has elevated relatively, at beginning with 10 mills in 1960 moved to 410 operated mills in 2008. At least 44 million tons of POME was produced and are increasing every year in Malaysia [1], particularly because of the initiative of the government to promote palm oil industry. While the palm oil industry has been recognized strongly for its contribution toward economic growth and rapid development, it has also contributed to environmental pollution due to the production of large quantities of by-products during the process of oil extraction [2, 3]. Furthermore, it is necessary to properly address the POME treatment so as not to contribute to human health hazards and environmental pollution.

POME is the wastewater produced by processing oil palm and comprises of different suspended materials. POME is 100 times more polluted than the municipal sewage which has a high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The effluent also contains higher concentration of organic nitrogen, phosphorus and different supplement substance [4]. POME is a non-harmful waste; however, it will pose environmental issue because of vast oxygen draining capacity to oceanic framework because of natural and supplement substance. It is also known to be a good source of nutrients [5]. The waste products generated during palm oil processing consist of oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), palm pressed fibers (PPF) and palm kernel shells, less fibrous material such as palm kernel cake and liquid discharge POME [2]. The wastes are in the form of high organic matter concentration such as cellulosic wastes with a mixture of carbohydrates and oils. The discharge of untreated POME creates adverse impact to the environment [6].

Nowadays, biological process is the most common practice way for the treatment of POME based on anaerobic and aerobic ponding system [2]. While the emerging technologies for the treatment of POME, the notion of nurturing POME and its derivatives as valuable resources should not be dismissed. Furthermore, it is necessary to properly address the POME treatment so as not to contribute to human health hazards and environmental pollution. At the point when contrasted with those routine wastewater treatment processes which introduce activated sludge and living floc to degrade natural carbonaceous issue to CO_2, and microalgae may acclimatize natural toxins into cell constituents, for example, lipid and carbohydrate, therefore attaining pollutant decrease in a more ecological friendly way [7]. Actually, microalgae have turned into the consideration for both wastewater treatment and biomass production as early as 1950s [8]. Small scale and economically viable technologies that combine wastewater treatment and energy production can treat the industrial effluents and enhance the availability of the energy simultaneously [9]. The feasible way that is more attentions in the present time is the use of microalgae, which is known to have the potential to treat wastewater [10] such as removal of CO_2 and NOx [11] and high capacity of nutrient uptake [12]. The idea of using microalgae in wastewater treatment has been investigated since 1950s by Oswald and Gotaas [8]. There are several important aspects to be considered during the current study. POME is the major source of water pollutant in Malaysia [13]. For example, in a conventional palm oil mill, 600–700 kg of POME is generated for every 1000 kg of processed fresh fruit bunches (FFB) [14]. By utilizing the ingredients present in POME, this study will play a major role to solve the pollution problem resulting from the POME as it will pollute the environment if it is improperly discharged into the environment.

2. Palm oil mill effluent

In particular, POME is a basic expression referring to the effluent from the last phases of palm oil manufacture in the mill. It incorporates different fluids, dirt, leftover oil and suspended solids. POME in its untreated shape is a high quality waste, relying upon the operation of the procedure. POME is generated mainly from oil extraction, washing and cleaning processes in the mill, and these contain cellulosic material, fat, oil and grease, and so on [15]. POME also contains substantial quantities of solids; both suspended solids and total dissolved solids in the range of 18,000 and 40,500 mg/L, respectively.

Oil palm is the most productive oil producing plant in the world, with 1 ha of oil palm producing between 10 and 35 tons of fresh fruit bunch (FFB) per year [15]. During processing of oil palm, more than 70% by weight of the fresh fruit brunch was left over as waste [16]. Usually, the harvested part is the fruit whereby oil is obtained from the fleshy mesocarp of the fruit. Despite the importance of the edible oil and fats extracted from the palm fruits, the POME contains residual oil which affects the environment cannot be ignored. Treatment and disposal of oily wastewater such as POME is presently one of the serious environmental problems. Palm oil mill wastes have existed for years but their effects on environment are at present more noticeable [15]. The oily waste has to be removed to prevent problems which are considered as hazardous pollutants particularly in the aquatic environments because they are highly toxic to the aquatic organisms. Discharging the effluents or by-products on the lands or release to the river may lead to pollution and might deteriorate the surrounding environment. In order to conserve the environment, an efficient management system in the treatment of these by-products is needed [17]. Treatment of POME is essential to avoid environmental pollution [18].

POME wastes are the fiber free non-oil components obtained from the clarification zone of an oil mills. The significant contamination comes out of the fresh fruit brunch (FFB). In fact, every ton of FFB is composed of 230–250 kg of empty fruit bunches (EFB), 130–150 kg of fibers, 60–65 kg of shell and 55–60 kg of kernels and 160–200 kg of unrefined oil [19]. POME contains high amounts of oil and grease (4000 mg/L) and COD (50,000 mg/L). Although the effluent is nontoxic, it has a very high concentration of biochemical oxygen demand (BOD) (i.e., 25,000 mg/L) which becomes a serious threat to aquatic life when discharged in relatively large quantities into watercourses. The high amount of total solids (40,500 mg/L) contributes to the large amount of nutrients available in the wastewater, hence possible algae bloom.

Most palm oil mills in Malaysia have adopted the ponding system for the treatment of POME [20]. In general, there are four types of treatment systems adopted by the palm oil industry, which are as follows:

- **a.** Waste stabilization ponds,
- **b.** Activated sludge system,
- **c.** Closed anaerobic digester and
- **d.** Land application system.

The most proper secondary treatment for POME is natural assimilation with the blend of anaerobic and aerobic ponds. Right now, the management of POME has developed from treatment of waste for transfer to gainful use of assets. POME contains generous amounts of significant plant supplement that shift as indicated by the level of treatment to which it is subjected. The potential utilization of recovery of water and natural issues from POME has been applied for different applications [21]. Commercial trials and applications of these technologies are currently underway, especially conversion of the solid residual materials into saleable value-added products.

2.1. Malaysian palm oil industry

In 2011, Malaysia was the second biggest oil palm producer in the world, with an aggregate of 16.6 million tons, a sum lesser than 1% from the total world's supply behind Indonesia. Since the oil palm industry is tremendous, with 67% of agricultural land secured with oil palm tree, biomass from oil palm contributes the most. As of now, 85.5% of the biomass residues are originating from the oil palm industry. Palm oil has a very good potential in producing alternative energy due to its calorific content. With 50% efficiency, biomass from oil palm can generate 8 Mton of energy and can save RM 7.5 billion per year of crude oil [14, 19]. More than 85% of palm oil mills in Malaysia have adopted ponding system for treating POME [20], while the rest have opted for open digesting tank [22]. These methods are regarded as conventional POME treatment method, whereby longer retention time and large treatment areas are required [23]. The effluent that comes out from palm oil mill is hazardous to the ecosystem due to its high-volume composition and nutrient. The discharge can lead to land and aquatic pollution if it is left untreated [24].

In view of the measurement estimation of aggregate unrefined palm oil generation in May 2001, the production of 985,063 ton of crude palm oil means, a total of 1,477,595 m^3 of water is being used, and likewise, 738,797 m^3 POME is discharged for a month. Without appropriate treatment, this wastewater will contaminate the encompassing surrounding. The present treatment technology of POME normally comprises of natural aerobic and anaerobic digestion. Biologically treated effluent is disposed via land provision system, hence providing vital supplements for growing plants. This system might be a decent decision for the disposal of treated effluent. However, acknowledging those rates of daily wastewater generation, for instance, around 26 m^3/d for an average palm oil mill with an operating limit of 35 t/d FFB, it is doubtful that the surrounding plantations receiving it might effectively absorb all the treated effluent [25].

2.2. Palm oil management

Around 44 million m^3 of POME were produced in year 2013 to yield 19.66 million tons of total crude palm oil [14]. Around 85% of palm oil mills have treated raw POME using biological treatment [26]. The biological treatment of POME is a series of pond systems, including anaerobic, facultative and aerobic pond systems [19, 27]. However, the final treatment by aerobic pond system is struggling to achieve the discharge standards because of inefficient operational design [3]. The final effluent of the treated POME must comply with the discharge standards set by the Department of Environment (DOE), Malaysia. There is a requirement for a sound and effective management system in the treatment of these by-products in such a way that will assist to protect the environment and check the deterioration of air and river water quality. Treatment of POME is vital to avoid environmental contamination [28].

2.3. Current state of POME treatment

Indonesia and Malaysia are the two biggest oil palm manufacturing nations and is rich in various endemic and forest dwelling species [29]. Malaysia has a tropical atmosphere and is prosperous with regular assets. Oil palm as of now involves the biggest real acreage of cultivated land in Malaysia [30, 31]. The total oil palm acreage from 1970 to 2000 has expanded from 320 to 3338 ha. In the year 2003, there were more than 3.79 million ha of land under palm oil cultivation, occupying more than 33% of the total developed area and 11% of the total land area of Malaysia [32]. Palm oil, edible oil, is derived from the meaty mesocarp of the fruit of oil palm (*Elaeis guineensis*). One hectare of oil palm produces 10–35 tons of fresh fruit bunches (FFB) per year [2, 33]. Malaysia produces about 41% of the world's supply of palm oil as shown in **Figure 1**. Malaysia also accounts for the highest percentage of global vegetable oils and fats trade in the year 2005 [34].

The oil palm has the expectancy of over 200 years, whereas the economic life is about 20–25 years. The nursery period is 11–15 months for plants, and first harvest is done after 32–38 months of planting. It takes 5–10 years for palm oil plant to reach the highest yield. The yield is approximately 45–56% of FFB, and the fleshy mesocarp of the fruit is used to get oil. The yield of oil from the kernel is about 40–50% [35]. Both mesocarp and kernel of fruit produce about 17 t ha^{-1} yr^{-1} of oil [6]. Starting with 5.8 ton of FFB about 1 ton of crude palm oil (CPO) is produced [2]. The world palm oil production is shown in **Table 1**.

While the oil palm industry has been recognized for its contribution toward economic growth and rapid development, it has also contributed to environmental pollution due to the production of huge quantities of by-products from the oil extraction process [2].

2.4. Characteristic of POME and utilization by microalgae

POME contains high content of degradable organic matter, which is due in part to the presence of uncovered palm oil [36]. The discharge of improperly treated POME creates adverse impact to the environment (**Table 2**). However, the substances in POME are able to support the growth of microalgae. Microalgae naturally exist in many palm oil mill processes, phenomena known as "algae bloom," hence declining the water quality. Because POME consists of large amount of organic compounds and inorganic compounds which is hazardous to environmental health, microalgae have been suggested as a potential candidate to remove these pollutants and able to breakdown the organic compounds present in it [37, 38].

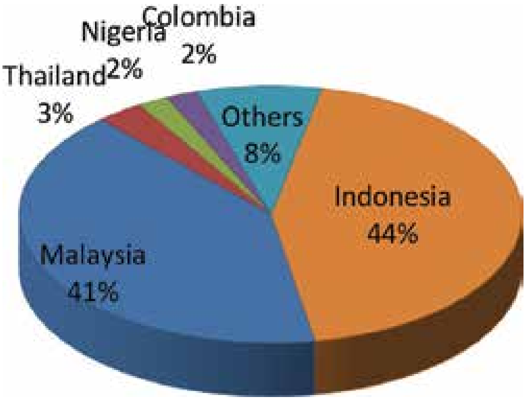

Figure 1. Palm oil production in 2007 [6].

Country	Share (%)	Amount (tons)
Indonesia	44	19,000
Malaysia	41	17,350
Thailand	3	1123
Nigeria	2	850
Colombia	2	832
Others	8	832

Table 1. World palm oil production [2].

Parameters	Concentration (mg/L)	Standard limit (mg/L)
pH	4.7	5–9
Oil and grease	4000	50
BOD	25,000	100
COD	50,000	—
Total solids	40,500	—
Suspended solids	18,000	400
Total nitrogen	750	150

Table 2. Characteristics of POME and its respective standard discharge limit by the Malaysian Department of Environment [19, 20].

Alternatively, culturing microalgae in wastewater offers an economy, which is alternative to the traditional types of wastewater treatment [39, 40]. In the meantime, microalgae can apply the nitrogen and phosphorus compound in wastewater to produce microalgae biomass for various kinds of lipid generation, which can serve as a substrate for biofuel production [38, 41].

POME is a colloidal suspension, starting from the blend of sterilizer condensate, separator sludge and hydrocyclone wastewater in a proportion of 9:15:1, respectively [1]. In total, about 2.5–3.0 tons of POME for huge amounts of produced crude palm oil is obtained in the extraction procedure [42]. Fresh POME is a thick brownish colloidal blend of water, oil and fine-suspended solids. It is hot (80–900°C) and has a high BOD, which is 100 times as contaminating as domestic sewage [1]. The effluent is not hazardous, as no chemicals are added to the extraction procedure [43], and also acidic with a pH around 4.5 as it contains organic acids in complex forms that are suitable to be used as carbon sources [44]. Palm oil mill effluent is a high-strength pollutant with low pH due to the organic and free fatty acids arising from partial degradation of palm fruits before processing. The characteristics of POME depend on the quality of the raw material and the production processes [24]. It typically contains large amounts of total solids (40,500–75,000 mg/L) and oil and grease (2000–8300 mg/L). Its total nitrogen in the range of 400–800 mg/L and suspended solids contents in the range of 18,000–47,000 mg/L. POME also has very high BOD and COD contents which are in the range 25,000–54,000 mg/L and 50,000–100,000 mg/L, respectively [45]. POME while fresh is hot acidic and pH range between 4 and 5, brownish colloidal suspension containing high concentrations of natural matter, high quantities of total solids (40,500 mg/L), oil and grease (4000 mg/L) COD (50,000 mg/L) and BOD (25,000 mg/L) [15]. However, it also contains appreciable amounts of N, P, K, Mg and Ca which are the vital nutrient elements for plant growth [46]. The characteristic of POME based on Malaysian Palm Oil Board is shown in **Table 3**.

According to Kamyab et al. [46], the raw or partially treated POME has an extremely high content of degradable organic matter. However, it has nontoxic nature and has fertilizing properties, POME can be used as fertilizer or animal feed substitute, in terms of providing sufficient mineral requirements. The Malaysian government provides an effort to reduce the effluent of palm oil through licensing system, which mainly consists of effluent standards and effluent charges. According to POME characteristic and standard discharge limit in Environmental Quality Act (EQA) 1974, the palm oil industry faces the challenge of balancing the environmental protection, its economic viability and sustainable development. The year 1978 witnessed the enactment of the Environmental Quality Regulations detailing POME discharge standards. **Table 4** shows the palm oil mill effluent discharge standard that must be followed.

Normally, the characteristics of POME may vary considerably for different batches, days and factories, depending on the processing techniques and the age or type of fruit as well as the discharge limit of the factory, climate and condition of the palm oil processing [19]. Occasional oil palm cropping and activities of the palm oil will also impact those quality and quantity of the discharged POME, thus influence the ecological treatment procedure of POME [27]. Hence, the variation of the characteristics of POME, in terms of its quality and quantity, is the main reason that causes selection in the treatment of POME in the palm oil industries [1, 47].

Parameter	**Mean**	**Range**
pH	4.2	3.4–5.2
Biological oxygen demand	25,000	10,250–43,750
Chemical oxygen demand	51,000	15,000–100,000
Total solids	40,000	11,500–79,000
Suspended solids	18,000	5000–54,000
Volatile solids	34,000	9000–72,000
Oil and grease	6000	130–18,000
Ammoniacal nitrogen	35	4–80
Total nitrogen	750	180–1400

*Units in mg/L except pH.

Table 3. Characteristics of POME [14].

Palm oil mill effluent discharge standards	1/7/78–30/6/79	1/7/79–30/6/80	1/7/80–30/6/81	1/7/81–30/6/82	1/7/82–31/12/83	1/1/84–there after
pH	5–9	5–9	5–9	5–9	5–9	5–9
BOD	5000	2000	1000	500	250	100
COD	10,000	4000	2000	1000	—	—
Total solids	4000	2500	2000	1500	—	—
Suspended solids	1200	800	600	400	400	400
Oil and grease	150	100	75	50	50	50
Ammoniacal nitrogen	25	15	15	10	150	100
Total nitrogen	200	100	75	50	—	—
Temperature °C	45	45	45	45	45	45

*Units in mg/L except pH and temperature.

Table 4. Environmental quality [14, 42].

2.5. Wastewater treatment technology

The wastewater treatment technologies are expensive, dependent on skilled personnel and hard to carry out, as the volume of contaminated wastewater is huge [38]. Furthermore, the common conventional treatment is unable to meet the regulations set by the Department of Environment (DOE) with the level of BOD at 100 mg/L. According to Ahmad et al. [19], large quantities of water are used during the extraction of crude palm oil from the fresh fruit bunch, and about 50% of the water results in POME. The disposal of this very contaminating effluent is turning into a noteworthy issue assuming that it may be not continuously treated appropriately as well as a severe standard boundary obligatory set by the Malaysian Department of Environment for the discharge of effluent. A POME treatment system based on membrane technology shows high potential for decreasing the ecological issue, and also, this alternative treatment system offers water reusing [19].

The utilization of wastewater for the microalgal growth is considered beneficial for limiting the utilization of freshwater, dropping the cost of supplement option, expelling nitrogen and phosphorus from wastewater and generating microalgal biomass as bioresources for biofuel or value-added by-products. Three primary sources of wastewater are municipal (domestic), agricultural and industrial wastewater which included a variety of elements. Some elements in the wastewater, such as nitrogen and phosphorus, are valuable components for microalgal cultures [48].

2.6. POME as nutrients source to culture microalgae

A life cycle assessment on microalgae cultivation has underlined that 50% of energy use and greenhouse gas emissions are associated with fertilizer (nutrients) [49]. In general, culturing of microalgae on a large scale required high nitrogen and other related chemical fertilizers, which driven the process toward non-environmental friendly. On the other hand, culturing microalgae can actually play an important role as a self-purification process of natural wastewaters [50].

Utilizing POME as supplements source to culture microalgae is not an another scenario in Malaysia. Most palm oil millers favor the culture of microalgae as a tertiary treatment before POME is released because of practically low cost and high impact. Consequently, vast majority of the nutrients such as nitrate and ortho-phosphates that are not detached during anaerobic digestion will be additionally treated in a microalgae pond. Thus, the cultured microalgae will be used as a food nutrition for live feed culture [50] Meanwhile, nitrogen source (usually

Source of POME/ concentration	**Microalgae**	**Growth condition**	**References**
POME collected from pond with no dilution	*Chlorella pyrenoidosa*	3 L PBR system Temperature: 24–26°C Mixing 60 rpm Lighting 8 h:16 h L:D pH 6.5–7.5 Light intensity of 150 μmol m^{-2} s^{-1}	[56]
Fresh POME with dilution 50% + 1 g/L urea	*Chlorella* sp.	1 L glass flask disk Light intensity 3000 lx pH 6.8–7.2, Temperature 28°C Mixing using aeration aquarium air pump	[4]
POME from anaerobic pond with 40% dilution	*Spirulina platensis*	1 L glass flask disk Mixing using aeration aquarium air pump pH 9–10.5 Light intensity, 4000–6000 lx	[57]
POME collected from pond with concentration 250 mg COD/L	*Chlorella sorokiniana*	Room temperature Light intensity-continuous illumination at intensity of ±15 μmol m^{-2} s^{-1}	[58]
POME collected from pond with concentration 250 mg COD/L	*Chlorella pyrenoidosa*	5 L HPBR reactor with turbine impeller Temperature, 30°C Light intensity, illuminated by four 32 W white fluorescence light continuous lighting (24 h) (Philip, Germany) C:N, 100:6 OLR, 36 kg COD m^{-3} d^{-1}	[46]
POME collected from pond with concentration 250 mg COD/L	*Chlamydomonas incerta*	250 mL Erlenmeyer flask Temperature, 30°C Light intensity, 15 μmol m^{-2} s^{-1} C:N, 100:7 OLR, 36 kg COD m^{-3} d^{-1}	[38]

Source of POME/ concentration	Microalgae	Growth condition	References
Fresh POME with dilution of 500 mL of POME in 400 mL deionized water	*Chlorella* sp.	1 L conical flask Pressure regulators bring down the pressure of both CO_2 and compressed air to 2 bars before entering their flow meters. The sparging tube of a flask culture was placed at the bottom of the flask Light intensity, 10,000 lx CO_2 concentration (% v/v), 16% Sparging rate (vvm), 0.8 vvm	[59]
Fresh POME with dilution of 1%	*Arthrospira platensis*	10 L of culture media in 20 L tank Outdoor	[60]

Table 5. Growth conditions for microalgae using POME.

appears in nitrate form) plays an important role in promoting microalgae growth. In order to grow microalgae effectively, the basic nitrate concentration required is in the range of 200–400 mg/L [51]. Others minerals such as Fe, Zn, P, Mg, Ca and K that are required for microalgae growth are also present in POME. Thus, POME emerged to be an alternative option as a chemical remediation to grow microalgae for biomass production and simultaneously act as a part of wastewater treatment process [50].

These days, there is an incredible and nonstop increment in industrialization, foundation and urban expansion in Asia, which has added to the critical wastes demand and water deficiency because of water contamination [52]. Industry in particular agro-based industry is one of the significant divisions releasing extensive amount of wastewater yearly influencing the other water sources and human life. The palm oil industry in Malaysia is generating the biggest amount of natural contamination loads into rivers [30, 33]. POME is a highly polluted waste having unpleasant odor. There is a greater need to find alternative way to utilize these organic pollutants for the good benefit of both human beings and the environment [21]. Microalgae cultivation in POME offers an alternative to conventional forms of tertiary wastewater treatments and spontaneously utilizes organic compounds present in POME to generate microalgae biomass for algae oil production [50]. There are several environmental and operational factors, which can affect the microalgae growth in order to make the cultivation fruitful. The natural effluent discarded from palm oil mill might be colloidal, dark and viscous, which should be considered prior media preparation for culturing the microalgae [53]. Vairappan and Yen [54] had found that for the marine *Isochrysis* sp., the concentration of POME at 5% dilution is the best concentration for culture media due to properties of POME. This dilution procedure will then enhance the light penetration into media for the algal growth in wastewater [55]. As described in **Table 5**, limited growth conditions are required for the growth of microalgae using palm oil mill effluent.

The concentrated nutrients (i.e., C, N, P, carbohydrate, lipid, protein and minerals) in POME are highly applied in biotechnology studies for growing microalgae [46]. The concentration extend about POME in various accepting water body may give high effect on the aquatic environments if the release surpasses the limit of standards set by Malaysia Environmental Quality Act.

Microalgae	Nutrient reduction (%)	Lipid production (%)	Growth rate (d^{-1})	Biomass productivity (g/L/d)	Duration (d)	Ref.
C. pyrenoidosa	—	42	—	2.19	18	[56]
Chlorella sp.	—	—	0.066	0.058	15	[57]
S. platensis	—	—	—	9.8	13	[57]
C. sorokiniana	—	28.27	0.099	8.0	20	[58]
C. pyrenoidosa	COD, 71.16%	68	1.8	0.13	10	[28]
Chlorella sp.	—	—	—	1.562	7	[59]
A. platensis	—	—	—	0.211	7	[60]

Table 6. Microalgae growth in POME.

Numerous species of microalgae exist in freshwater, seawater or brackish make them appropriate to be grown in great scale reactor on unfertile lands. The usage of macroalgae and microalgae in the utilization or remediation of the excess nutrients and CO_2 present in natural water resources, lagoons and ponds is called as phycoremediation [55]. This biological remediative treatment was introduced about 40 years ago when it was usually used in tertiary wastewater treatment [61]. The performance of microalgae growth cultivated in POME is shown in **Table 6**.

As seen from **Table 6**, Kamyab et al. [28] have done their studies by focusing on the nutrients reduction in POME, lipid production and microalgae growth. Meanwhile, it can be found that other researchers have not focused much on nutrient reduction, which is to be considered more important in relation to the growth of microalgae.

3. Conclusion

Malaysia is the biggest generator and exporter of palm oil. Palm oil processing is achieved in palm oil mills where oil is removed from a palm oil fruit bunch. Expansive amounts of water are utilized throughout the extraction of crude palm oil from the fresh fruit bunch, and around half of the water consequences in POME, which is a highly polluting wastewater that pollutes the environment if discharged directly due to its high COD and BOD concentration. In conclusion, the research was carried out mainly to investigate the influence of discharging POME from the treatment plant especially in tropical region like Malaysia and the effect on microalgae growth efficiency in POME. In other words, a combination of wastewater treatment and renewable bioenergies production would be an added advantage to the palm oil industry.

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Conflict of interest

The authors declare that there is no conflict of interest.

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Section 3

Applications of Palm Oil and its Industrial Wastes

Biomaterial from Oil Palm Waste: Properties, Characterization and Applications

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Additional information is available at the end of the chapter

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Abstract

Oil palm are among the best known and most extensively cultivated plant families, especially Indonesia and Malaysia. Many common products and foods are derived from oil palm, its making them one of the most economically important plants. On the other hand, declining supply of raw materials from natural resources has motivated researchers to find alternatives to produce new materials from sustainable resources like oil palm. Oil palm waste is possibly an ideal source for cellulose-based natural fibers and particles. Generally, oil palm waste such as oil palm empty fruit bunches, oil palm trunk, oil palm shell and oil palm ash are good source of biomaterials. Lack of sufficient documentation of existing scientific information about the utilization of oil palm waste raw materials for biomaterial production is the driving force behind the this chapter. Incorporation of various types of biomaterial derived from oil palm waste resources as reinforcement in polymer matrices lead to the development of biocomposites products and this can be used in wide range of potential applications. Properties and characterization of biomaterial from oil palm waste will not only help to promote further study on nanomaterials derived from non-wood materials but also emphasize the importance of commercially exploit oil palm waste for sustainable products.

Keywords: waste as green potential, cellulose fiber, oil palm particle, nanocellulose, biocomposites

1. Introduction

Sensitivity and concern for ecology and technology have sparked a new tendency towards the use of environmentally friendly materials in the world. Environmental-friendly "waste to wealth" programs are becoming increasingly important as a step to exploit and use biomass materials as raw material for biocomposite products for added value and new products. Biomass fibers (natural fibers, agricultural waste fibers, industrial timber waste etc.) have many techno-economic advantages over synthetic fibers such as glass fibers, carbon fiber and so on. Even in 1938, history has shown how Henry Ford uses soybean residues as a major raw material for the production of car interior frames components.

In general, there is continuous attempts to produce more high-value products from biomass. For example, biomass fibers from palm oil (OPBF) can be found continuously from oil palm fractures during pruning activities, when processing from oil palm stems during replanting (after 25 years) and periodic processing. Until this day, palm oil processing activities yield only 10% palm oil and palm kernel oil while the remaining 90% remain in the form of biomass or waste is still not used for the industry.

The oil palm industry has been producing a lot of oil palm biomass wastes in field and oil palm mills. The waste from mill consist of pressed fruit fibers (PFF), empty fruit bunch (EFB), oil palm shell (OPS), palm oil mill effluent (POME), whilst the other wastes from the plantation comprises of oil palm trunks (OPT) and oil palm fronds (OPF) during replanting after achieving its economic life spans [1]. The increase in oil palm plantation has been producing the waste in large quantities during the replanting; especially oil palm fronds (OPF) and oil palm trunk (OPT). Generally, 24% of OPF obtained from each oil palm trees in a year during harvesting at fresh fruit bunches (FFB) in the field. Meanwhile, OPT accounted for 70% of the replanting activities [2]. This means the potentiality of OPT availability would increase continuously as plantation is increasing and replanting is done throughout the year. Along with these two wastes, there are also other wastes like empty fruit bunch (EFB), oil palm shell (OPS) and waste (effluent) palm oil mill effluent (POME) [3].

These renewable biomass sources can be used for the development of biocomposites, power generation, paper production, construction board fillers, solid wood, mulching and soil conditioning as well as many other uses. Availability, price, performance, and biodegradable nature are among the factors that act as catalysts to promote the use of lignocellulose fiber of oil palm wastes as a value-added product. The oil palm sector generates a large number of biomass categorized as agricultural wastes which up to now only 10% are used as alternative raw materials for biocomposite-based industries, industrial raw materials, fertilizers, animal feeds, chemical derivatives and others. Much of this residual waste is not used but contributes to severe environmental problems when left in processing factories and farms just like that. Previous research on biomass and other agricultural waste has shown potential in its use for the production of various types of value-added products such as medium-density panel, chip board, thermoset composite and thermoplastic, nano biocomposite, pulp and paper manufacture [4, 5].

Through intensive research and development attempts, the world's oil palm biomass has been commercialized in a variety of biomass-based products. The use of lignocellulosic material from oil palm biomass for various types of value-added products through chemical processing, physical and biological innovation is now evolving.

2. Oil palm waste as green potential

Palm oil is one commodity which demand is growing very rapidly in world and provide an important contribution to economic development. Increased demand for palm oil in the form of vegetable oils encourage the countries to spur the development of oil palm plantations. Consequently, with the increasing development of the palm oil industry will cause the increase in palm oil mill effluents.

Despite this enormous production, the oil consists of only a minor fraction of the total biomass produced in the plantation. The remainder consists of a huge amount of lignocellulosic materials in the form of fronds (OPF), trunk (OPT), empty fruit bunches (EFB), pressed fruit fiber (PFF), pruning oil palm frond (POPF), and oil palm ash (OPA). Fortunately, all of the wastes are categorized as organic wastes that are environmentally degradable. However, owing to the large quantities generated, these wastes have the potential to pollute the environment. Sumanthi et al. [6] reported that the amount of biomass produced by an oil palm tree, include oil and lignocellulosic materials, is 231.5 kg dry weight/year.

Globally, oil palm biomass is produced and utilized in million metric tonnes annually. With the anticipated higher fresh fruit bunch yields and increase in planted areas in the world expected to produce more than 295 million tonnes of wastes annually. In Malaysia, the oil palm waste are produced of 135 million tonnes annually [7]. Meanwhile, Indonesia produced 143 million tonnes of the oil palm biomass annually [8, 9].

Solid wastes of EFB and OPT has higher potential for commercial exploitation than the other types of biomass waste [8]. Consequently, EFB and OPT, which collectively comprise the bulk of lignocellulosic waste are available for commercial exploitation. However, producer countries of oil palm in the world such Malaysia and Indonesia, the zero-waste strategy must applicated to maintain the competitive edge of oil palm industry [9]. Other potential biomass wastes were OPF from the plantation fields. Fronds are obtained during regular pruning on FFB harvesting, when trees exceeding the economical age are felled [10].

An oil palm tree reaches an average volume of 1.638 m^3 after its commercial life span [11]; therefore, more than 20 and 18.5 million m^3 of biomass from OPT are available annually in Malaysia and Indonesia, respectively. Bakar et al. [11] also reported that, the high OPT that can be used only 2/3 parts and recovery of oil palm lumber (outer part) generated an average of several patterns is tested is 30% [11], it can be generated about 5 million m^3.

The oil palm wastes can be utilized to produce various types value added products which mean the resources of the substitute's material on wood-based industry. Many studies have investigated the utilization of solid oil palm wastes, utilization of EFB as alternative of fertilizer using EFB waste and liquid waste of oil palm factory as filler in biocomposites have been done for particleboard or fiberboard using cement as adhesive or thermosetting adhesive such as an urea formaldehyde have been conducted [3]. EFB can also be used as a major component of specialized construction materials [12, 13]. Previous studies and the latest on oil palm biomass waste have shown the potentiality in its use for the production of various types of value-added products such as medium density panels, block board, laminated veneer lumber (LVL), mineral-bonded particleboard, plywood, chipboard, thermoset and thermoplastic composites, nanobiocomposite, pulp and paper manufacturing [14]. Islam et al. [15] used OPS as activated carbon. Abdul Khalil et al. [16] investigated the conversion of OPT and oil palm EFB into new plywood. Other researchers such as Zaidon et al. [17] and Deraman et al. [18] worked on making particleboard by mixing EFB and rubber wood. Oil palm biomass wastes in field and oil palm mills is illustrated in **Figure 1**.

The motivation for using OPT as plywood was initially due to the difficulty in obtaining good quality timber, as well as the abundance of OPT in developing countries like Malaysia and Indonesia [3]. However, oil palm-based plywood mills only utilize about 40% of the OPT and the other 60% is discarded as waste due to its insufficient properties [19]. Only the outer part of OPT can be used for plywood, while the inner part of OPT, which is not strong enough to use as lumber, is discarded in large amounts. It is highly susceptible to degradation agents due to its high moisture content (around 80%) [19]. Abdul Khalil et al. [16] investigated the development of hybrid plywood by utilizing OPT and oil palm EFB. The results showed that hybridization of EFB with OPT improves some of the properties like bending strength, screw withdrawal, and shear strength of the plywood.

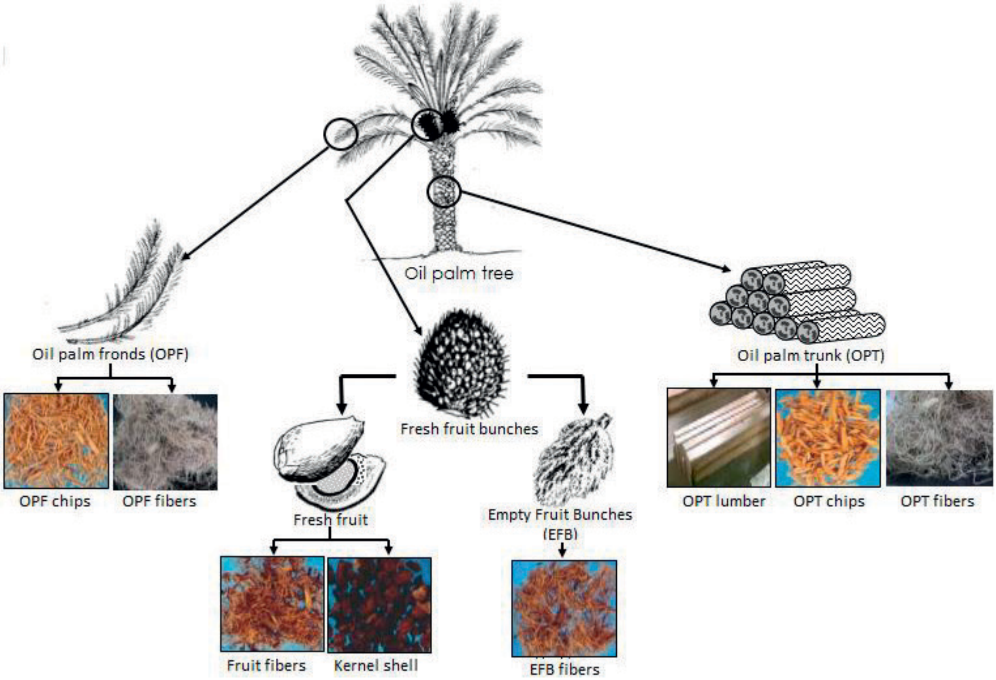

Figure 1. Various oil palm waste form and its derivative.

3. Properties and characterization of various oil palm waste and their products

3.1. Structure and morphology of oil palm tree

The cell wall structure of oil palm fibers consists of primary layer (P) and secondary layer (S1, S2 and S3). In general, oil palm fibers have varied variations in size, shape and structure of cell walls. Almost all the fiber structures are round. The layers of S1, S2 and S3 are strongly bonded and form structures such as sandwiches where microfibrils S1 and S3 corners are parallel to S2 layers. This sandwich structure provides additional strength to fiber for resistance to water strain, curve resistance to compressive strength, and bending stiffness to bending force. The primary walls of all oil palm fibers look like a thin layer. Some primary walls are clearly distinguishable between the middle lamella to each other.

Studies show that the S2 layer is the majority layer of cell wall. This layer affects the strength of a single fiber. OPT fibers are found to have the most thick S2 layers of 3.43 μm. According to the S2 layer thickness, the OPT is estimated to have the highest strength as the fiber strength is dependent on the cellulose microfibrils that are in line with the fiber axis of the S2 layer [13, 20, 21].

3.2. Properties of various oil palm wastes

EFB fibers are hard and strong multicellular fibers that have a central part called lacuna. Its porous surface morphology is important to provide better mechanical links with matrix resin for composite fabrication [22]. The fiber cross section is a polygon with a bundle or a vascular packet that is compact and surrounded by thickened layers of cells. Vascular fibers in monocytes are usually surrounded by several layers of thick cell walls that serve to provide tensile strength to side compression power [23]. OPF fibers consist of various sizes of vascular bundles. Vascular files are widely found in thin-walled parenchyma tissues. Each bundle consists of round gloves, vessels, fibers, phloem, and parenchyma tissue. The xylem and phloem tissues are clearly distinguishable where the phloem is divided into two separate parts in each bundle [12].

Different chemical compositions according to plant species and parts in the plant itself. It also varies by location, geographical condition, age, climate and soil conditions [24]. **Table 1** shows the differences in chemical composition between various types of oil palm biomass waste.

In order for many applications, oil palm solid waste has physical and mechanical properties. **Table 2** shows the properties include physical and mechanical of different part of oil palm solid waste. These properties are very important in reinforcement of biomass in polymer composites. Dungani et al. [34] investigated that physical, mechanical and chemical properties of various oil palm waste were examined to assess for many applications.

Fibers	Extractive (%)	Holocellulose (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
EFB	2–4	68–86	43–65	17–33	13–37	1–6
OPF	2–5	80–83	40–50	34–38	20–21	2–3
OPT	4–7	42–45	29–37	12–17	18–23	2–3
OPS	0.9–2	40–47	27–35	15–19	48–55	1–4

Sources: [25–29].

Table 1. Chemical composition of oil palm biomass waste.

Properties	EFB	EFB	EFB	OPT
Density (gr/cm^3)	0.7–1.55	—	—	1.1
Tensile strength (MPa)	0.1–0.4	71	51.73–82.40	300–600
Young modulus (GPa)	1–9	1.7	0.95–1.86	15–32
Elongation et break (%)	8–18	11	9.5–12.15	—

Sources: [30–33].

Table 2. Physical and mechanical properties oil palm solid waste.

3.3. Isolation and characterization of cellulose fibers from oil palm waste

Many researcher investigated the isolation and characterization cellulose fibers from oil palm waste. They studied about isolation of cellulose from many part of oil palm waste, which are chemical treatment and mechanical treatment. There are several ways to isolate cellulose from oil palm solid waste, such as homogenization, ultrasonication, electrospinning, acid hydrolysis, and steam explosion [33]. The main purpose of extracting cellulose is to remove existing non-cellulose components such as hemicellulose, lignin, extractive compounds to obtain cellulosic nano fiber [35].

The following are the results of several researchers who conducted their research on oil palm solid waste. Nasution et al. [36] report their research has isolated cellulose from EFB with hydrochloric acid. The result show that the microcrystalline cellulose (MCC) was found in the form of alpha cellulose. From SEM analysis this treatment affected the structural of morphological of resulting of microfibrillated cellulose. Chieng et al. [37] investigated extraction nanocellulose from OPMF by acid hydrolysis. They used sulfuric acid to remove amorphous region of cellulose to found nanocellulose crystalline. The result show that increased crystallinity of cellulose after removing hemicellulose and lignin. After analysis process the fiber surface to be smoother and reduction in diameter and size. The diameter of nanocellulose about 1–6 nm and rod-like shape.

Nordin et al. [38] also isolated cellulose with sulfuric acid from OPF. The result show that nanocrystalline cellulose improved. From TEM analysis showed good dispersion of individual fiber resulted from chemo-mechanical treatment. They were subjected that the nanocellulose derived from OPF is suitable for many application such as tissue engineering, medical implants, drug delivery, wound dressing and cardiac devices due to their excellent properties. Nazir et al. [39] produced cellulose from EFB with formic acid and hydrogen peroxide. Owolabi et al. [40] studied isolation of cellulose from OPF rachis vascular bundle using sodium hydroxide and hydrogen peroxide.

Shanmugarajah et al. [41] studied isolation of nanocellulose from EFB and investigated with sulfuric acid. Indarti et al. [42] produced cellulose nanocrystal from EFB by TEMPO mediated process follow with ultrasonication. They studied the effect of drying and solvent exchange process on thermal stability.

3.4. Production and characterization of particles from oil palm waste

Several methods has been implied by researcher to produce nanoparticle such as mechanical process, supercritical fluid extraction and solvent extraction [43]. These methods are intended for removing the residual impurities from sources including mechanical pressing. Nanoparticles as one form of nanomaterials like nanotubes and nanolayer, depend on the numbers of dimensions in nano range. Nano particles are small size, narrow size distribution, high dispersion tendency and lower aggregation form [44]. Producing nanomaterials could be preparing by different methods, such as mechanical treatments, chemical treatments, electrospinning method and so on.

Abdul Khalil et al. [43] investigated that OPS as nanoparticles for reinforcement in polymer composites. In prepared the nanoparticles, they used solvent extraction method. From analysis, the shape and surface of defatted OPS particles were angular, crushed shapes and irregular. Liauw et al. [45] stated that the bioresources when used extraction with supercritical fluid, the high purity of oil could produced.

Many researchers also concerned to produce oil palm nanoparticles in the form of activated carbon and oil palm ash. Ruiz et al. [46] produced and characterized the activated carbon particle from OPS. Sukiran et al. [47] studied biochar particles from EFB by pyrolysis process by using fluidized bed reactor. Biochar particles can be used as fuel in form of briquettes, reinforcement in polymer composites, as antifouling in polymer membranes, biocatalyst and ink. Abdul Khalil et al. [48] investigated nanoparticles from oil palm ash (OPA) which is rich siliceous material. They successful reduce the size with ball mill process for 30 hours. Saba et al. [44] investigated nanoparticles from EFB with physical treatment and chemical treatment. To reduce macromolecular size to nano-size used high energy ball mill. Nasir et al. [49] succeeded to produce reduced rapheme oxide from rapheme oxide using OPL, PKS and EFB.

4. Potential application of oil palm waste-based composites

Over the past few decades, the polymer science have been development in a wide spectrum since emergence natural fiber-reinforced polymer composite materials. Its natural fiber composites have used in various applications such as automotive components, package trays, door panels, headliners, dashboards and interior parts [50].

Type of conventional composite	References
Veneer and plywood	Mokhtar et al. [54] and Rosli et al. [55]
Compressed lumber	Choowang and Hiziroglu [56] and Choowang [57]
Sandwich panel	Srivaro et al. [58] and Srivaro [59]
Fiberboards	Onuorah [60] and Ramli et al. [53]
Particleboards	Sudin and Shaari [61] and Haslett [62]

Table 3. Conventional composite based on oil palm waste.

Biocomposites	References
EFB/polyester	Abdul Khalil et al. [63]
OPF/phenol formaldehyde	Sreekala et al. [64]
OPF/glycidyl methacrylate	Rozman et al. [65]
Oil palm fibers/rubber	Ismail et al. [66]
Oil palm wood flour/natural rubber	Ismail et al. [67]
EFB (carbon black)/epoxy	Abdul Khalil et al. [68]
EFB/polycaprolactone	Ibrahim et al. [69]
EFB/phenol formaldehyde	Chai et al. [70]
Short palm tree fibers-polyester	Kaddami et al. [71]
Short palm tree fibers-epoxy	Kaddami et al. [71]
Polyethylene modified with crude palm oil	Min et al. [72]
EFB fiber/poly(butylene adipate-*co*-terephthalate)	Siyamak et al. [73]
EFB fiber/polyethylene	Arif et al. [74]
EFB fiber/poly(vinyl chloride)	Abdul Khalil et al. [75]
OPT fiber/polypropylene	Abdul Khalil et al. [76]

Table 4. Thermoset based on biocomposite polymer and elastomer.

Utilization of natural fiber like oil palm empty fruit bunch (EFB) in polymer composites have some advantages such as low density, low cost, renewability, and biodegradability [51, 52]. The use of biomass from oil palm wastes has been demonstrated at the laboratory and pre-production levels as alternative raw wood materials for biocomposite production, for example particleboard, medium density fiberboard (MDF) and others [53]. These are the essential features and properties of fibers that are important and enable integration of oil palm biomass waste into existing industries for the purpose of product production.

4.1. Oil palm waste-based conventional composite

The biomass wastes include trunk, empty fruit bunch, leaf, mesocarp fiber, etc. are convertible into various biocomposite products. The type of conventional composite performance can be tailored to the end use of the product with each category classification is simple low and high density. Conventional composites are used in some structural and non-structural product applications, including panels for internal closure purposes to panels for outdoor use in furniture and multi-building support structures. Review on each potential biocomposite products can be manufactured from oil palm waste is presented in **Table 3**.

4.2. Oil palm waste-based polymer composites

This section provides an overview of use of oil palm waste fiber in the field of composite material. Bio-based polymers such as polylactic acid (PLA), polyhydroxybutyrate (PHB), cellulose ester, soy-based plastic, starch plastic, polymer trimethylene terephthalate (PTT), functional

Biocomposite	References
Polyethylene/tapioca starch/EFB biofilm	Roshafima and Wan Aizan [77]
Polypropylene/EFB	Rozman et al. [78]
High-density polyethylene composites/EFB	Mohd Ishak et al. [79]
High-density polyethylene composites/OPF/EFB	Rozman et al. [80]
Poly(vinyl chloride)/EFB	Bakar et al. [81]
Polyurethane/EFB	Rozman et al. [82]
Polypropylene/EFB-oil palm derived cellulose	Khalid et al. [83]

Table 5. Thermoplastic-based biocomposites polymer.

Hybrid composites	References
Oil palm fiber-glass fiber/epoxy	Jawaid and Abdul Khalil [84]
EFB-glass fiber/polypropylene	Rozman et al. [85]
EFB-glass fiber/polyester	Abdul Khalil et al. [26]
EFB bio-composites hybridized-kaolinite	Amin and Khairiah [86]
Oil palm fibers-glass fiber/polyester	Kumar et al. [87]
EFB-glass fiber/phenol formaldehyde	Sreekala et al. [64]
Sisal-oil palm fibers/natural rubber	Khanam et al. [88]
EFB-glass fiber/vinylester	Abdul Khalil et al. [89]
EFB-jute/epoxy	Jawaid et al. [90]

Table 6. Oil palm fiber-based hybrid composites.

vegetable oil-based resin and thermoset and elastomer biocomposites (**Table 4**) has revolutionized the plastic and petroleum world with biodegradable polymer.

Additionally, oil palm fiber can be used as a filler in thermoplastics and thermoset composites (**Table 5**). This composite has extensive applications in automotive furniture and components. In Malaysia, research and development in this area has finally reached commercialization levels to develop the thermoplastic composite, thermoset and elastomer composite for components used in the manufacture of proton cars [6]. In addition, hybrid composites also have lower modulus of storage than non-hybrid oil palm/PF composite composites. Research and production of various hybrid composites based on oil palm fiber are listed in **Table 6**.

5. Conversion of oil palm waste-based lignocellulosic to nanocellulose

Lignocellulosic of oil palm fibers such as hemicellulose, lignin and especially cellulose are also potentially exploited in nanotechnology. The pulp fiber from the oil palm fiber to produce a network structure unit such as nano-sized mesh called cellulose microfibril, it are obtained through mechanical treatment of pulp fibers which include smoothing process and high-pressure homogenizer process. The degree of fiber fibrillation of the pulp will increase the flexural flexibility of the fiber [75, 84]. This increase is due to the complete fibrillation of most fibers. The use of pulp (cellulose) as a reinforced booster with additional high pressure homogenization, composite strength will increase linearly against water resistance values and other properties [91].

In general, related materials such as hydrolyzed microcrystalline cellulose will rapidly clot when it is drained [92]. This, will complicate the next process. Therefore, surface modification should be carried out so that cellulose has compatibility with the matrix. Examples of applications for surface-made nanofibrillar celluloses are high-performance films and materials of nanocomposites, materials with superb hydrophobic surfaces as well as optical properties, electrical conductivity, magnetic or unique adsorption, new wood-based fibers with nanoscans or modified surface textures [93]. Products include filters, textiles, films, packaging materials, casting and mold components.

There are various methods had been reported for isolation of oil palm waste-based lignocellulosic to nanocellulose or nanoparticles, its can either in chemical treatment, mechanical treatment, and chemo-mechanical treatment processes [39, 94, 95] considered that alkali treatment seems to be effective in the removal of lignin and hemicelluloses components in palm oil EFB fiber. Mazlita et al. [96] suggested that chemical-sonication process were successfully generated from oil palm trunk (OPT) lignocellulosic biomass.

The characteristic of nanocellulose of oil palm wastes has great potential in applications such as strength enhancers polymer composites has been studied since the first half of the twentieth century. Nanocellulose extracted from oil palm biomass lignocellulosic can be classified in two main subcategories, nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). Research on the isolation nanofibres from oil palm biomass such as empty fruit bunch have

Event	References
Cellulose nanofibers were produced by hydrolyzing OPEFB with sulfuric acid	Fahma et al. [39]
Microfibrillated celluloses from OPEFB	Goh et al. [100]
Production defatted OPS nanoparticles	Dungani et al. [101] and Rosamah et al. [102]
Nanofibrillated from EFB using ultrasound assisted hydrolysis	Rosazley et al. [103]
EFB nanocrystalline cellulose was isolated from OPEFB microcrystalline cellulose	Rohaizu and Wanrosli [104]
Nanocellulose from OPF using alkaline processes	Mohaiyiddin et al. [105]
Production cellulose nanocrystals from OPF by hydrolysis treatment	Saurabh et al. [106]
Isolation of cellulose nanowhiskers from oil palm mesocarp fibers by acid hydrolysis and microfluidization	Adriana et al. [107]
Production cellulose nanocrystals from OPF by chemo-mechanical treatment	Nordin et al. [38]
Oil palm mesocarp fiber as a source for the production of cellulose nanocrystals	Chieng et al. [108]
Nanofillers obtained from OPA	Abdul Khalil et al. [7]
The utilization of OPA as a nanofiller for the development of polymer nanocomposites	Bhat and Abdul Khalil [109]
Nanocellulose was extracted from OPT fibers by a chemi-mechanical technique	Surip et al. [110]
Cellulose nanocrystals were isolated from OPT using acid hydrolysis method and total chlorine free method	Lamaming et al. [111]

Table 7. Events in the exploration of isolation nanocellulose from oil palm biomass with various methods and their related applications.

been conducted over the years [97]. It has been reported that cellulose nanofibers from cellulosic oil palm fiber can used as a reinforcing agent in composites materials. Meanwhile, research in the use of oil palm waste nanofiller such as oil palm shell and oil palm ash for manufacturing of wood composites have been carried out by Dungani et al. [98] and Sasthiryar et al. [99]. In general, the results of these studies indicate that, the addition of nanofiller can improve the properties of composites. The research development of isolation of nanocellulose of oil palm biomass and its related methods in various treatment are shown in **Table 7**.

6. Conclusion

The oil palm industry produces a high amount of waste during harvesting, replanting and processing at the plant. Generally, up to this day only 10% of the use of oil palm biomass residues is used as a biocomposite industrial raw material or as an alternative substitute material for wood raw materials. Oil palm waste that has lignocellulose content can be produce biomaterial as reinforcement in conventional biocomposite products (molded product panel, plywood, fiberboard, hybrid biocomposite, etc.) and advanced biocomposites (thermoplastics, thermosets and elastomers). Biomaterial can produce with or without treatment. That mean is the biomaterial from oil palm tree can be made from the fiber and isolated the cellulose content. Biomaterial from oil palm waste played an important role in the polymer composites and it can classified according to their origin. The types of biomaterial can be prepared from trunk, empty fruit bunch, frond, and shell. Reinforcement of biomaterials from different part of oil palm tree in thermoplastics and thermoset will give different characteristics. The different characteristic because of the physical and mechanical properties of oil palm fibers are mainly depended on their chemical content. The reinforcement oil palm waste into polymer composites have shown the sensitivity of certain mechanical and thermal properties to moisture absorption. These phenomena can be decreased by the employ fiber surface treatment.

In additions, biomaterial from oil palm waste reinforce in polymer composites could increase biodegradability, decrease environmental pollution, reduces cost and hazards. The waste disposal issue has directed most scientific research into eco-composite materials that can be readily degraded and assimilated by biological agent. The characterization of biomaterial reinforce in polymer matrix give some performance like, physical properties, chemical properties, mechanical composition, and also interaction between fiber as nanomaterial and matrix.

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Conflict of interest

The authors have declared that no competing interest exists.

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Chapter 4

Potential Application of Oil Palm Wastes Charcoal Briquettes for Coal Replacement

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Additional information is available at the end of the chapter

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Abstract

This study is aimed at investigating the potentials of oil palm wastes as an alternative to fossil fuels (coal) for domestic heat generation via briquettes (solid fuels) production. In this study oil palm wastes such as empty fruit bunches (EFB), mesocarp fiber (MF) and palm kernel shell (PKS) were pyrolyzed at temperatures of 400°C for 120 min and a heating rate of 10°C min^{-1}. The biochar and bio-oil obtained were blended in the ratio of 60:40 weight percentages and compressed at a constant pressure of 400 kg cm^{-2} for charcoal briquettes production. The combustion profiles, heat release of the charcoal briquettes and Malaysian sub-bituminous coal were analyzed and compared through thermogravimetric analysis (TGA). Comparably, MF and PKS charcoal briquettes had higher HHV of 26.15 and 25.99 MJ kg^{-1}, individually than coal which has 24.21 MJ kg^{-1}, while EFB charcoal briquette showed the lowest value 23.93 MJ kg^{-1}. Therefore, it can be said that all the charcoal briquettes showed a positive sign to replace coal. The maximum and minimum heat released of 0.059 and 0.048 W were obtained from the combustion of EFB and MF charcoal briquettes. It was established that in each ton of raw (dry basis) of EFB, MF, and PKS, there is 0.177, 0.212 and 0.228 tons of charcoal briquettes which correspond to 1.866, 2.055 and 2.414 MW of heat. Therefore, the findings in this study could contribute toward achieving the targeted 500 MW of green energy initiated in 2005 by the Malaysian government. Furthermore, the production of charcoal briquettes could be one of the proper methods to minimize the agricultural disposal problem in Malaysia.

Keywords: oil palm wastes, charcoal briquettes, coal replacement, heat generation

1. Introduction

1.1. Energy demand

International Energy Agency (IEA) in its new policy scenario stated that the world energy demand is anticipated to persistently rise yearly to about 1.2% from 2008 to 2035, with 70% of the demand imminent from the developing countries. However, the majority (87%) of this energy demand will be obtained mainly from fossil fuels. The rise of the entire global energy demand is associated with the increase in the world population and global economic growth [1, 2]. Furthermore, the energy uses in the main cities of developing countries is related to stages of greenhouse-gas (GHG) emissions and are anticipated to increase [3]. Global warming has been one of the fundamental environmental problems for many decades. However, the quantity of CO_2 in the atmosphere will persistently increase, except key modifications are made in the manner fossil fuels are utilized in the energy production [4, 5]. Fossil fuels still control the world's energy market value of about 1.5 trillion United States Dollars (USD). For example, the World Energy Council (WEC) estimated in 2007 that recoverable coal mineral deposits would be about 850 billion tons in 2006 [6].

The burning of coal generates more CO_2 emissions than combustion of both oil and natural gas by 1.5 and 2 separately [7]. Malaysia is not an exception in the use of fossil fuels for power generation. As at 2010, the coal generation in Malaysia is derived majorly from six mines in Sarawak. There are about 1724 million tons of coal resources of which 274 million tons are identified, 347 million tons indicated and the balance of 1102 million tons as inferred [2]. Presently, community and political sensitivities to environmental problems and energy security have focused on the promotion of non-fossil fuel energy sources instead of fossil fuels. Renewable energy sources such as small hydropower, solar, wind, geothermal and biomass have presently contributed 14% of total world energy consumption, of which 62% is biomass [8].

1.2. Renewable energy sources

Renewable energy is an energy source which does not vanish. These types of energy sources have been in use since the beginning of human civilization. They are abundantly available because they exist naturally in our environment [9]. There are three sources of energy and these include; fossil fuels, renewable and nuclear power sources. However, among these energy sources, renewable energy is the only source that can be used to generate energy repeatedly. They can also be used easily to provide the domestic energy demand for local communities. **Table 1** presents the global renewable energy scenario as predicted by the year 2040. Sun is the largest source of all energies. Renewable energy sources (RES) have advantages for the alleviation of greenhouse gas emission, minimizing global warming by replacing conventional energy sources and reducing disposal of a lot of wastes. Renewable energy sources such as biomass, hydropower, geothermal, solar, the wind and marine energies provide about 14% of the total world energy demand. The percentage is predicted to improve extensively to about 30–80% by 2100 as shown in **Table 1** [10].

1.3. Biomass energy

Among the renewable energies, biomass is the largest and an essential one that has been employed in both developed and developing countries. Biomass is formed when carbon dioxide

Decades	2001	2010	2020	2030	2040
Total consumption (million tons oil equivalent)	10,038	10,549	11,425	12,352	13,310
Biomass	1080	1313	1791	2483	3271
Large hydro	22.70	266	309	341	358
Geothermal	43.20	86	186	333	493
Small hydro	9.50	19	49	106	189
Wind	4.70	44	266	542	688
Solar thermal	4.10	15	66	244	480
Photovoltaic	0.10	2.00	24	221	784
Solar thermal electricity	0.10	0.40	3.00	16	68
Marine (tidal/wave/ocean)	0.05	0.10	0.40	3.00	20
Total RES	1365.5	1745.5	2964.4	4289	6351
Contribution of RES in (%)	13.60	16.60	23.60	34.70	47.70

Table 1. Global renewable energy scenario by 2040.

and solar energy (sunlight) with water are mixed via photosynthesis. However, burning of biomass results in the release of carbon dioxide into the atmosphere accompanied by the conversion of stored chemical energy in the biomass into thermal energy [11]. Biomass supplies a clean, renewable energy source that could considerably improve our environment, economy and energy security by reducing the burning of fossil fuels, emission of greenhouse gasses (GHG) and environmental pollution [12].

Biomass can be used to generate heat and power for industry and domestic purposes. This particular value over wind power and solar energy via photovoltaic cells makes biomass a significant pillar in the energy contribution today and in the future. Biomass such as wood, energy crops, forest and agricultural residue, industrial and municipal wastes could be the prominent alternatives to coal [12, 13]. Moreover, according to statistics from the IEA, biomass contributed about 10% of primary global energy demand in the year 2005. Biomass can be converted into gas and liquid fuels (bio-oil, biodiesel, and bioethanol) through gasification and pyrolysis, transesterification and fermentation respectively [14].

Biomass is a lignocellulosic material obtained from living organic substances such as wood and agricultural wastes. However, non-lignocellulosic substances, like an animal and municipal solid wastes (MSW) are also regarded as biomass. The three major constituents of biomass [15, 16] are cellulose, hemicellulose, and lignin. It also contains water extractives and ash [16]. The constituents are highly associated and chemically bonded by noncovalent forces. They are cross-linked collectively, thus bearing composition and firmness of the plant [15]. The basic structures of biomass lignocelluloses components can be written as $(C_6H_{10}O_5)m$, $(C_5H_8O_4)m$ and $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}]m$ for cellulose, hemicellulose, and lignin respectively, where m is a degree of polymerization [14].

1.4. Oil palm biomass in Malaysia

Palm oil has made significant and continued development in the worldwide market in the past few decades. Malaysia and Indonesia are the top producing countries of palm oil in the world, which together produced about 85% of the total world palm oil. Additional producing countries comprise Thailand, Columbia, Nigeria, Papua New Guinea and Ecuador [17]. Oil palm is the most important product that has changed the situation of the agricultural sector and economy in Malaysia. It is projected that in the period 2016–2020, the standard yearly production of palm oil in Malaysia will achieve 15.4 million tons. Lignocellulosic biomass which is produced from the oil palm industries incorporate oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB) and palm pressed fibers (PPF), palm shells, and palm oil mill effluent (POME). The occurrence of these oil palm wastes has created a significant disposal crisis, but the primary objectives of waste management in Malaysia are to limit and reuse the waste and recuperate the energy. This principally applies to agro-industrial wastes, for example, palm oil residues as applied to municipal waste. One of the significant advantages of oil palm wastes is that the palm oil mill is independent in energy, utilizing PPF, EFB, and shell are used as fuel to generate steam in waste fuel boilers for handling, and power-generation with steam turbines [18].

The oil extraction rate is just around 10% of the palm oil production with the larger part 90% remaining as biomass. For instance, in 1 kg of palm oil about 4 kg of dry biomass is generated [19, 20]. The oil palm wastes generated from palm oil industry in Malaysia is among the most excellent biomass residues. After being lignocellulosic biomass, they also show non-edible characteristic which makes them attractive globally [21]. Specifically, Malaysia produced around 9.9 million tons of palm oil wastes as a fundamental of biomass sources including EFB, shell, and fiber, which continues to expand at 5% yearly [22]. However, the proportions of agricultural residues generated from oil palm include mesocarp fiber (13.5%), palm kernel shell (5.5%) and empty fruit bunch (22%). Palm shell and palm fiber were utilized as fuel to power the steam boilers, whereas empty fruit bunch is used for mulching in the plantation area [23].

In 2009, the oil palm wastes rendered in Malaysia were 7.0 million tons of EFB, 11.6 million tons of PKS and MF, 44.8 million tons of fronds and 13.9 million tons of trunks. However, the eminent expected utility of these wastes is assumed to circumscribe [24]. Between the oil palm biomass, mesocarp fiber contains a high calorific value in comparison with palm shell and EFB [23]. These oil palm residues comprise various chemical composition and high heating value of about 18–19 MJ kg^{-1}. They are better complement and ingredients for fuels in the form of pellets and briquettes [25]. It has been declared that in the year 2012 there were profitable oil palm wastes (dry weight) of about 83 million tons in Malaysia. Moreover, it will eventually ascend to 100 million tons in few years to come (2020) [24]. These wastes will continue to contribute to the agricultural wastes disposal problem in Malaysia except necessary action are taken.

1.5. Thermochemical conversion of biomass

The direct combustion of biomass is not the best way to use it as burning fuel. Some processes can be used to upgrade the standard of biomass for better and proper application. Some of these processes include dewatering and drying, pulverization or grinding, and densification process such as pellets. Besides the above-mentioned conventional pre-treatment, there is also another important and efficient method for upgrading biomass as a fuel known as torrefaction [11]. Torrefaction can be described as a thermochemical process carried out in the temperature range of 200–300°C under an oxygen-free condition with a purpose to upgrade the quality standard of biomass [26].

Pyrolysis conversion process is one of the prominent thermochemical methods through which biomass are converted into three major by-products namely; solid char, bio-oil, and gases [27, 28]. A pyrolysis procedure is divided into slow pyrolysis and fast pyrolysis. Slow pyrolysis yields more biochar yet less bio-oil with around 35% as biochar, 30% as bio-oil and 35% as syngas. However, fast pyrolysis gives a yield of around 15% biochar, 70% bio-oil, and 13% syngas [20]. The pyrolysis parameters such as temperature, retention time, heating rate, particle size, inert gas and reactor type give different pyrolysis product yields. Temperature and holding time are among the most significant operating parameters. As the temperature and residence time rise, the biochar yield is reduced because of gasification of the solid biochar. With increased temperature up to 500°C, the greatest bio-oil yield can be accomplished. However, the yield drops with further increment in temperature. Interestingly, gas products are favored at high temperature and long holding time not surprisingly because of the quantity of volatiles released with increasing temperature [20]. For woody biomass, the liquid product is typically maximized at a temperature around 500–520°C for fast pyrolysis. However, lower temperatures favor the production of biochar [29].

1.6. Biomass briquetting for solid fuels

Briquetting is a process of compressing materials into a small portable size with a diameter ranging from 30 to 100 mm and of any length depending on the technology applied, which could either be screw or piston compression [30]. The briquetting process is perhaps regarded as a way to improve the application of low-grade wastes materials. Briquetting is mainly used for compacting of biomass and none biomass sources such as plastic, many types of milled paper wastes and other combustible wastes [31]. Municipal solid waste (MSW), industrial waste and sludge are used to produce fuel briquettes in some countries [32]. It is well-known and believed that biomass residues could be utilized as a replacement to fuel for combustion at coal-fired power plants [33]. There are many processes for briquetting; they include pre-treatment and operational parameters (factors) that controlled the quality of fuel briquettes. Furthermore, physical properties such as a binder, moisture content, particle size and compressing forces (pressure) are among the factors that influence the quality of briquettes regarding durability and resistivity during transportation [34]. However, a briquette quality significantly depends on the drying process [35].

In this research, the potential application of empty fruit bunches, mesocarp fiber and palm kernel shell for coal replacement was investigated. These biomasses were pyrolyzed and the bio-oil and biochar obtained were used to form charcoal briquettes (solid fuels). The viscosity of bio-oil was improved by the addition of 10% starch and used as a binder.

2. Materials and methods

2.1. Biomass sample collection and preparation

The oil palm biomass used in this study include mesocarp fibers (MF), empty fruit bunch (EFB) and palm kernel shells (PKS) as shown in **Figures 1–3**. They were obtained freshly from a palm oil mill located in Nibong Tebal, Pulau Pinang, Malaysia. These biomass samples were the by-products from different procedures such as pressing and nut cracking in the milling process industries where crude palm oil is generated. The biomass samples were dried to a moisture content lower than 10 wt%, for 24 h at 105°C. EFB sample was cut into smaller sizes, and all the samples were stored into desiccators before experiments and analyses. The Sago starch was obtained from MYDIN shopping mall located at Bukit Jambul, Pulau Pinang, Malaysia. Sub-bituminous coal was supplied by a company based in Sarawak, Malaysia.

2.2. Physiochemical characterization

Proximate analysis was carried out by ASTM E871 for moisture content, ASTM E872 for volatile matter content, and ASTM E1755-01 for ash content, from which the difference was used to determine the amount of fixed carbon. Elemental analysis was conducted to analyze the percentages of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O). It was performed using a Perkin Elmer 2400 analyzer, and 2–2.8 mg of sample was used to measure the percentage weight of each element present. The higher heating value (HHV) was determined using bomb calorimeter system IKA C 200, and oxygen station C248 with an empty water hose. For each test run, 0.5–0.8 g of the sample was measured and placed in the crucible joined to the thread from the ignition wire, which was then closed, and oxygen gas was pumped in. The lignocellulosic compositions of the materials were measured according to the procedure prescribed by Sukiran [22].

2.3. Pyrolysis experiment

The pyrolysis experiment was conducted three times separately using a stainless-steel reactor of 150 mm length and 70 mm internal diameter; about 180 g of raw biomass was weighed and placed inside the electric furnace. The reactor was heated at a temperature of 400°C for 120 min and at a heating rate of 10°C min^{-1}. During the pyrolysis, the reactor temperature was monitored using a K-type thermocouple, and nitrogen (N_2) was used as the reaction gas at a rate of 2 l/min as shown in **Figure 4**.

Figure 1. Oil palm EFB as received.

Figure 2. Oil palm fiber as received.

Figure 3. Oil palm kernel shell as received.

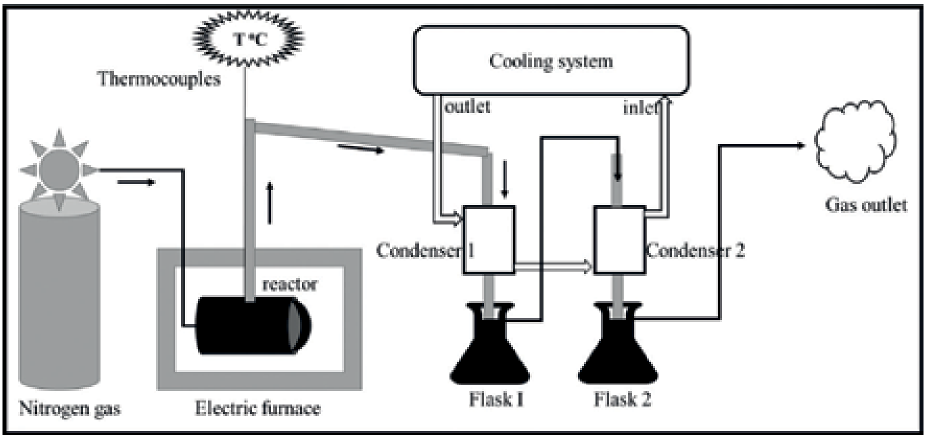

Figure 4. A schematic of the pyrolysis system.

2.4. Briquetting tools and methods

The cylindrical briquetting mold used was made from hardened steel with an inner diameter of 19.4 mm and a height of 50.2 mm. Other briquetting parts are press piston of 65.0 mm and stop piston of 10.0 mm. The manual hydraulic pressing machine (briquetting machine) used is purposely manufactured for experimental work. It has a maximum pressuring capacity of only 1000 kg cm^{-2} (98.07 MPa). For each bio-briquettes made, about 10–20 g of the mixture was placed into a mold and compressed at a constant pressure of 400 kg cm^{-2} for 2–5 min until no more change occurred on load reading. This procedure was replicated for all the briquettes produced. The mold and piston, and schematic briquetting machine setup are displayed in **Figures 5** and **6**, respectively.

The starch was ground to powder and mix with the bio-oil of about 50 ml and warmed. The mixture was stirred vigorously until a uniform solution was observed (bio-oil binder). The biochar and bio-oil (binder) were mixed in the ratio of 60:40 weight percentages. The mixture was allowed to dry for 10 min at room temperature before feeding into mold and press. The weight of briquette produced was recorded instantly and placed under ambient conditions for about 7 days to dry. The briquette procedure is summarized in **Figure 7**.

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on the sample using a Perkin Elmer STA 6000 thermogravimetric analyzer. Thermal analysis was used to examine the thermal performance of the samples by observing the weight alteration that happened as the samples were heated, concerning hemicellulose, cellulose, and lignin, and identifying their thermal degradation behavior. The analysis was carried out in the presence of nitrogen (N_2) gas flow under a 10°C min^{-1} heating rate, with a sample size of 250–355 μm and the samples were heated from ambient temperature to about 850°C.

After the charcoal briquettes had been manufactured and dried, they were ground and subjected to combustion together with coal via TGA from a temperature range of 30–850°C at a constant heating rate of 10°C min^{-1} under oxygen environment at a flow rate of 50 ml min^{-1}. In the combustion analysis, the combustion profiles such as peak temperature, ignition temperature, and burnout temperature at each combustion zone were determined. Also, the amount of weight loss, briquettes burnt, combustion rate and heat release during combustion were analyzed. The graph of DTG %/min versus temperature was used to determine the combustion properties of the briquettes. The combustion rate and heat release were computed with the equations shown below [23].

$$\text{Combustion rate} = \text{total mass of burnt briquette/burning time} \tag{1}$$

$$\text{Heat release} = \text{calorific value} \times \text{combustion rate} \tag{2}$$

Figure 5. Briquette mold and piston.

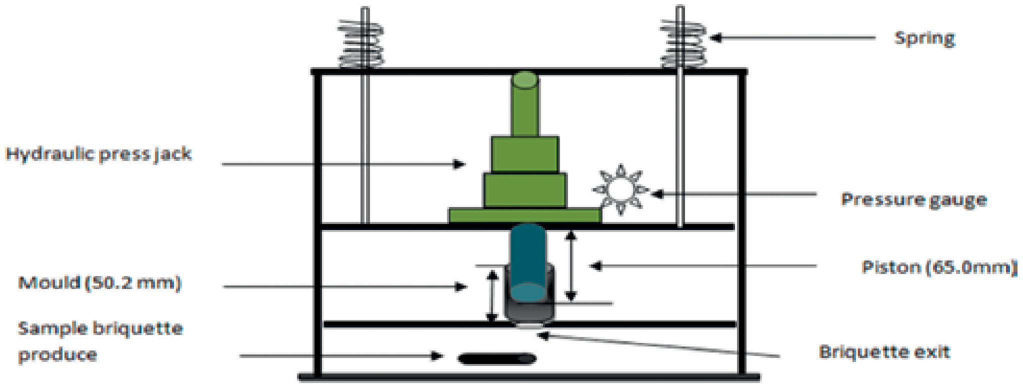

Figure 6. A schematic briquetting machine.

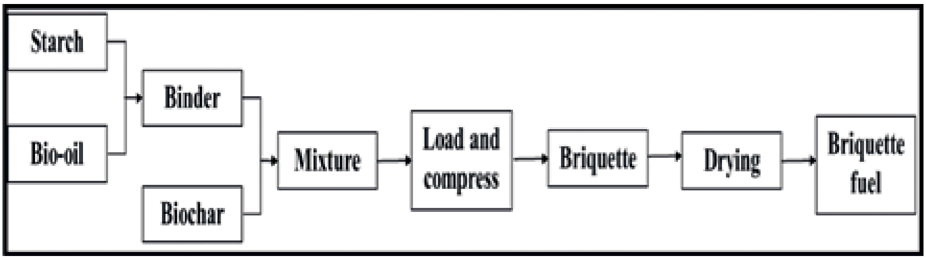

Figure 7. Briquetting processes.

3. Results and discussion

3.1. Lignocellulosic components of oil palm wastes

The composition of cellulose, hemicellulose, lignin, and extractive in the oil palm wastes was in the range of 20–39, 23–35, 20–49 and 3–10 wt%, respectively as shown in **Table 2**. Comparatively, empty fruit bunch has high cellulose and hemicellulose, and low lignin and extractives contents than others. Mesocarp fiber has a high content of extractive than PKS and EFB, which could be responsible for it higher heating value than others. The high lignin content in palm shell resulted in a high yield of biochar. The cellulose, hemicellulose, lignin, extractive and ash components of oil palm wastes were respectively found in other research to be 33.9, 26.1, 27.7, 6.9 and 3.5 (% dry wt.) for MF. While, 38.3, 35.3, 22.1, 2.7 and 1.6 (% dry wt.) for EFB, 20.8, 22.7, 50.7, 4.8 and 1.0 (% dry wt.) for PKS [20]. The percentage compositions of lignocellulosic play a vital role in the pyrolysis products yield. The lignocellulosic components of wood and Switchgrass were 35–50 and 30–50% cellulose, 20–30 and 10–40% hemicelluloses, and 25–30 and 5–20% lignin, respectively [36].

3.2. Proximate and elemental analysis

The results from the proximate analysis of oil palm biomass are given in **Table 2**. The moisture, ash and fixed carbon contents were 7.30, 7.51 and 10.09 wt% for EFB, 6.2, 7.02 and 15.83 wt%

Properties (wt%)	EFB	MF	PKS
Cellulose	39.80	32.60	20.70
Hemicellulose[b]	35.90	29.20	23.30
Lignin	20.40	27.90	49.50
Extractives	3.90	10.30	6.50
Moisture content	7.30	6.2	4.90
Volatile matter	82.40	77.15	75.40
Ash content	7.51	7.02	8.70
Fixed carbon[b]	10.09	15.83	15.90
Carbon	42.80	46.37	50.29
Hydrogen	6.20	5.52	6.35
Nitrogen	0.47	0.59	0.48
Sulfur	0.09	0.12	0.08
Oxygen[b]	50.44	47.47	42.82
HHV (MJ kg^{-1})	16.9	19.06	19.5
LHV (MJ kg^{-1})	15.5	17.9	18.1

[a]Weight percentage dry basis (wt%).
[b]By difference.

Table 2. Physiochemical properties of oil palm wastes.

for MF, and 4.9, 8.7 and 15.9 wt% for PKS, respectively. The volatile matter content was between 75 and 82 wt%, whereby EFB has high volatile matter than MF and PKS. Relatively, similar results in (wt%) can be found in the other study [28]. Comparing with other biomass sources, EFB has similar volatile matter content with Sawdust (82.20 wt%) and lower than that of Rice husk (61.81 wt%). However, the cotton stalk has high fixed carbon and high ash content than all the oil palm wastes studied [37]. The percentage of volatile matter, fixed carbon, ash content, and moisture are reasonable parameters of pyrolysis product yields. Jahirul et al. reported that the percentages of volatile matter, fixed carbon, ash content, and moisture are suitable parameters of pyrolysis product yields. Biomass with high volatile matter generates large amounts of bio-oil and syngas, whereas fixed carbon enlarges the biochar generation. Moisture content in biomass influences the heat transfer system with primary outcomes on product distribution. Also, an increase in moisture content increases liquid product yield and reduces the yield of solid and gas product. Which could be associated with the huge amount of condensate water generates from the moisture in the liquid phase [36].

The chemical composition of oil palm wastes stipulates the elements present. The results of the analysis in **Table 2** above revealed that the PKS comprises a high carbon content of 50.29 wt% and low oxygen content of 42.82 wt% than the contents in MF and EFB, respectively. The hydrogen, sulfur, and nitrogen contents were found to be respectively 6.20, 0.09 and 0.47 wt% for EFB, 5.52, 0.12 and 0.59 wt% for MF, and 6.35, 0.08 and 0.48 wt% for PKS. Other oil palm wastes such as oil palm frond and oil palm trunk have high and low content of oxygen (50.88 and 53.12 wt%) and carbon (42.76 and 40.64 wt%), respectively [38, 39], than EFB, MF, and PKS. For rice husk and Sawdust, they have a carbon content of 47.80 and 46.90 wt% [37] above that of EFB and MF.

3.3. Calorific heating value

The calorific value is used to measure the energy content and thermal efficiency of materials. In this work, the higher and lower heating values (HHV and LHV) of oil palm wastes was determined and calculated, respectively. The results acquired disclosed that the HHV of EFB, MF and PKS were respectively found as 16.9, 19.06 and 19.5 MJ kg^{-1} as shown in **Table 2**. Other fuels such as Sub-bituminous Malaysian coal and Olive husk possess a high heating value of 24.6 MJ kg^{-1} [23] and 21.80 MJ kg^{-1} [37], respectively in relative to oil palm wastes studied in this work. The LHV was computed to be 15.5 MJ kg^{-1} for EFB, 17.9 MJ kg^{-1} for MF and 18.1 MJ kg^{-1} for PKS, respectively.

3.4. Thermogravimetric analysis

Figure 8 displays the TGA and differential thermogravimetry (DTG) curves of the sample. The samples showed similar behavior during pyrolysis. The first small peak corresponds to the evaporation of moisture and the early weight loss at a temperature lower than 150°C for all the palm biomass samples. The degradation of hemicelluloses commences at temperatures of around 270°C for EFB, 290°C for MF, and 300°C for the PKS. It is reported by Sulaiman and Abdullah that DTG curves for PKS and MF attain separate peaks for hemicellulose at around 300°C and cellulose above 300°C [40]. In this study, the peak at about 310°C and the two peaks at 360°C correspond to the degradation of cellulose for EFB, MF, and PKS, respectively. Though the breakdown of cellulose and hemicelluloses is a constant progression, the weight loss of these constituents was sustained throughout nearly the whole heating period. However, the maximum decline speeds of the celluloses are between 300 and 360°C, and for the hemicelluloses,

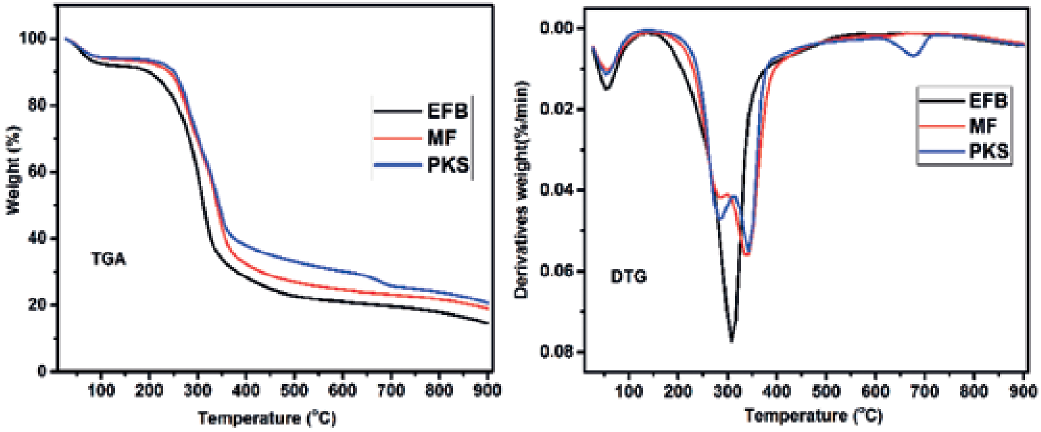

Figure 8. Thermal analysis (TGA and DTG curves).

they are between 270 and 300°C. The degradation of lignin is seen at 650°C, but PKS shows high resistance to temperature due to its high lignin content. The total weight losses between 100 and 450°C are 78.6, 75.71, and 98.5% for EFB, MF, and PKS, respectively.

3.5. Pyrolysis products yield

The biochar, bio-oil and gas yields obtained from the pyrolysis of oil palm wastes at a temperature of 400°C, a heating rate of 10°C min^{-1} and for 120 min holding time are shown in **Figure 9** for EFB, MF, and PKS. Jahirul et al. reported that the decomposition of lignocellulosic components relies on temperature, heating rate, and other contaminants because of their different molecular structures. Hemicellulose ordinary decomposes easily, followed by cellulose, while lignin decomposes at last. However, during pyrolysis lignin and hemicellulose do not affect each other but both can influence the pyrolysis of cellulose. They also reported that the percentages of volatile matter, fixed carbon, ash content, and moisture are suitable parameters of pyrolysis product yields. [36].

3.5.1. Biochar yield

As evident in **Figure 9**, PKS and MF were distinguished as the samples that yielded a huge quantity of biochar compared with EFB. The quantities of biochar yield were 42.11% for EFB, 45.12% for MF and 46.57% for PKS, respectively. The influence of lignin (fixed carbon) and cellulose on biochar yields were observed accordingly. It was shown in **Table 2** that PKS and MF comprehend eminent quantity of lignin and fixed carbon, and less amount of cellulose than did EFB and therefore, they give rise to a large amount of biochar compared to EFB. It is known that biochar is from lignin content. Thus, biochar elemental composition is near to that of lignin [36].

The yield of biochar could be associated with either primary or secondary decomposition of raw samples during pyrolysis which consequently influenced the pyrolysis conversion processes. Moreover, the disintegration of cellulose, hemicelluloses, and lignin during the pyrolysis plays a vital function in the yield of biochar [28, 41]. The high yield of biochar at low temperatures demonstrates that the material has been only partially pyrolyzed [41]. It

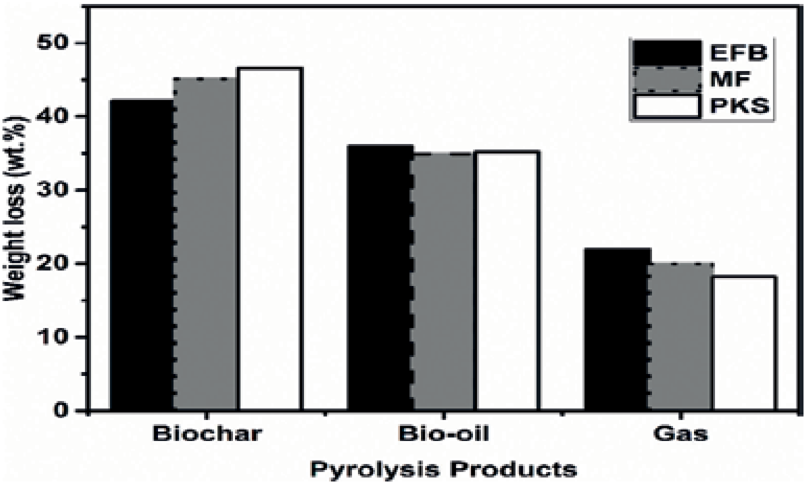

Figure 9. Pyrolysis products obtained from EFB, fiber and shell.

has been reported that during the pyrolysis process cellulose, hemicelluloses and lignin were respectively found to demonstrate the highest to the lowest disintegration rate. At temperature more than 400°C the cellulose content was almost pyrolyzed with a little quantity of solid remnant [42].

3.5.2. Bio-oil yield

The bio-oil yields as seen in **Figure 9** indicated that the quantity of bio-oil produced was between 34 and 35%. However, EFB and PKS produced the maximum and minimum quantities of 35.97 and 35.20% of the bio-oils, respectively. The fact that the EFB and MF generated a high amount of bio-oil than PKS could be attributed to the high amount of cellulose and hemicelluloses as shown in **Table 2**. It has been [36] noted that cellulose is principally responsible for bio-oil production during the pyrolysis of biomass (around 500°C). However, best quality of bio-oil can be generated from biomass with high lignin content. Biomass with high volatile matter generates large amounts of bio-oil and syngas. Moisture content in biomass has an influence in the heat transfer process with significant effects on product distribution [36]. The bio-oil binder viscosity has improved to 40 cP with addition of 10% starch from the initial value of 3 cP.

3.6. Combustion characteristics of charcoal briquettes and coal

The charcoal briquette samples produced, and its physical properties are displayed in **Figure 10** and **Table 3**, respectively. The physical and combustion properties of charcoal briquettes obtained in this work were compared with Malaysian sub-bituminous coal (Coal) for replacement purposes.

The proximate analysis and HHV of the charcoal briquettes are shown in **Table 3**. From the results, volatile matter, fixed carbon, ash, moisture content and HHV were respectively found to be between 41 to 49, 39 to 50, 6 to 11, 2 to 4 wt% and 23 to 26 MJ kg^{-1}. The maximum volatile matter of 49.74 wt% was received from EFB solid fuel, while the minimum value of 41.92 wt% was acquired from PKS solid fuel. Coal had shown the highest fixed carbon followed by MF, PKS and EFB solid fuels, respectively. The sequence of the calorific values was MF first, followed by PKS, coal and then EFB at last. The sequence could be according to the volatile matter

Figure 10. Charcoal briquettes samples.

Properties (wt%)	EFB	MF	PKS	Coal
Moisture content	4.23	3.87	2.91	2.65
Volatile matter	49.74	43.23	41.92	42.05
Ash content	11.20	6.61	8.15	7.44
Fixed carbon[b]	39.06	50.16	49.93	50.51
Carbon	58.11	62.93	65.07	64.66
Hydrogen	5.03	5.87	6.11	7.91
Nitrogen	0.97	0.98	0.93	1.16
Oxygen[b]	35.89	30.22	27.89	26.27
HHV (MJ kg^{-1})	23.93	26.15	25.99	24.21

[a]Weight percentage dry basis (wt%).

[b]By difference.

Table 3. Physiochemical properties charcoal briquettes and coal (solid fuels).

content and other factors present in the solid fuels that determine the quality of fuel. However, the low volatile matter and high ash content could make fuel difficult to ignite and thus, could not be recognized as good combustible fuel. Comparably, MF and PKS charcoal briquettes had higher HHV of 26.15 and 25.99 MJ kg^{-1}, individually than coal which has 24.21 MJ kg^{-1}, except EFB charcoal briquette which showed the lowest value 23.93 MJ kg^{-1}. Therefore, it can be said that all the charcoal briquettes showed similar properties with coal. And, therefore regarded as the best choice to replace coal.

It was previously stated that for a solid fuel to ignite and burn easily, it must contain a moderate percentage of volatile matter. It was observed that high moisture and ash contents could lead to ignition and other combustion difficulties [37, 43]. The significant benefits that biomass has as a combustion fuel are the high volatility and high reactivity of the fuel and the resulting char [44]. Based on these reasons, and since all the charcoal briquettes obtained in this study had similar properties or even better than coal, the choice of the best fuel is established on volatile, ash and moisture contents, respectively because of their role during combustion. All the solid fuels were subjected to combustion at 10°C min$^{-1,}$ and the results of combustion profiles acquired using DTG is shown in **Figure 11**.

Before analysis, the combustion temperature starting from 30 to around 850°C is partitioned into zones as shown in **Table 4**. It is seen from the figure that all the solid fuels showed a comparable peak between the temperature of 30 and 200°C. This peak could be ascribed to dehydration of moisture during the combustion. However, inside the primary zone, coal showed the highest weight reduction of 8.825 wt% and a peak temperature of 77°C, while MF demonstrated the least weight reduction of 3.382 wt% and a peak temperature of 59°C as seen in **Tables 4** and **5** respectively.

The second zone began from 140 and lasted to around 560°C. This zone showed the greatest weight reduction and most astounding peak temperature, and ignition temperatures. As apparent from **Table 5**, EFB and coal showed the most elevated weight reduction of 30.728

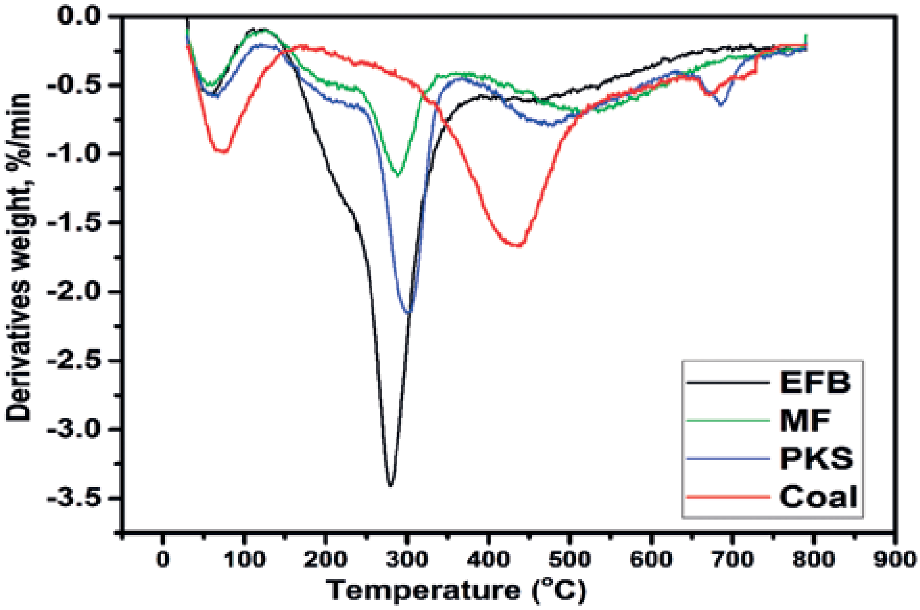

Figure 11. DTG curves for solid fuels combustion.

Solid fuels	Temperature intervals (°C)		
	First zone	Second zone	Third zone
EFB	30–140	140–360	360–644
MF	30–140	140–356	356–780
PKS	30–140	140–351	351–739
Coal	30–200	200–557	557–780

Table 4. Temperature intervals for different zones.

Zones	Weight loss, wt%			
	EFB	MF	PKS	Coal
I	3.539	3.382	4.461	8.825
II	30.728	12.00	18.868	29.603
III	14.408	20.247	21.62	10.278

Table 5. Weight loss of solid fuels at different zones, % by weight.

and 29.603%, individually. The ignition temperature of the solid fuels in **Table 6** was 235°C for EFB, 254°C for MF, 265°C for PKS and 368°C for coal. Along these lines, peak temperature took after ignition temperature and the value recorded was displayed in **Table 6**.

Temperature extends between 356 and 780°C is perceived as zone three. It can be seen from **Figure 11** that the rapid combustion of MF and PKS proceeded in this zone with a most extreme weight reduction of 20.247 and 21.62 wt%, individually as listed in **Table 6**. The recorded burnout temperature was 675, 788, 786 and 770°C for EFB, MF, PKS, and coal separately. The peak around 700°C for PKS could be because of the breakdown of calcium carbonate.

3.7. Heat generated from the combustion of solid fuel

The combustion period for solid fuels was around 45 min. The amount of fuel consumed, and time taken to reach burnout temperature for each fuel was ascertained. The time taken was evaluated and found to be 40, 44, 44 and 42 min for EFB, MF, PKS, and coal individually. Likewise, the burning rate and heat discharge from the initial temperature to burnout temperature was additionally determined as displayed in **Table 7**.

As seen from **Figure 11**, the solid fuels showed diverse conduct amid combustion particularly inside zones II and III. In this manner, the amount of fuel consumed ought not to be equivalent because the time taken for each fuel to approach the burnout temperature is additionally not equivalent. As apparent from the figure and **Table 7**, EFB fuel indicated high reactivity and therefore brought about high burning rate and heat discharge. The most extreme fuel consumed and heat discharge for EFB were separately observed to be 5.248×10^{-6} kg and 0.059 W. MF fuel discharge less amount of heat since it is less reactive as shown in **Figure 9** which prompted moderate amount of fuel consumed.

Nonetheless, low heat discharged by MF (0.048 W) amid burning could be identified with the low amount of fuel burnt (1.443×10^{-9}). Equivalently, combustion of MF, PKS, and coal may

Solid fuels	Peak temperature (°C)			Ignition temperature	Burnout temperature
	I	II	III		
EFB	57	280	472	235	675
MF	59	287	513	254	788
PKS	67	303	473	265	786
Coal	77	440	671	368	770

Table 6. Peak and burnout temperatures of solid fuels.

Solid fuels	Fuel burnt (kg)	CR (kg/s)	Heat release (W)
EFB	5.248×10^{-6}	2.187×10^{-9}	0.059
MF	3.810×10^{-6}	1.443×10^{-9}	0.048
PKS	4.830×10^{-6}	1.830×10^{-9}	0.051
Coal	5.001×10^{-6}	1.985×10^{-9}	0.052

Table 7. Combustion rate and heat release as at burnout temperature.

Solid fuels	Briquettes (ton)	Power (MW)
EFB	0.177	1.866
MF	0.212	2.055
PKS	0.228	2.414

Table 8. Power generated per 1 ton of raw oil palm biomass.

require higher temperature and longer burning time to finish the conversion. This might be because of the presence of a lot of inorganic material. It can, therefore, be presumed that MF fuel could be viewed as steady since it might deliver heat for an extended period.

It can be established from **Table 7** that in every 1 mg of EFB briquettes consumed; there is 0.0112 W of heat release. Therefore, based on these, the amount of heat that can be generated from 1 ton of EFB briquette is evaluated and shown in **Table 8**. It can be noticed that 1 ton of raw EFB can deliver 0.177 ton of briquettes which corresponds to 1.866 MW of heat. Furthermore, **Table 8** demonstrated that in every ton of raw MF, roughly 0.212 tons of briquettes could be obtained, which can give up to 2.055 MW of heat. For 1 ton of raw PKS, 0.228 tons of briquette can be delivered, and this connects to around 2.414 MW of heat.

4. Conclusion

During the combustion the primary zone, coal showed the highest weight reduction of 8.825 wt%. In the second zone, EFB showed the highest weight reduction of 30.728%. The rapid combustion of MF and PKS proceed in zone III with a most extreme weight reduction of 20.247 and 21.62 wt% individually. It was found that EFB is the easiest to ignite at 235°C due to high volatile matter content while MF attained the highest burnout temperature of 788°C. The maximum and minimum heat release of 0.059 and 0.048 W were obtained from the combustion of EFB and MF respectively. It was established that in each ton of raw (dry basis) of EFB, fiber, and PKS, there is 0.177, 0.212 and 0.228 tons of charcoal briquettes which corresponds to 1.866, 2.055 and 2.414 MW of heat respectively. Therefore, the findings in this study could contribute toward achieving the targeted 500 MW of green energy initiated in 2005 by the Malaysian government. It can also reduce dependence on fossil fuels for heat generation which in turn reduce the global warming, and minimize deforestation globally. Most importantly, the 100 million tons of oil palm wastes that will be generated in the year 2020 in Malaysia can easily be converted to useful products for heat generation. Also, application of various types of biomass for briquettes production can create job opportunities and enhance environmental sanitation in developing countries.

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Conflict of interest

The authors have declared no conflict of interest.

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Chapter 5

Pulp and Paper Potentials of Alkaline Peroxide Pre-Treated of Oil Palm Waste and Industrial Application

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Abstract

This chapter explores the potentials of the alkaline peroxide pre-treated oil palm vascular bundle (oil palm waste) in the industrial production of pulp, paper and other cellulosic products like microcrystalline cellulose. Management of this escalating waste is a herculean task and creates environmental hazards hence urgent action is needed to create value out of these waste biomass. The pulp and paper industry being a large consumer of lignocellulose materials preferred the use of coniferous and deciduous trees for pulp production and papermaking because their cellulose fibres in the pulp make durable paper. In addition to this, the global population explosion and the economic development has resulted in the significant increase in demand for paper. With improvements in pulp processing technology through the use of environmental benign technology like alkaline peroxide pre-treatment it has been considered as suitable for paper pulp and other cellulose based products such as microcrystalline cellulose. Characterization of the alkaline peroxide pre-treated oil palm vascular bundles using the scanning electron microscope (SEM), Fourier transmission infra-red (FTIR) spectroscopy and X-Ray Diffraction (XRD) analyses confirm the micro-sized cellulose fibres. Use of these lignocellulosic materials can reduce the burden on the forest while supporting the natural biodiversity.

Keywords: alkaline peroxide, FTIR, oil palm waste, pulp and paper, SEM, oil palm vascular bundle, industrial production of pulp and paper

1. Introduction

As the global demand for palm oil increases in the global markets, many tropical countries like Malaysia, Indonesia, Nigeria and others, have invested heavily in its plantation and production of Crude Palm Oil (CPO) and Palm Kernel Oil. Indonesia is the world's largest producer of palm oil contributing about 44% of the total world supply, which is followed by Malaysia, with 43% of the total world supply of palm oil (year 2006–2009) [1, 2]. The palm oil industry contributes $7.3 billion annually to the Malaysian GDP through export [3]. In Malaysia, over 75% of oil palm plantation in Malaysia spread within four states, which include, Sabah, Johor, Pahang and Sarawak, each of which has over half a million hectares under cultivation. It was reported that about 4.3 million ha lands were utilized for oil palm plantations in 2007 which has increased to 4.49 million hectares in 2009 and it is predicted that the annual production will be increased to 50 million tons by the year 2030 [4, 5]. With the proposed increase in the oil palm plantation, there is expected increase in the oil palm waste generation. From the present estimated 83 million tonnes (dry weight) of oil palm waste generated, Awalludin and coworkers [5] reported that, it is expected to rise by 40% dry weight by 2020. From the oil palm production activities, 10% of the products goes to the oil palm produce while the remaining 90% are considered as waste biomass [6]. These waste biomass include, Oil Palm Trunk (OPT) generated after 25 years replanting scheme and Oil Palm Fronds (OPF) generated during monthly pruning during and replanting season. Although these are either used as main source of energy for power generation in oil palm mills or as organic fertilizers for natural decomposition. OPF which is the largest waste generated through the activities of the oil plantation is reported to generate about 15 tons per hectare of dried of OPF and are pruned and left to rot away at the plantation site [7]. This has been reported to constitute environmental menace to the dump sites [8]. Mushtaq and coworkers [8] reported that during oil-palm fruit harvesting, about 44 million tonnes of OPF dry weight are generated. The management of these enormous wastes has demanded the attention of researchers to proffer ways of value addition. Other oil palm waste generated is empty fruit bunches (EFB) from the oil mills, oil palm shells, kernel cake and mesocarp fibres [9]. Apart from palm oil mill effluent (POME), other oil palm wastes generated are lignocellulosic wastes which represents an extraordinarily large amount of renewable bio-resource available in the universe and has wide array of applications as raw material especially for cellulose based materials [10].

The quality of the cellulosic products from this cellulose depends on the source of the original cellulose, the type of treatment and the kinds of the extraction procedures [11]. The effective utilization of lignocellulosic is conversely, not totally devoid of challenges. Among the range of the challenges associated with the use of lignocellulosic biomass apart from byproducts generated during pretreatment are, resistance of the plant cell wall due to integral structural complexity of lignocellulosic fractions and strong hindrance from the inhibitors [12]. Similarly, the knowledge of suitable pretreatment method and extent of cell wall deconstruction for generation of value-added products are equally very important in the choice of the pretreatment methods. The pretreatment techniques for overcoming biomass resistance could be selected over an array of methods which include: avoidance of cellulose fibre size reduction, preservation of the hemicellulose, minimization of bye products, reduction in energy consumptions, use of low cost pretreatment catalyst and should justify the cost of downstream processing steps [13]. Oil palm lignocellular wastes fibres have been proven to be suitable as ideal source for pulp and paper, cellulose based micro and nanofibres. It's a fast growing accumulation that has been considered as an advantage. Based on extensive studies on the use of cellulosic plant fibres for various industrial applications, oil palm wastes are reported as being sustainable, reusable, and eco-friendly. Research studies into the properties of the oil palm wastes show that the processing is cheap and low cost since they are considered as wastes. The polymer reinforced green composite obtained by their application has been characterize as having low energy consumption, light weight, low environmental hazard, and are renewable [14].

1.1. System with alkaline peroxide pretreatment of lignocelluloses

Hydrogen peroxide is a mild oxidant [15]. Its highest efficiency in bleaching and delignification is observed when the reaction is conducted in alkaline medium. In the presence of sodium hydroxide, and absence of any stabilizing agents like diethylenetriamine penta- acetic acid (DTPA), or ethylene diamine tetraacetic acid (EDTA) etc. hydrogen peroxide is unstable [16]. Hydrogen peroxide readily decomposes (Eq. 1) to generate more active radicals such as perhydroxyl acid, hydroxide ions, superoxides, which play prominent role in dissolving lignin hence releasing the fibre for paper making [17]. The mechanism of alkaline peroxide delignification reaction of hydrogen peroxide revealed that it is strongly pH dependent [18] with an optimum at pH 11.5–11.6, pKa for the dissociation:

$$H_2O_2 \Leftrightarrow H^+ + HOO^- \tag{1}$$

Under these conditions, the active species responsible for the elimination of chromophoric groups from lignin are hydroperoxide anion (HOO−) [19]. **Table 1** shows the list and characteristics of active radicals and anions from hydrogen peroxide decomposition in alkaline medium [20].

H_2O_2 decomposition products such as ·OH and O_2^{-}·, are the primary lignin oxidizing species. The delignification reaction witnessed the evolution of O_2 from the reaction mixture indicating H_2O_2 decomposition. The alkaline peroxide delignification procedure is a lignin-retaining bleaching of mechanical, thermomechanical, chemimechanical, and semichemical pulps [21].

Reactants	Name	Type	Nature	Function	pH range
HOO^-	Hydroperoxide anion	Anion	N	Reductant	Alkaline
OH^-	Hydroxide ion	Anion	N		Alkaline
HOO•	Hydroperoxyl Radical	Radical	E	Oxidant	Acidic
HO•	Hydroxyl radical	Radical	E	Oxidant	Acidic
O_{2^-}	Superoxide anion radical	Radical, Anion	N	Oxidant	Alkaline/neutral

Source: [20].

Table 1. Active radicals and anions from H_2O_2 decomposition in alkaline medium.

If the reaction contribution is not properly controlled, these radical materials are likely to redeposit on the biomass surface. Pulp brightness may be achieved by either lignin removal (delignification) or lignin decolonization [22]. This anion was found to be a strong nucleophile that is site specific, during bleaching, preferentially attacks ethylenic and carbonyl groups present in lignin. As a consequence, such chromophores as quinones, cinnamaldehyde, and ring-conjugated ketoses are converted to none chromophoric species [20]. On the other hand, radical species such as hydroxyl radicals (HO•) generated from the hydrogen peroxide alkaline decomposition, are responsible for delignification and solubilization of hemicelluloses [21]. Sequel to the mechanism of alkaline peroxide delignification, Gould [19] reported the use of alkaline peroxide in the delignification of agricultural residues to enhance enzymatic conversion of the cellulose-rich residue to glucose. According to the report, approximately one-half of the lignin is dissolved. Most of the hemicellulose present in agricultural residues such as wheat straw and corn stover was solubilized when the residue was treated at 25°C in an alkaline solution of hydrogen peroxide.

2. Characterization of alkaline peroxide pre-treated oil palm waste fibre

Screening the effect of the alkaline peroxide pre-treated vascular bundle fibre particles was carried out with three different alkaline peroxide concentrated liquors: low (H_2O_2: NaOH; 1.5:1.0), medium (H_2O_2: NaOH; 2.5:2.0) and high (H_2O_2:NaOH; 5.0:4.0) at alkaline peroxide pretreated oil palm frond vascular bundles (AP-OPF VB) reaction duration ranging from 10 to 60 min, with 0 min serving as control.

After the reaction period, the solid pulp was dried at 103°C and subjected to Fourier Transform Infrared (FTIR) spectroscopy to elucidate the changes in the functional groups predominating the samples before and after pulping. To further exploit the effect of the AP pretreatment, extracted cellulose fibre, crystallinity and the thermal analysis through the study of the thermogravimetry analysis TGA and derivative thermogravimetry (DTG) as reported by Lamaming and coworkers [22] were used to characterize the extracted cellulose fibres in terms of thermal stability, miscibility, and the reaction enthalpy that occur during the temperature-dependent phase transition. Also the TGA was used to characterize the thermal stability of materials through the study of the thermal degradation of the fibre at varying temperature. The knowledge of the X-ray diffraction pattern XRD of the cellulose fibres is used to estimate the purity of the AP treated biomass. This is based on the crystallinity values. The result and surface morphology of the produced OPF VB fibres and Handsheet were studied with the aid of the scanning electron microgram (SEM).

2.1. Evaluation of the pulp fibres from AP pre-treated OPF vascular bundles

Two-way ANOVA of the AP level and pretreatment duration as independent factors on the screened pulp properties (screen yield, kappa number and the CSF), the paper mechanical properties (Tensile, Burst and Tear indexes) and ISO brightness shows significant difference in the pretreatment study. The result shows that the time factor, the AP pretreated concentration factor and the interactive effect of the time and the AP treatment factors are statistically significant at 95% confidence level. This development led to the determination of the level of significant effect through post hoc test conducted on the AP pretreatment on the pulp and strength properties of the formed handsheet with the different alkaline peroxide dosage as displayed in **Table 2**. The significant differences in the AP concentration levels for the homogenous subset of all the independent variables namely: Screened yield, kappa number, Canadian freeness test (CFS), Tensile, Burst and Tear indexes and ISO brightness (**Table 2**) shows that the pulp and paper properties increased with an increase in the AP concentration. The result shows best pretreatment is obtained for papers prepared at a high concentration of AP pretreatment. The differences among the alkaline peroxide concentration pretreatment levels were tested, by using Duncan Multiple Range test and the significant distinctions are denoted by letters a, b, and c (**Table 2**).

From the result obtained, there is generally increase in the pulp and paper properties investigated with the AP pretreatment of the oil palm vascular bundles, with the increase in the AP concentration. The increase in the pulp and paper properties as observed with increase in the AP concentrations is attributable to the dissolution of lignin fragment and the loss of some extractives from the OPF VB. This shows that an increase in the concentration of AP results in gradual reduction in lignin molecule and hemicellulose removal. A reverse trend, however, was obtained for high AP concentration in the screened yield. A general drop in the pulp screened yield between 50.44 and 57.70% was apparent at high AP concentration. This observation could be attributable to the gradual increase in the rate of lignin dissolution resulting in the lignin modification and hemicellulose loss as conspicuously shown on the result obtained from the TGA/DTG curves and FTIR spectra (**Figures 1–4**) respectively. The decline in the screened pulp yield obtained at high AP concentration is also attributable to the high rate of micro-to-nano scale cogenerated fibrils that escaped the P200 screen during screening stage, resulting in low screened pulp yield. This presence of these fines particles enhances the water retention of the pulp web resulting in the low value of the CSF as shown in **Table 2** at high AP concentrations. Conversely, an increase in alkaline peroxide level is attributable to better extent of lignin removal. As a result, an increased amount of delignification agents was available to access the more remote chromophoric groups within the OPF structure. This

Treatment	PH	Yield (%)	Kappa Number	CSF (ml)	Tensile Index (mN/g)	Burst Index (kpa m^2/g)	Tear Index (mN m^2/g)	ISO Brightness
Low	13.45	40.21b	114.55a	780a	1.59c	2.87c	2.33b	28.528a
Medium	13.70	42.67a	101.10b	550b	9.085b	5.95b	5.37a	27.806b
High	14.00	38.07c	91.20c	241.67c	13.34a	7.90a	5.63a	24.183c

Means within a column with different letters are significantly different at $P < 0.05$.

NB: a = Highest significant; b = Lower significant; c = Least significant.

Table 2. DMRT for AP significantly different effects on pulp and paper properties.

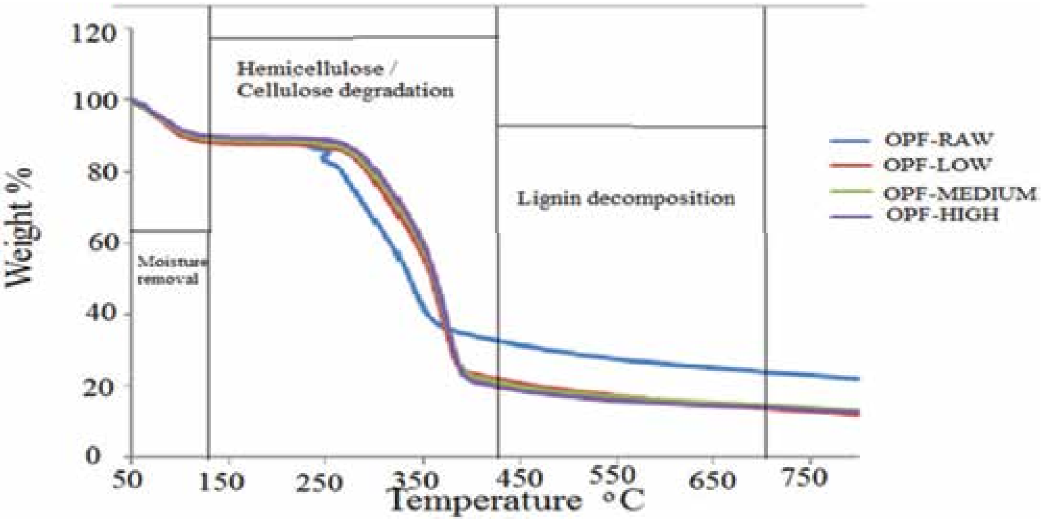

Figure 1. TGA curves for OPF vascular bundle fibres [7].

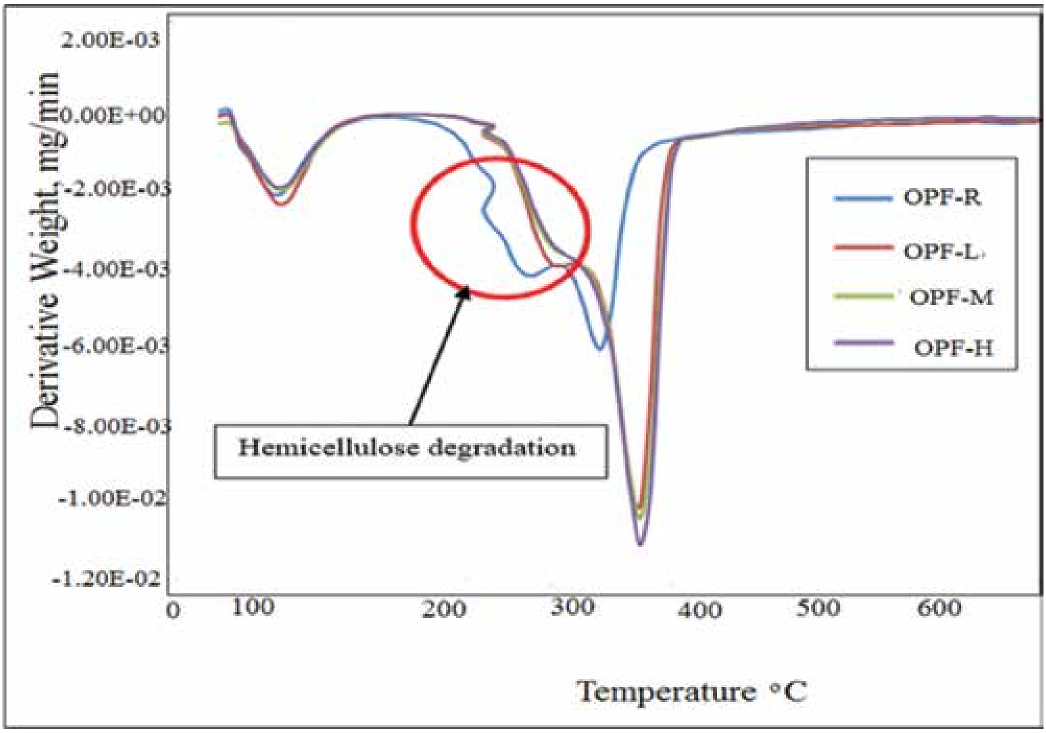

Figure 2. DTG curves of the raw and extracted OPF vascular bundle fibres [7].

contributed to the low Kappa number obtained at high AP concentration **Table 2**. Despite the general decrease in the Kappa number with time with the increase in the concentration of chemical charge, the high Kappa number results (**Table 2**), is attributable to the weak oxidizing

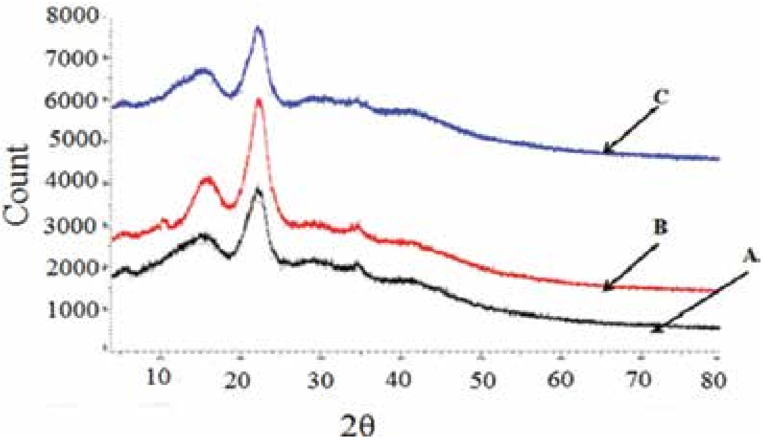

Figure 3. X-ray diffractometry patterns of APMP pulp from OPF vascular bundles [7].

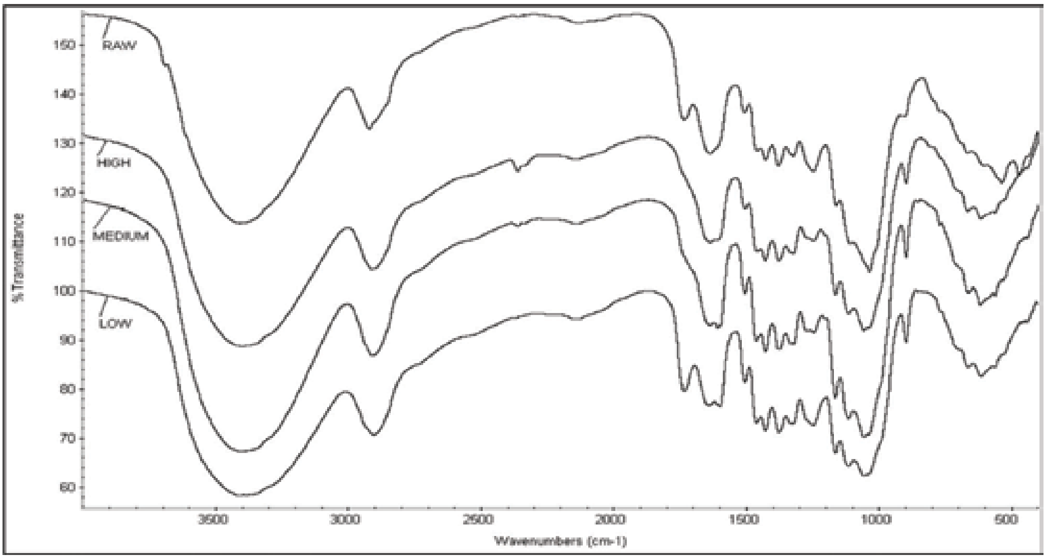

Figure 4. FTIR spectra of OPF vascular bundle fibres at different AP pretreatment.

power of alkaline peroxide [23]. About 50% lignin was reportedly removed from a couple of lignocelluloses biomass (corn stover, oak shavings, kenaf, straw and wheat straw, which has been reported possessed similar morphological properties) treated with 2% (w/v) solution of alkaline peroxide [15]. Also, the same observation was reported when alkaline peroxide was optimized at 8.6% (w/v) [19]. With the treatment of alkaline peroxide for wheat straw, 60% reduction in lignin was recorded [23]. A similar result was reported by sun and coworkers [17] that treatment with the alkaline solution of hydrogen peroxide on rye straw resulted in 60% delignification. The overall result shows a reduction in the lignin by 25.56, 32.05 and 38.43% for pulp generated from the low, medium and high AP concentration pulping system. Since Kappa number is a measure of the total amount of residual lignin in the pulp that is oxidizable with $KMnO_4$, its value is used to determine the residual lignin content in the pulp. Result in **Table 2** also shows that the optical properties are significantly affected by the AP pre- treatment concentration. The decrease in brightness at high concentrations of the AP liquor is attributable to the redeposition of the alkaline leachate on the surface of the biomass hence resulting to the phenomenon of alkaline darkening. This is similar to the observation reported by Liu and co-workers [24].

3. Characterization of alkaline peroxide pre-treated OPF fibres

The extracted fibres were next characterized for their thermal properties and functional groups.

3.1. Thermal characterization of OPF AP pulp

Thermogravimetric analysis (TGA) was measured to access the thermal stability of the extracted fibres. It provides quantitative information on weight change during heating process [25]. From the result shown in **Figures 1** and **2**, the thermogravimetry analysis TGA and derivative thermogravimetry DTG curves obtained for both the raw and the extracted OPF fibres at different AP concentrations. Where (a) untreated represents fibre OPF-R, (b) Fibre pre-treated at 1.0% NaOH: 1.5% H_2O_2—OPF-LOW, (c) Fibre pre-treated at 2.0% NaOH: 2.5% H_2O_2—OPF-Medium, and (d) Fibre pre-treated at 4.0% NaOH: 5.0% H_2O_2; OPF-High AP concentrations. From the graph, the initial weight loss was observed to occur between 50 and 106°C for the raw sample while the weight loss for the extracted samples were observed between 50 and 110; 50 and 118 and 50 and 119°C for cellulose from low; medium and high AP concentrations, respectively. This first stage of weight loss, which is not accompanied with samples thermal degradation, corresponds to loss in the volatile materials and vaporization of water because of the hydrophilic nature of the lignocellulose fibres in all the samples [26]. The second stage of weight loss, was observed between 230 and 282; 262 and 366; 254 and 366; and 270 and 366°C for raw and the extracted fibres at low, medium and high AP concentrations, respectively. This corresponds to hemicellulose, pectin and cellulose degradation as previously found by Eriksen and coworkers [27].

From DTG (**Figure 2**), the maximum thermal degradation peak corresponds to 342; 366; 374 and 382°C for untreated OPF fibre and cellulose fibres obtained at low, medium and high AP concentrations, respectively and this corresponds to the decomposition temperature of cellulose [28]. This weight loss was attributed to thermal depolymerization and cleavage of the glycosidic linkages of cellulose [29]. From the DTG curves (**Figure 2**), the lower temperature peak at around 290°C was observed from raw (untreated fibre) and AP extracted fibres at H_2O_2: NaOH 1.5:1.0, corresponds to the decomposition of hemicellulose [25]. This temperature peak was found to shift to a higher temperature and remained as a shoulder for AP-treated fibres at H_2O_2: NaOH of 2.5:2.0 and H_2O_2: NaOH of 5.0:4.0, indicating partial removal of hemicellulose from the fibre. From the DTG result it could be deduced that, the extracted cellulose has higher thermal stability than the raw OPF fibre. The third decay stage of the thermal decomposition graph, presents thermal degradation peaks of lignin compound as a result of the breakdown of ether and carbon–carbon linkages [30]. With further heating beyond 400°C, all the fibres at the specified AP concentrations, had residual weight of approximately 27.47, 12.71, 13.55 and 13.34% for untreated OPF fibre and cellulose fibres obtained at low, medium and high AP concentrations, respectively. The residual char obtained at the end of the heating exercise was ascribed to the combination of the residual lignin and ash in the samples. This is in line with the result of Rosa et al. [30], and Sonia and Dasan [26]. The amount of the residual char after the thermal decompositions reflects the amount of residual lignin and the ash. The result shows that the residual char reduces significantly compared to the raw OPF-VB biomass. This is attributable to the successful removal of the amorphous part of the extracted fibres [22].

3.2. X-Ray diffraction

The cellulose chain contains the crystalline (ordered) regions and the amorphous (disordered) regions [29]. **Table 3** shows the values of the fibre crystallinity of the OPF-VB fibres obtained from AP pretreatment systems. Crystallinity values are calculated by the formulae reported by Segal and team [31]. From **Table 3**, it is evident that there is an increase in the cellulose crystallinity as the alkaline peroxide concentrations increases from low AP concentrations to the medium AP concentrations. The percentage crystallinity dropped for fibres extracted at high AP concentrations.

The observed drop in the percentage crystallinity of the extracted fibre at high AP concentrations was as a result of a high amount of fines generated in the high AP concentration in the AP pretreatment system. This is in line with the observation reported by Segal and team [31] who similarly witnessed the loss of crystallinity upon excessive refining. Similarly, both Habibi and coworkers [32] and Lamaming and team [20] independently reported changes in crystallinity index of the respective substrate due to pretreatment. Trache and coworkers [33] reported that during refining, the intermolecular hydrogen bonds of cellulose are broken, causing the collapse of the crystal structure of the cellulose fibre. The x-ray diffraction patterns of the cellulosic fibres at different AP concentrations are shown in **Figure 3**, matching with the monoclinic sphenodic structure characteristic of cellulose 1 polymorph (which is unmodified form of natural cellulose) [34]. The similarity in the three X-ray diffraction patterns in **Figure 3** shows that the AP treatment at different concentrations maintains the natural cellulose 1 polymorphs structure of the biomass.

AP fibre Samples	Crystallinity
Low-AP	28.1%
Medium-AP	35.7%
High-AP	27.4%

Table 3. Crystallinity index of the OPF VB fibres.

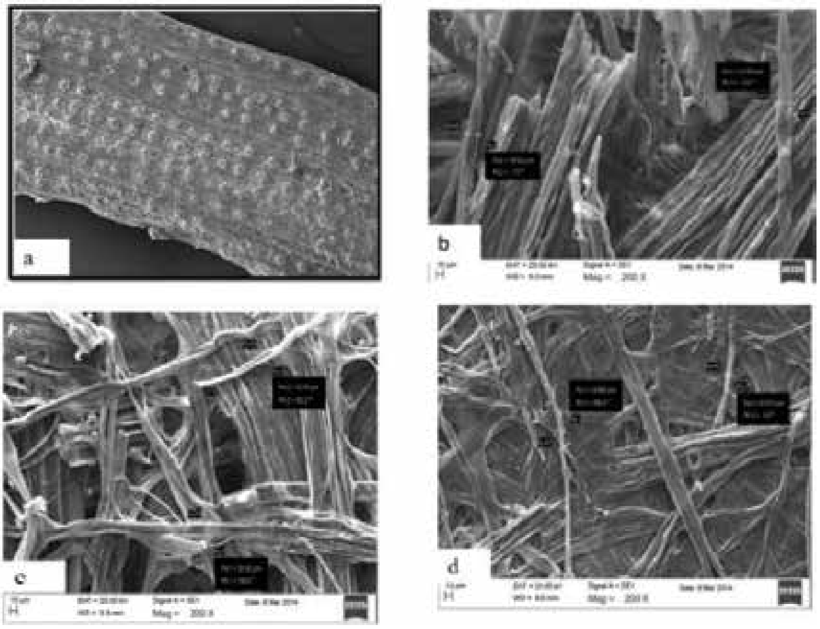

Figure 5. SEM images of (a) Raw OPF sample (b) AP treated fibre at low AP concentration (1.0 :1.5), (c) AP treated fibre at Medium AP concentration (2.0 : 2.5) and (d) AP treated fibre at high AP concentration (4.0 : 5.0) paper web at different AP concentrations.

It is evident from **Figure 5** that the peaks at 22.20°, 22.40°, and 22.10° corresponding to A, B, and C, respectively are characteristic of native cellulose I polymorph [20, 31]. The X-ray diffraction technique revealed that the extracted cellulose fibres could be easily hydrolysed into the crystalline sample. Due to the softening effect of the treated fibres at high AP concentrations, the high fibrillations, cell wall delaminations aid the production of fibrillar fines at high AP concentrations; expose the crystalline cellulosic materials in OPF in a more profound manner.

The observed drop in the fibre crystallinity observed at high AP concentration treatment is attributable to the presence of certain threshold of fines content in the pulp. In a separate reports, Segal and coworkers [31] reported that fibre crystallinity could be lost by refining while Rafiee and Keshavarz [34] reported that fibre crystallinity could be lost due to high chemical treatment. This trend in the fibre crystallinity is in agreement with the report in the literatures [34]. The X-ray diffraction technique revealed that the extracted cellulose fibres could be easily hydrolysed into the crystalline sample.

3.3. Correlation between FTIR spectroscopy, DTG and XRD

The FTIR spectra of the raw and pulped fibres are shown in **Figure 4**, which shows the FTIR spectra of OPF fibre (A) Raw OPF vascular bundle fibres (B) OPF isolated at 1.5%:1.0%; H_2O_2:NaOH AP concentrations (C) OPF isolated at 2.5%:2.0%; H_2O_2:NaOH AP concentrations (D) OPF isolated at 5.0%:4.0%; H_2O_2:NaOH AP concentrations. Analysis shows that despite the similarity, there are some shifts, disappearance and appearance of some signals of samples after APMP process. This is apparent from the result in **Figure 4**. From the result, among the common bands were the 3400–3300 cm^{-1} region, which is attributed to the stretching of O-H groups, whereas those around 2900–2800 cm^{-1} were due to the stretching of C-H [20]. The appearance weak band at 2362–2135 cm^{-1} for the AP pretreated pulp at different concentrations is attributed to the C-C stretching vibration. This peak could be the result having phenyl ethynyl group that was generated during lignin dissolution [35] suggesting also lignin dissolution with AP treatment. The peak located at 1734 cm^{-1} in the raw OPF was assigned to the C=O stretching of the acetyl group in hemicellulose [37] or ester linkage of the carboxylic group in the ferulic and p-coumaric acids of either lignin or hemicelluloses [36]. The FTIR spectra reveal (as shown in Section 4) a shoulder at 1733 cm^{-1} for fibres generated via AP pretreatment system employing the medium and high AP concentrations. This characterizes the significant dissolution of hemicelluloses with the medium and high AP systems, in agreement with the DTG result in **Figure 4**. This observation is in contrast with the report by Ghazali and co-workers [17] that an increase in alkaline solution of hydrogen peroxide concentration caused an increase of lignin oxidation through a reduction in the aromatic rings. The peak at 1247 cm^{-1} could also be associated to the C=O stretching of the aryl group in lignin [35]. The shift of this peak coupled with weak absorbance was believed to be due to the reduction of lignin after the chemical treatments, while the weak signal indicates the presence of residual lignin [22]. The absorbance between 1426 and 1427 cm^{-1} for the raw OPF and OPF pulps is associated to the CH_2 symmetric bending [14]. The stretching of C=O and O-H can be observed as peaks around 1112–1114; 1054–1056 cm^{-1} and 897 cm^{-1} in all the pulp samples.

It is characteristic of glycosidic linkage between sugar unit samples [33], which are not present in the spectra of the raw samples. The absorbance peak at 1160–1164 cm^{-1} in the OPF raw sample and pulp is due to the anti-symmetrical deformation of the C-O-C band [36]. However the vibration peak at 897 cm^{-1}, which was absent in the raw sample, appear in the OPF pulp at the various concentrations. This was assigned to the glycosidic bonds, which are symmetric in polysaccharides [35].

3.4. Effect of alkaline peroxide pretreatment concentration on paper properties

Statistically, significant differences in the effects of AP concentration treatment level on the strength properties (tensile index, burst index and tear index) are also shown in **Table 1**. The ANOVA result shows that all the paper properties are significantly affected by the AP treatment except the burst index. The study showed that increase in the AP concentrations enhances the strength properties of the paper formed, which is in agreement with the trend already established with the paper apparent density. The impact of the high AP level on the fibrillation of OPF vascular bundle fibres become more apparently portrayed on the pulp web strength properties, and this stems from the higher probability of the lignin transformation to low molecular weight fragments and hence easily leached at high AP concentration treatment [17]. Furthermore high AP concentrations level produces higher fibrillation, which enhances fibre bonding and reduces fibre coarseness, thus leading to improved mechanical strength of the paper. Unlike the other strength properties, the ANOVA for AP treatment and time effect on AP strength properties (**Table 1**), the burst strength show no significant effect on the AP and time interaction effect. This observation is attributable to the fact that the bursting strength of paper is a composite strength property that is affected by various other properties of the sheet, principally tensile strength and stretch [27]. The reason for the low burst index at low and medium AP concentrations is attributed to the presence of hemicellulose in the pulp fibre [27]. The extraordinary improvement in the burst index at high AP concentrations is attributed to the refining effect of well softened OPF biomass. The refining process is expected to increase the fibre swelling, hydration and extend of fibrillation degree, which result in an improved fibre flexibility and thus, bonding and strength of the paper. This enhances paper physical properties and burst index [22].

3.5. Surface Morphological Transformation of Papers from OPF

The paper samples obtained from the three AP pre-treatment concentrations (Low, Medium and High) were examined with Scanning Electron Microscope analysis (SEM) (**Figure 5**) to monitor the morphological transformation of the paper surface.

Figure 5 shows SEM images of (a) raw OPF vascular bundle and (b–d) handsheet surface corresponding to AP of (b) low; (c) medium; (d) high AP concentrations.

Overall as apparent in SEM analysis, the alkaline peroxide pretreatment has two effects on the fibre: In synergy with refining it increases the uniformity of paper arising from better interlocking of fibre and because of the softening effect of the alkaline peroxide chemical treatment, the treated samples displaced a greater degree of fibre collapsibility at high concentration. It exposes more cellulose of the biomass by modifying the lignin and leaching out the fragmented lignin.

4. Conclusion(s)

The study revealed that alkaline peroxide pretreatment of the OPF-VB at various AP concentrations produced a high quality pulp that could be attributed to easier fibre extraction from the biomass. Apart from the physical and mechanical properties, spectroscopic analyses confirm the ability of the pulping protocol to effectively remove non cellulosics such as hemicelluloses, reduce the lignin content while realizing pulp and paper of high ISO optical brightness. The thermal analysis showed that the AP pretreated cellulose fibres have higher thermal stability than the raw sample, which made them suitable as biodegradable raw material in the polymer composite. The FTIR spectra is consistent also with the crystallinity values of the extracted cellulose fibres, which increased with an increase in the AP concentrations but decreased at high AP concentrations due to an increasingly generated fines materials, forming as a result of disruption of fibrous cell walls. The study showed that these extracted fibres will be useful in paper production and with further processing could be used as raw material for biodegradable composites with improved qualities.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Oleochemicals from Palm Oil for the Petroleum Industry

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Additional information is available at the end of the chapter

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Abstract

Waste vegetable oils as a sustainable, low-cost and low-toxicity feedstock are attracting more interests for the production of oleochemicals that are excellent substitutes for petroleum-based chemicals widely used in the petroleum industry. The compounds resulting from transesterification-epoxidation-sulfonation of waste vegetable oils have great potential as bio-based surface active agents with extensive application in the petroleum industry. The oleo-surfactant from vegetable oils is gaining increasing attention as alternative to the costlier and non-biodegradable petrochemical-based surfactants currently in use. This chapter reports on cost-effective processes to convert waste palm oil into high-grade surfactants aiming at its filed application in petroleum production to enhance recovery of crude oils from reservoir. The first section focused on the formulation of a high-performance bifunctional solid catalyst with basic and acidic sites that are able to mediate simultaneous esterification and transesterification reactions. In the second part, the methyl esters were epoxidized and then sulfonated to produce the anionic surfactant. The feedstock and the methyl ester produced were analyzed with gas chromatography-mass spectrophotometer (GC-MS) and the sulfonated functional group (S═O) was detected using Fourier-transform infrared spectroscopy (FTIR) analysis.

Keywords: oleochemicals, waste palm oil, surfactants, bifunctional catalyst, esterification, transesterification, epoxidation, sulfonation, enhanced oil recovery

1. Introduction

A cost-effective and sustainable supply of energy sources is of enormous importance to the economy and national security. Oleochemicals are chemicals derived from sustainable resources that are majorly oils and fats of vegetable and animal origin [1]. These resources are widely available or can be easily cultivated (virgin vegetable oils) or cheaply sourced (waste vegetable oils and animal fat) in virtually all parts of the world. These ecological and economic advantages are responsible for the growing importance of oleochemicals as energy resources and intermediates for manufacturing of industrial chemicals [2, 3]. This is responsible for the renew research interest in oleochemicals as one of the most cost-effective and widely available substitutes for a number of industrial chemicals and fuels currently derived from fossil fuels [2, 4].

Basic oleochemicals include fatty acids, methyl esters, fatty alcohols of these fatty acids and glycerol [1, 5] as well as fatty amines [6]. With a better understanding of oleochemistry, researchers now variously functionalize triglycerides in vegetable oils to manufacture different useful products [7]. The structure of oleochemicals with the presence of long-chain methylene sequences facilitates a ready functionalization into a wide range of products [8]. The approaches include epoxidation, acrylation of epoxies, transesterification reactions [7, 8] and amidation and amination to generate esters, amides and amines [1]. The sustained interest in the chemistry and conversion of fats and oils and the industrial applications of the bio-based or oleochemicals produced therefrom is being spurred by many factors. Prominent among the drivers is the fast depletion of the world fossil resources, the concern over extreme climatic conditions [7] leading to more stringent environmental standards and regulations and the growing demands for green fuels and cleaner technology with significantly reduced carbon and environmental footprints.

Also there is a growing surplus of fats and waste vegetable oils worldwide resulting in disposal and management challenges. Chhetri et al. [9] citing several sources reported that in 2008, the US produced about 100 million gallons of waste vegetable oil every day. The figures are 135,000 tons/year in Canada, 900,000 tons/year in EU countries while UK produced over 200,000 tons per annum. This is in addition to millions of tons of chicken fats being produced globally every year. The use of waste vegetable oils and non-edible oils in the production processes in place of refined vegetable oils has led to a significant improvement in the economics of oleochemical processes [5]. The conversion of the hitherto waste materials into industrial fuels and chemicals also significantly reduce the environmental impact of the production processes [5].

These have led to the growing awareness of the potentials of waste vegetable oils as sustainable and cost-effective feedstock [10] for the production of industrial chemicals and as energy carriers. Methyl esters produced from the transesterification of triglycerides molecules in the vegetable oils and animal fats with an alcohol [11] are used directly as green fuels (due to its lower emissions of particulate matter and greenhouse gasses) and as chemical intermediates due to its high functionality. Also aiding the extensive uses is the fact that vegetable oils are inherently biodegradable as well as its low toxicity [7]. Epoxidized methyl esters from vegetable oils are used as chemical intermediate to manufacture a variety of industrial chemicals that are ready substitute for petrochemicals [7].

Surfactants are employed in all stages of petroleum production and processing. Usual applications include the use of non-ionic surfactants as demulsifying agents [12], anionics as defoamers and amphoterics and cationics as corrosion inhibitors and biocides [13]. Surfactants are also essential additives in drilling process operations [14] to reduce water loss and as additives in drilling, completion and fracking fluids to enhance lubricity (for better flow) and pumpability (to control foaming) [15]. It is also put into effective use in the clean-up of crude oil spillages serving as oil slick dispersants or spreader [16] or as oil herder for easy burning [17]. The world production of synthetic surfactants reaches 13 million tons annually, making it an economically important chemical [18].

However, commercial surfactants used in these processes are usually expensive and required in large quantities which limit the economics of the process [19]. Most of these petroleum-based surfactants are also toxic raising concern of their environmental impact [20]. Thus, a less hazardous and cost-effective but high performance surfactant formulation for an efficient oil recovery is required. These have led to interest in green and cost-effective processes for the manufacturing of commercial surfactants from sustainable feedstock [21]. Bio-based surfactants, due to their biodegradability and lower critical micelle concentration [22] are therefore becoming more attractive for the application in the petroleum industry [12]. It was reported that the global biosurfactant market value is expected to grow to around $25 billion by 2018–2020 [23].

Surfactant is one of the oleochemicals that can be produced from epoxidized methyl esters from palm oil [1]. The sulfonation of the esters has been used to produce methyl ester sulfonate surfactants [15, 18]. The anionic surfactant possesses good surface-active properties [15], excellent detergency and is less sensitive to water hardness [24]. It is therefore projected that the global market for methyl ester sulfonates will experience significant growth as demand for biodegradable surfactants increases [18]. The first-generation feedstock employed to obtain the esters are coconut and soybean oils [25]. These edible oils still dominate the process accounting for more than 95% of biodiesel production [26]. Though easily cultivated and produced, these are relatively costly feedstock and have been the food materials that have ignited the food versus fuel issue [26]. Also, as the cost of edible oils rise due to growing demands, the cost of their derivative surfactants will increase as well [27].

This led to the interest in employing waste vegetable and non-edible oils as the preferred feedstock for commercial production of alternative surfactants [28]. However, a wider utilization of waste vegetable oils for bio-based chemicals production is still limited by the cost of pretreatment [2]. The poor quality of the waste vegetable oils due to high content of free fatty acids and water poses some challenges. Of equal interest is the heterogeneity of these cheap feedstocks in terms of compositions that necessitate pretreatment steps which led to increased cost of production and lower the competitiveness of the bio-products against petroleum-derived alternatives. This chapter presents cost-effective processes to produce a sulfonated surfactant from waste palm oil using heterogeneous bi-functional solid catalysts.

The goal is to synthesize a cheaper and less hazardous surfactant that will be both economical and effective for surface activity as well as reservoir rock wettability alteration to achieve a significant improvement in oil recovery.

2. Application of surfactants to enhance oil recovery

Surfactants are surface active polymeric molecules that contain amphiphilic molecules with hydrophilic part (that is, water soluble or polar) and a hydrophobic or lipophilic part (that is, oil soluble or nonpolar) [29]. These moieties will therefore partition preferentially at the interface of a immiscible fluid system with different degrees of polarity [29]. When introduced into a water-oil system for instance, the surfactant hydrophilic head interacts with water molecules and the hydrophobic tail interacts with the trapped oil [30]. Hence, they dissolve in both aqueous phase (water) and oleic phase (or organic solvents) resulting into reduced interfacial tensions between the phases. They as well alter the wettability of the reservoir rock surface by adsorbing to the liquid-rock interface, thus making the rock surface have a strong attraction toward one of the immiscible fluids, preferably water [31].

In petroleum production, crude recovery from matured fields are declining at a rate faster than the discovery and production of new fields needed to maintain or increase the production rate to meet the energy demand. Therefore, resources are being committed to maximize oil recovery from matured reservoirs and tight rock formations. More than half of the original oil in place (OOIP) remains trapped in the petroleum reservoirs, after conventional production operations. This is attributed to poor sweep efficiency and oil droplets trapped by capillary forces due to high interfacial tension (IFT) between oil and water. There is therefore the need to economically recover more of this residual (or tail end) crude in declining and abandoned wells [12].

More effective enhanced oil recovery (EOR) methods that ensure an economical production of the tail end (trapped oil) from these oil fields are being continuously researched. Such technologies include thermal flooding (steam injection, in-situ combustion), chemical (surfactants, polymers, solvents, alkali) flooding, miscible and immiscible gas displacement, and microbial EOR to produce the hard-to-recover oils in older fields [32–34]. Among these techniques, chemicals flooding techniques have emerged as one of the most effective techniques to improve crude oil recovery from maturing fields. Chemicals (also referred to as micellar) flooding is widely employed due to ease of application and availability of wide range of chemicals. It involves injections of surfactants, polymers and alkali, and their various combination into the reservoirs to mobilize the trapped oil and improve recovery [35].

The alkali-surfactant-polymer (ASP) flooding is the most cost-effective technique, so far having recorded as much as 68% improved recovery from abandoned and depleted oilfield, particularly field past its peak production stage. ASP flooding involves the injection of a mixture of alkali, surfactant, and polymer into the reservoir. It is an effective chemical EOR technique due to the fact that it employs the synergy of the three techniques [35]. It has been employed in the oil industry to, among others, allow for better sweeping of the reservoir by lowering the interfacial tension (IFT) between oil and water (by the surfactant), alter reservoir rock wettability from oil wet to water wet (using the alkali), and to increase the crude mobility ratio (with the polymer). The technique has resulted considerably to improve the recovery factors at additional cost estimated to be as low as US$2.42 per additional barrel for an onshore field.

A microemulsion of hydrocarbons and water dosed with a large amount of surfactants was found to significantly improve crude recovery [36]. Surfactant flooding is widely employed to manipulate the phase behavior of the reservoir fluids to counteract the high capillary force trapping oil in the pores of the reservoir during enhanced oil recovery process [21, 37, 38]. Surfactant improves the microscopic displacement efficiency by lowering the interfacial tension between oil and water to form a highly stable water-in-oil emulsion as well as between crude oil and rock thus increasing the capillary number, which combines to facilitate greater mobilization of the oil droplets trapped in the reservoir rock [35, 39, 40]. The surface active chemical promotes the formation of microemulsions at the crude oil and the displacing fluid (mostly water) interface [41, 42] thus causing a significant lowering of the fluids' interfacial tension. This is required to efficiently mobilize a substantial percentage of the residual oil toward the production wells to enhance overall crude recovery [43]. Behind the oil bank, the surfactant prevents the mobilized oil from being re-trapped [44].

In the 2000s, oil fields subjected to surfactant-polymer and ASP flooding yielded higher oil recovery compared with those in the late 1970s and 1980s [25]. Improvement in the chemical functionality as a result of better insight into the process schemes is the principal reason for this accomplishment [21]. Since then, surfactants have been considered as an excellent enhanced oil recovery agents due to their ability to considerably reduce the interfacial tension and modify reservoir wetting characteristics. Depending on the nature of the hydrophilic group (head group), the surfactants are classified as anionic, cationic, zwitterionic or amphoteric or nonionic [45]. Typically in this field, anionic surfactants are used in sandstone rock matrices while for carbonate rocks, cationic amphiphiles are surfactants that are more effective. Nonionic surfactants are ideal for high salinity reservoirs, but are most often used as co-surfactants due to their lower surface activity ability [35, 45].

A major challenge with micellar flooding is the loss of surfactant through interaction with reservoir rock [46] and surfactant partitioning into the oil interface [47]. The high cost of production of surfactants makes this potential loss an issue. As previously mentioned, most of the commercial surfactants are petroleum-based and toxic raising concern of sustainability and environmental impact [20]. It is therefore imperative to find alternative, environmentally friendly, and cost-effective processes to produce surfactants on industrial scale from sustainable feedstock. Oleochemical surfactants aside from being biodegradable and less toxic possess other excellent properties suitable for several potential applications in the petroleum industry and a good substitute for the petroleum-based commercial surfactants. These include functionality under extreme conditions and the inherent high specificity [48].

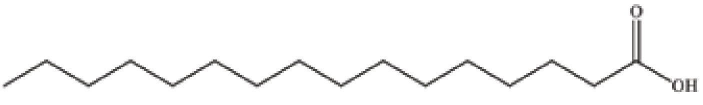
3. Production of methyl esters from waste palm oil

Fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE) are produced from transesterification of glycerides with methanol and ethanol, respectively. The triglycerides which serve as the starting material for the alkyl esters production are found in all vegetable oils, and other edible oils [49] and animal fats. Conventional feedstocks for the alkyl esters production are vegetable oils from palm, sunflower, groundnut, soybean, cotton, coconut, rapeseed, palm kernel, olive and nonedible oils (for instance, oil from Jatropha, sesame, rubber seed, tobacco seed, rice bran, camelina, and karanja) [50]. Other renewable resources such as oils from plant carbohydrates, sucrose, glucose, sorbitol, starches, animal fats and so on, have also been reported for FAME production [51].

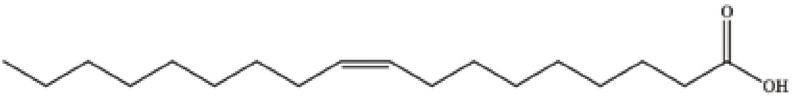
Triglycerides (also referred to as phospholipids or triacylglycerols) are triesters of fatty acids [52] comprising of three fatty acid units attached to a three-carbon backbone [53]. A fatty acid is a carboxylic acid containing a long unbranched aliphatic chain of an even number of carbon atoms, from 4 to 2, which can be either saturated or unsaturated [54]. If all carbon atoms of the fatty acid are attached to single bonds, they are considered saturated. Fatty acid molecules are further grouped as monosaturated if the fatty acid molecules have one double bond and polysaturated if it contains more than one double bond (as shown in **Figure 1**). The fatty acid composition of a specific oil sample has a major influence on its reactivity as well as on the physical and performance properties of the esters obtainable therefrom [54]. When the fatty acid molecule is attached to other fragments, it is referred to as free fatty acid (FFA).

Palm oil is a triacylglycerol obtained from the oil palm *Elaeis guineensis* [6]. The fact that palm oil predominantly consist of short-chain (C_8-C_{10}) and medium-chain (C_{12}-C_{14}) fatty acids (as shown in **Table 1**) therefore makes it a valuable feedstock for the manufacturing of oleochemicals [55]. In fact, close to 60% of the palm kernel oil and about 5% of the palm oil were used for the manufacture of oleochemicals [56]. The rapid increase in production in the last decade has made palm oil the most consumed vegetable oil in the world [57, 58]. Global consumption of vegetable oils in 2016 was reported to be around 184 million tons, of which palm oil accounted for 38.7% while soybean oil, rapeseed oil, and sunflower oil accounted for 28.9, 15, and 8.5%, respectively [59]. An estimated 58 million metric tons of palm oil was reportedly produced in 2016 [60].

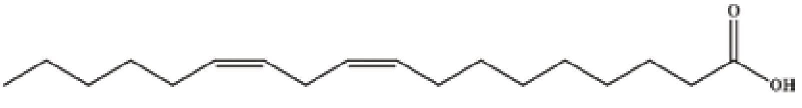
Waste or used vegetable oils are cheap source of triglycerides and are widely available in large quantities worldwide. About 29 million tons of waste cooking oil are generated every year [29],



Palmitic acid - Saturated Fatty Acid



Oleic acid - Monosaturated Fatty Acid



Linoleic acid - Polysaturated Fatty Acid

Figure 1. Classification triglyceride molecules.

Fat/oil	**Carbon chain (%)**										
	8	**10**	**12**	**14**	**16**	**18**	**18:01**	**18:02**	**18:03**	**20:01**	**22:01**
Tallow				4	30	20	40	5	1		
Palm				2	42	5	41	10			
Soya					8	5	28	53	6		
Palm kernel	4	5	51	15	7	1	15	2			
Coconut	8	7	48	17	9	1	7	2	1		

Table 1. Fatty acids distribution of common oils and fat.

a figure that is expected to increase rapidly as a result of growth in human population and increase in food consumption [61]. Some of waste vegetable oil is utilized in soap making, but the larger volumes are dumped into rivers and landfills with its attendant environmental pollution [62]. The use of waste cooking oil to produce oleochemicals will assist in the reduction of this environmental issue [9] and, at the same time, lower the cost of production. However, the high FFA contents, solids and water impurities in waste vegetable oils will impact on the yield, product quality, and the economic feasibility of the process [63]. A relatively high FFA content in the feedstock will promote saponification of triglycerides forming by-products such as soap and water as illustrated in **Figure 2** [64] .

This has resulted in poor yield as well as need for products purification [63, 65]. Waste cooking oils also contain water, which if not removed will promote hydrolysis of triglyceride to form more FFA [66]. The choice of the catalyst is a key factor when producing biodiesel via catalytic transesterification, which is also dependent on the FFA existent in the oil [67]. For virgin vegetable and other oils with a lower FFAs content, base-catalyzed reaction gives a significant conversion in a reasonably short time whereas for oils containing higher FFAs stock, acid-catalyzed esterification followed by transesterification is the best option [68] to prevent hydrolysis of the esters product.

In this work, the goal is to use the fatty acid esters from waste vegetable oils to produce bio-based surfactants. The processes involved simultaneous esterification and transesterification of waste palm oil over bifunctional heterogeneous catalyst to produce alkyl esters (majorly methyl or ethyl esters) and glycerol. The catalyst esterified the FFA into methyl esters in a one-step process and hence eliminated the pretreatment step. The first section of this study focused on formulation of a high performance bifunctional solid catalyst, CaO/Al_2O_3, with basic and acidic sites that are able to mediate simultaneous esterification and

$$R-\overset{O}{C}-OH + CH_3OH \xrightleftharpoons{\text{Acid catalyst}} R-COOCH_3 + H_2O$$

Figure 2. Esterification of free fatty acid reaction.

transesterification reactions for the production of methyl esters from waste vegetable oils. This is necessitated by the high FFA content of waste palm oil. The acidic oxide eliminated the need for the removal of the FFA by converting it to esters via the esterification reaction. The esterification step faciliatted by the acidic oxide eliminate acid pretreatment step which is required to remove the FFA and hence costly and as well required disposal of the fatty acid (wastes). The reaction with methanol was investigated over the catalyst in a well stirred batch reactor at an optimum reaction condition.

3.1. Catalysts preparation and characterization

Due to difficulties encountered during homogeneous transesterification, attention was shifted to heterogeneous catalyzed transesterification for methyl ester production [69–74]. The most studied solid heterogeneous catalysts are metal oxides of alkaline earth metals (Mg, Ca, Be, Ba, Sr), mixed oxides, zeolites, γ-alumina as well as hydrotalcites [11, 75]. CaO is mostly utilized due to its cheap price, high activity (due to a relatively high basic strength), long catalyst life as well as moderate reaction conditions [76]. Presently, most of the industrial processes for the production of methyl esters involve the reaction between edible oils and methanol in the presence of an alkaline catalyst [11]. But as mentioned earlier, waste and other cheap oils contain high amounts of FFA and water and are therefore not suitable for the process using an alkali (or even acidic) catalyst owing to simultaneous saponification reaction which lowers yield of the esters.

Teng et al. [77] reported that the presence of water at 4 wt% in rapeseed oil lowered the conversion to 86% from 98%. This is attributed to hydrolysis of the triglycerides in the presence of water. This also causes serious separation and emulsification problems. Consequently, a two-stage process [78] where the feedstock is first pretreated to reduce the content of FFA was developed. It is achieved by the use of catalysts such as ferric sulfate or iron sulfate and sulfuric acid (to remove the FFA), followed by the use of a basic catalyst to produce methyl esters [79]. Patil et al. [80] also reported a two-step process to convert waste cooking oil to methyl esters. The process included esterification reaction for the conversion of FFA to esters using iron sulfate, followed by transesterification of the triglycerides using KOH. However, the two-stage process still faced the issue of catalyst removal in both steps. It was suggested that in the first step, the catalyst removal issue can be prevented by acid catalyst neutralization and by using high quantities of alkaline catalyst in the second step [81]. But the use of extra amount of catalyst will not only add additional costs to methyl ester production, the catalysts must still be removed from the product stream.

Bimetallic solid oxide catalysts with acidic and basic oxide sites are able to efficiently convert high FFA oils into esters due to their ability to facilitate simultaneous esterification and transesterification reactions. These catalysts are also more tolerant of the water in the feedstock while given better esters yield in shorter reaction time [82]. Processing cheap oils with these catalysts requires no neutralization step (to remove the FFA contents) and since they do not dissolve in the reaction mixture, simple products purification steps are required. The catalysts being recyclable give a more sustainable resource management as well.

CaO/Al_2O_3 catalysts with different oxide ratios were studied in the production of methyl esters from waste palm oil. Alumina (Al_2O_3) was chosen as the acidic oxide due to its exceptionally thermal and mechanical stability, large pore size and pore volume, and high specific surface area [83]. The catalyst was produced via the co-precipitation method and characterized using thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Brunner-Emmett-Teller (BET) analysis, scanning electron microscopy with energy dispersive X-ray (SEM-EDX), and transmission electron microscopy (TEM) techniques. All chemicals utilized for the catalyst synthesis were of analytical reagent grade and were used without prior purification. Calcium and aluminum nitrates were used as the basic and acidic oxide precursor salts, while sodium hydroxide was used as the precipitating agent.

A 80% CaO/20% Al_2O_3 (by weight) catalyst is prepared using NaOH to co-precipitate the respective oxyhydroxides from a solution containing the calculated amount of the respective metal nitrates. The required amount of $Al(NO_3)_3{\cdot}9H_2O$ (Kimix, 98%) and $Ca(NO_3)_2{\cdot}4H_2O$ (Merck, 99%) were introduced into a 2 L flask. Just enough deionized water to dissolve the salts but to avoid splashing of the solutions during the vigorous stirring was added. The solution was heated to boiling over a Heidolph MR 3001 K hot plate fitted with a thermocouple (Heidolph EKT 3001). The flask and the hot plate are arranged under a Dragon Lab OS20-S overhead stirrer setup. The required amount of NaOH pellets (Merck, 98%) is dissolved in deionized water and brought to boiling as well and added to the boiling nitrate solutions. The solution is maintained at 90°C and stirred vigorously for about 15 min to promote the nucleation-dissolution processes. The stirrer speed was initially set at 1000 rpm, but increased gradually to 2200 rpm as the solution viscosity due to nucleation rises using the high power overhead stirrer.

The solution was allowed to cool for about 20 min and then filtered in a Buckner filter setup fitted with a vacuum pump. The precipitate was washed several times with warm distilled water until the filtrates were free of nitrate confirmed with the silver brown ring test. The precipitates were placed in a convective oven and dried overnight at a temperature of 120°C, to decompose the oxyhydroxides into the desired hydroxides (and possibly oxides). The above procedure was repeated to synthesize other test catalysts but with different basic to acidic oxides ratios, 70% CaO/30% Al_2O_3 and 60% CaO/40% Al_2O_3. A higher ratio of basic (CaO) oxide was used in all cases due to the prevalence of triglycerides in the waste oils.

Prior to reaction, the catalyst powder was calcined to decomposes the hydroxides, activate and stabilize the crystalline structure. First, the calcination temperature required was determined using TGA. The dried precipitate was calcined in a well-defined pattern (**Figure 3**).

This is done with an induction furnace (Kiln Contracts) fitted with Gefran P800 programmable temperature controller with ramping capacity, in flowing air set at the flow rate to fluidized the powder in a fluidized bed reactor. The calcination step involves thermal decomposition, crystallization, and recrystallization processes and some degree of sintering. This step will remove interstitial water in the sample and other volatiles from the solid catalyst precursor. It also helps to convert and stabilize the particles in the crystallite form.

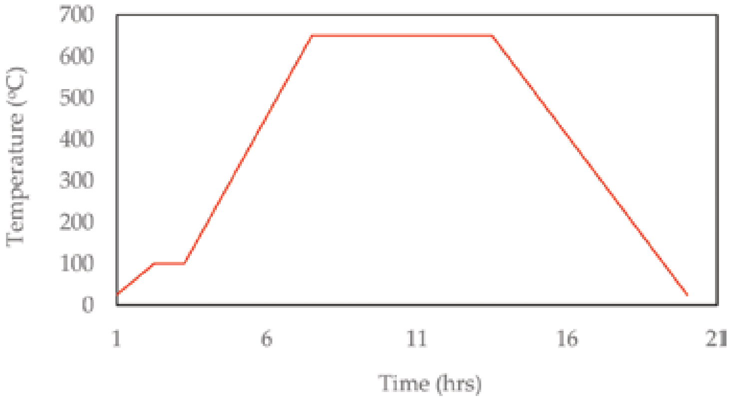


Figure 3. Catalyst calcination pattern.

Samples of the catalyst were characterized to determine among others the thermal behavior, the morphological properties, and elemental compositions. The BET, SEM-EDX, and TEM analyses were used to determine the surface area, particle size, particle size distribution, pore size, the pore volume distribution, elemental composition, and distribution. The bulk phases present were studied using XRD, whereas the reducibility and the maximum degree of reduction of the metal oxides were studied by means of the TGA method.

3.1.1. Thermal stability

Thermogravimetry analysis (TGA) continuously measures the mass and the rate of change in the weight of a sample subjected to a steady increase in temperature in a controlled atmosphere. The TGA profile will typically exhibit weight loss corresponding to various stages in the degradation of the substance. The thermal degradation behavior of the catalyst was performed on the dried sample to obtain the optimum calcination temperature and hence before the calcination step above. This was carried out with a Perkin Elmer TGA7 bench model thermogravimeter analyzer. The dried sample (20 g) was heated from room temperature to 900°C with high flow of nitrogen (100 ml/min) at a heating rate of 20°C/min. The weight change presented in **Figure 4** corresponds to water removal, possible carbon burning, and metals oxidation (Eqs. (1) and (2)) stages.

$$Ca(OH)_2(s) \xrightarrow{\Delta} CaO(s) + H_2O(g) \tag{1}$$

$$2Al(OH)_3(s) \xrightarrow{\Delta} Al_2O_3(s) + 3H_2O(g) \tag{2}$$

There was a sharp weight loss at 300°C and then at 600°C to around 750°C. These reduction are as a result of the decomposition of the respective hydroxides to the oxides. Using the thermal profile, 750°C is selected as the calcination temperature for this study.

3.1.2. Scanning electron microscopy analysis

After calcination, the morphology of the catalyst was studied with SEM as shown in **Figure 5**. The figure shows aggregated (interconnected) particles.

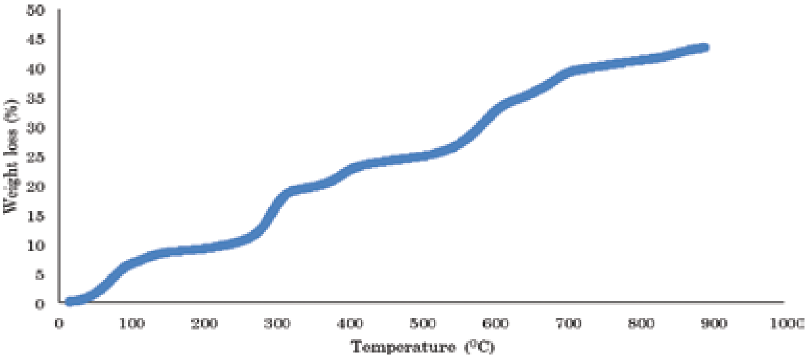


Figure 4. TGA curve for 80% CaO/20% alumina catalyst before calcination.

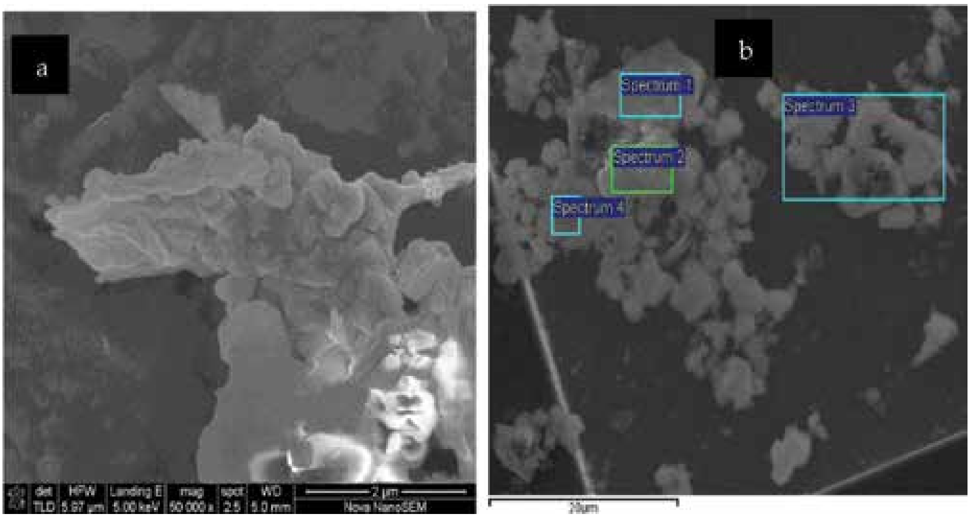


Figure 5. SEM-EDX micrograph of (a) the 80% CaO and (b) showing the areas chosen for EDX analysis at different magnifications.

Figure 6 shows the elemental composition of areas examined (determined by 4 replicates of EDX) for the catalyst sample. The SEM-EDX analysis of the catalyst confirmed the presence of Ca(CaO) and Al(Al_2O_3).

The SEM image also shows that Ca particles were well distributed on Al regardless of the 4.6:1 ratio obtained instead of the expected 4:1 which could have been caused by the impurities in the salts. It also showed a significant homogeneity of the CaO/Al_2O_3 catalyst which was visible in the value of Al and Ca acquired from the EDX analysis.

3.1.3. *Transmission electron microscopy analysis*

The morphology of the particles of the 80% CaO catalyst was studied with the transmission electron microscopy (TEM). **Figure 7** shows the micrograph of the catalyst particles. Most of

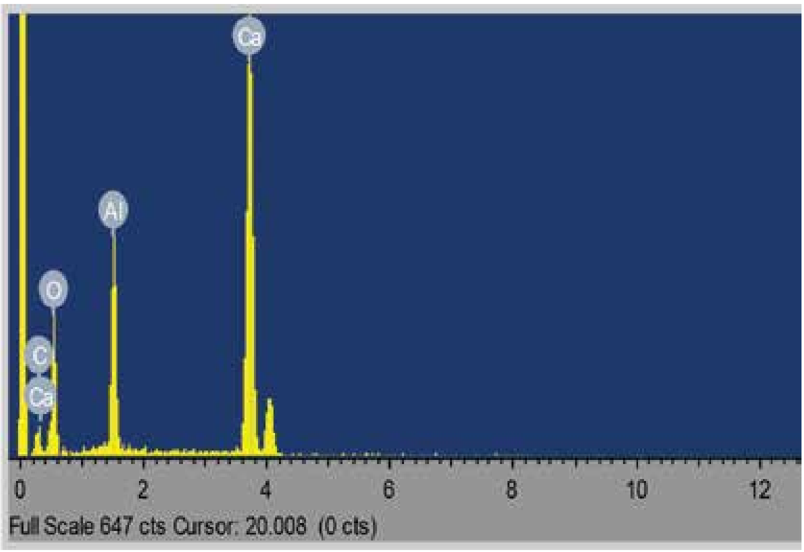


Figure 6. EDX spectrum for 80% CaO/Al_2O_3 catalyst.

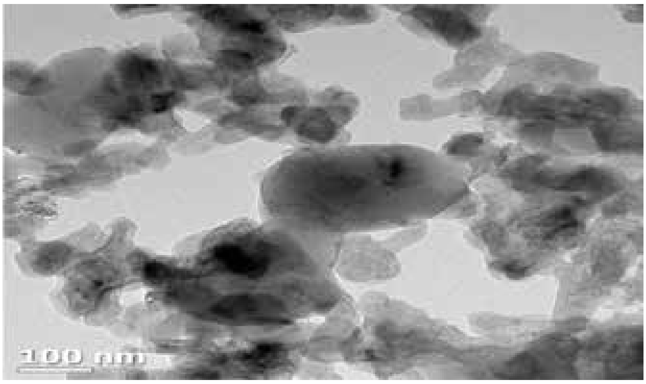


Figure 7. TEM images of the catalyst.

the particles were in the range of 10–100 nm. The porosity of the catalyst particles was confirmed by the TEM image and most of the crystal particles were in rectangular shape.

3.1.4. Bulk phase of catalyst

The qualitative and quantitative X-ray diffraction spectra XRD patterns of the 60, 70, and 80% CaO on Al_2O_3 used in this study are shown in **Figure 8**. The XRD of the catalysts showed expected peaks. A broad reflection of the CaO crystalline phases was clearly observed at 2θ range of 20.0–40.0° for 60, 70, and 80% CaO/Al_2O_3 which supports the presence of highly dispersed CaO particles in all CaO on Al_2O_3 catalysts.

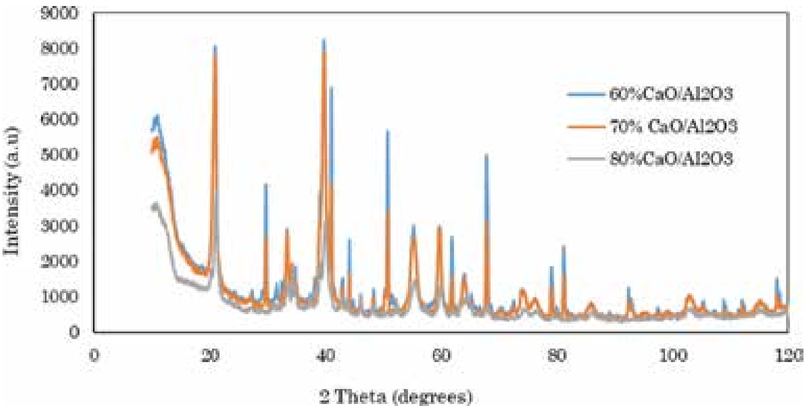


Figure 8. XRD pattern of 60, 70, and 80% CaO wt% catalysts.

There were also some diffraction peaks detected at ~51 and 68°2θ angles which did not correspond to CaO crystalline phases but were identified as hydrated calcium aluminate and alumina crystalline phases. The formation of these phases is expected due to the adsorption of water and CO_2 from air which must have occurred during the XRD analysis [84].

3.2. Methyl esters production

Waste sunflower and waste palm oil were used in this study. The samples FFA contents were found via titration to be 0.3825 and 76.96 mg/g, respectively. These oils were transesterified with a methanol at methanol/oil molar ratio of 9:1 and reaction temperature 65°C for 4 h. The optimum catalyst loading selected for the transesterification of both waste oils was 4 wt% based on previous studies [85, 86]. The effect of basic/acidic oxides ratio on the yield of FAME was investigated by varying the catalyst CaO ratio as 60, 70, and 80%. The yields of the esters are presented in **Figure 9**.

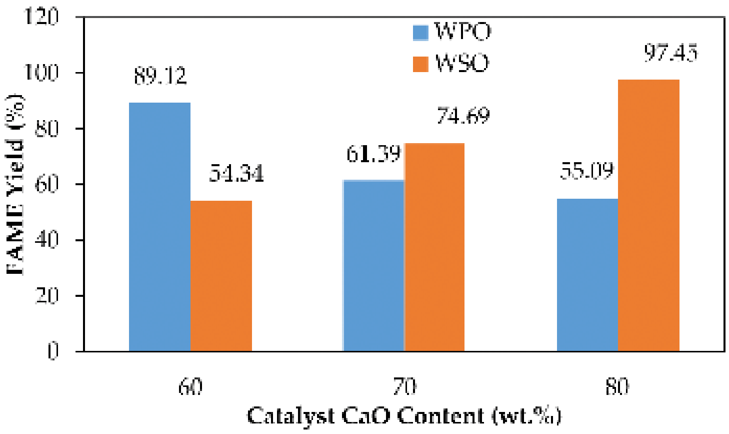


Figure 9. Methyl ester yield versus catalyst CaO content.

A 60% CaO/40% Al_2O_3 catalyst was found to be optimum for waste palm oil, whereas the optimum catalyst ratio for the waste sunflower oil was 80% CaO/20% Al_2O_3 at the same reaction conditions. This is due to the fact that waste palm oil contains higher amount of FFAs, and hence requires more acidic sites on the catalyst to esterify the FFA to FAME. The high yield of FAME obtained despite the low quality of the oils used demonstrated that the use of a bifunctional catalyst will provide an opportunity to lower the cost of production as well as assist in disposal of the waste vegetable oils.

4. Surfactants productions from the methyl esters

Currently, increasing research efforts are going into formulating cheaper, biodegradable, and nontoxic surfactants, because the existing commercial surfactants are mostly slow-degrading compounds produced from petrochemicals [13]. In many instances, the products from their degradation are detrimental to the environment or to humans [87]. The high cost of commercial surfactants imposes additional challenges and limits their widespread application in the petroleum industry. Therefore, to cut down on the surfactant production cost and to satisfy the intended specifications, increasing attention is being giving to agriculturally and waste resources [13] as substitutive feedstock to petroleum for surfactants manufacturing.

Waste and nonedible vegetable oils for the production of surfactant are of interest because utilizing these waste materials will result in low material and processing costs, thus making biosurfactants attractive in large scale applications. It is also biodegradable [18] and the relatively high interfacial tension reduction potential or surface active properties are comparable to synthetic surfactants [15]. Most of ionic and nonionic surfactants are derived from C_{12} and C_{14} fatty acids which are abundant in palm kernel and palm oil [1]. The longer chain fatty acids exhibit a high hydrophobicity making it unsuitable for micelle formation and, hence, are used only after necessary modification to increase their polarity [1]. The esters produced in the preceding step were further subjected to epoxidation reaction to reduce the mono- and polyunsaturated esters content and obtain more stable epoxides. Finally, the sulfonated surfactant is produced using sulfonating agents such as sulfuric acid, oleum or chlorosulfonic acid. The fatty acid composition of the methyl esters produced used is analyzed using a GC-MS. The spectra are as shown in **Figure 10**.

The GC-MS confirmed the fatty acids distribution as, saturated fatty acids: palmitic acid (16:0), stearic acid (18:0), arachidic acid (20:0), heneicosylic acid (21:0), behenic acid (22:0), and palmitoleic acid (16:1). The monounsaturated groups are gadoleic acid (20:1) and oleic acid (18:1) while the polyunsaturated fatty acids are linoleic acid (18:2) and linolenic (18:3). The saturated fatty acids content was found to be 19.95%, which is considered to be quite high.

To reduce the saturated fatty acids contents and to epoxidize the unsaturated fatty acids, investigations regarding the effects of solvent-free and solvent in the epoxidation reaction at 25, 30, and 50°C using formic acid were conducted. Formic acid was utilized in this study owing to the fact that the performic acid formation rate is superior in comparison to that of peracetic acid and the formic acid method is well-known to progress at a faster rate [88, 89].

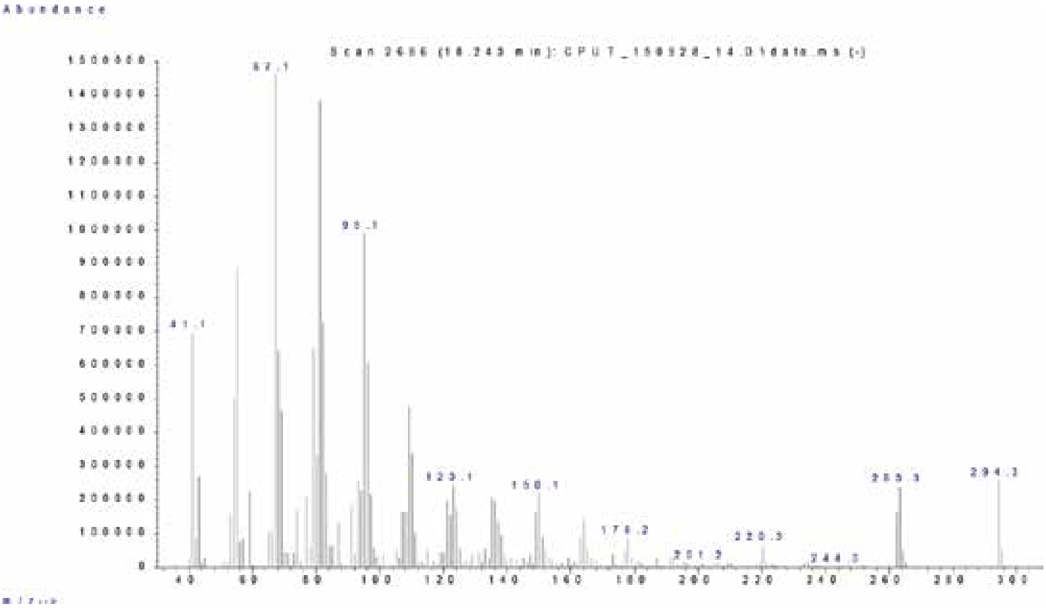


Figure 10. Chromatogram of the palm oil methyl esters.

Moreover, to generate peracetic acid in high concentrations, the use of a catalyst is required [89]. The chemicals utilized for the epoxidation of methyl esters are formic acid (99.81% CH_2O_2), sodium bicarbonate (7.5% aqueous $NaHCO_3$), sodium chloride (ACS reagent, ≥99.0% NaCl), hydrogen peroxide (30% aqueous H_2O_2), diethyl ether (≥99.0% $CH_3(CH_2)_2O$), toluene (anhydrous, 99.8% C_7H_8), n-hexane (anhydrous, 95% C_6H_{14}), and propan-2-ol (anhydrous, 99.5% $CH_3CHOHCH_3$). These were purchased from Sigma Aldrich.

4.1. Epoxidation with no solvent

The epoxidation reaction was performed in a temperature controlled batch reactor. About 10.7 g of CH_2O_2 and 100 g of FAME is added to the reaction vessel. The vessel is connected to a condenser and placed in a water bath maintained at 25°C. 58.8 g of H_2O_2 was added dropwise to the vessel through the top of the condenser which then formed peroxyformic acid by reacting with the formic acid (Eq. (3)) and allowed to stand for 4 h. The principal product is epoxidized methyl ester (EFAME) with oxirane rings at the position of double bonds. Possible by-products include keto compounds due to the redisposition of oxirane group or vicinal dihydroxy because of oxirane hydrolysis.

$$CH_2O_2 + H_2O_2 \rightleftharpoons CH_2O_3 + H_2O \tag{3}$$

Epoxidized FAME purification step was carried out to remove the unreacted H_2O_2 and the excess acid. About 20 ml of diethyl ether (Sigma Aldrich, 99.9%) is added to the EFAME in a 250 ml separation funnel and stirred well. First, the EFAME/ether solution is washed thrice with deionized water to get rid of the excess acid. Then, the product was washed again with about 10 ml of aqueous sodium bicarbonate solution (5 g $NaHCO_3$/100 g H_2O) which neutralized the residual acid and peroxide. As the bicarbonate solution was added to react with the rest of the acid and slowly agitated, the stopper of the separating funnel was pointed away and into the fume hood and occasionally opened to allow produced gasses to be discharged safely from the funnel. This was repeated until pH paper indicated that it was neutral, showing that the only components remaining in the organic layer was the epoxidized methyl esters. If the solution was too basic, it was rinsed again with water, and if it was too acidic, it was rinsed again with $NaHCO_3$ solution.

Then, about 10 ml of sodium chloride solution (5 g NaCl/100 g H_2O) is added to remove the remaining H_2O from the organic phase. The aqueous layer was decanted from the reaction system and disposed of. The organic layer was vacuum distilled in a rotary evaporator (Buchi Rotavapor Model R-205) for 30 min at 80°C to evaporate both the ether and any residual H_2O from the organic phase.

4.2. Epoxidation with solvent

Carrying out epoxidation reaction at lower temperatures and in the presence of organic solvents will minimize oxirane degradation and by-products formation [53, 90, 91]. The presence of organic solvents also has some stabilizing effect on the oxirane formed during the peroxyformic or peroxyacids epoxidation of oils and FAMEs [91]. Moreover, solvent can control the reaction temperature thus reducing the adverse temperature effects [92]. Solvent use also offers good solubilization for all inorganic and organic substances thus promoting good mass transfer.

The epoxidation reactions were conducted with toluene at 25, 30, and 50°C. The approach of Akintayo et al. [90] was used. 100 g of FAME was dissolved in 50 ml of toluene and 4 mol of CH_2O_2 was added at temperature of 25°C with stirring. Hydrogen peroxide (100 ml) was then added while keeping the temperature constant. Afterward the reaction was allowed to continue for 4 h. Reaction mixture was then allowed to settle and the aqueous layer removed using a separating funnel. The organic layer was repeatedly rinsed with warm H_2O until free of acid. The residual toluene and H_2O were removed under reduced pressure in the Buchi rotary evaporator. The same procedure was repeated at 30 and 50°C.

The produced epoxy fatty acid methyl esters are analyzed using a GC-MS to detect and determine the different epoxy acids present. From the results, it is noted that performing epoxidation reactions at 30 and 50°C and in presence of the organic solvents minimized side- and by-products formation and ring-opening reactions especially to hydroxyl compounds. Deshpande [93] argued that the presence of an inert solvent-like toluene stabilizes the epoxide product and reduced the adjacent reactions. Reaction at lower temperature of 25°C showed lower rate of epoxidation and high rate of hydrolysis of the product to various by-products.

When the temperature was increased from 30 to 50°C, a change in the composition of the fatty acid methyl esters to epoxy esters and a decrease in side reactions were observed. The results obtained at 50°C with the use of a solvent suggest simultaneous decrease in the side reactions that open the epoxy ring and minimization of the rate of hydrolysis (oxirane cleavage) of the product. This is in agreement with Ahmad et al. [92]. At 50°C and in the presence of a solvent, the epoxidized FAME showed a very low or no hydroxyl formation compared to the solvent-free epoxidation and at 25°C. Furthermore, increasing temperature demonstrated a favorable influence on the formation of performic acid. The results further showed substantial reduction in the percentage composition of saturated and unsaturated fatty acids in product composition for epoxidation reactions carried at higher temperatures. It can be concluded, therefore, that moderate temperature of 30°C were most suitable for epoxidation of oleic acid with PFA (performic acid generated *in-situ* for optimum oxirane levels and minimal hydrolysis rate).

4.3. Production of epoxidized methyl ester sulfonate

A number of methods for the preparation of sulfonated fatty acid esters from oleochemicals can be found in literatures. The sulfonation reaction of fatty acid methyl esters using SO_3 was studied in detail by Stein and Baumann [94], and products with distinct carbon chains which have excellent properties for surfactant formulation were obtained. Triglycerides with the required number of carbon chains can be found in coconut oil (~48% C_{12}, 17% C_{14}), palm oil (~46% C_{16}), palm kernel oil (~50% C_{12}, 17% C_{14}), and tallow (~26% C_{16}, 23% C_{18}) as mentioned earlier. In general, unsaturated esters contained in vegetable oils and tallow (comprising approximately 43% oleic acid) result in the bad color of the ester sulfonates. Thus, the esters must be hydrogenated or distilled before sulfonation so that their iodine number is less than 0.5.

For surfactant synthesis, chlorosulfonic acid (97% HSO_3Cl), pyridine (99.5% C_5H_5N), sodium carbonate (99.5% Na_2CO_3), sodium bicarbonate (7.5% aqueous solution of $NaHCO_3$), n-butanol (99.5% C_4H_9OH), and diethyl ether [$(C_2H_5)_2O$] were purchased from Sigma Aldrich. About 2.63 g of chlorosulfonic acid (HSO_3Cl) was added very slowly while stirring (at 800 ppm) to 15 ml of pyridine (C_5H_5N) in a 500 ml round bottom flask placed in ice-cooled water bath for 15 min. 2.60 g of the epoxidized fatty acid methyl ester solution obtained above was introduced slowly to the round bottom flask with continuous stirring, for another 30 min. The reactor and its contents were afterward heated to a temperature of 65°C in a water bath until the solution turned clear. For the second step, the reaction was quenched and the solution is poured into an ice-cooled 500 ml flask containing 33 g in 300 ml solution of sodium carbonate (Na_2CO_3) and enough (approximately 30 g) solid sodium bicarbonate ($NaHCO_3$) to keep the solution saturated with inorganic sodium salts.

The sulfonated product was extracted into 40 ml of n-butanol (C_4H_9OH) using a separating funnel. The solvent was removed from the crude product via drying with a rotary evaporator. The powder obtained is redissolved in 200 ml of water. Then, the organic impurities were eliminated from the aqueous solution of sodium epoxidized methyl ester sulfonate (SEMES) via extraction with 50 ml of diethyl ether. The crude product is concentrated and dried under vacuum for 24 h. Since C_4H_9OH and Na_2CO_3 are typically utilized in CEOR as co-solvent and alkali, the sulfonated esters produced were analyzed without further purification so as to reduce the cost of surfactant manufacturing [25].

A FTIR spectrophotometer was utilized to analyze the composition and the chemical functional group present in the synthetized surfactants. The synthesized (SEMES) powder was grinded and mixed with potassium bromide (KBr) to obtain a fine powder. The powder was then compressed into a thin pallet for analysis. About 15 mg of this pallet in each case was put on the Attenuated Total Reflectance (ATR) sample holder of a Perkin Elmer spectrum 100 FTIR spectrometer (model JASCO FT/IR-4100). The sample was recorded in the range of 4000–500 cm^{-1}, baseline was corrected, and the spectra smoothened.

FTIR spectra in the range of 500–4000 cm^{-1} of SEMES are shown in **Figure 11**. All the IR absorption bands were investigated with respect to the spectrometric identification of organic compounds by Silverstein et al. [95].

The peak at 1450 cm^{-1} is typically assigned to the disproportional stretching vibration band of methyl group (C—H). Elraies et al. [25] obtained a similar peak for epoxidized methyl ester sulfonate from jatropha oil. The symmetric and asymmetric C—H stretching vibration of the —CH3 group appears at 2497 and 2926 cm^{-1}. Analogous peaks between 2473 and 2955 cm^{-1} were reported by Babu et al. [96] for sulfonated methyl esters synthetized from castor oil and the ricinoleic acid methyl ester was sulfonated without the epoxidation step. The peak at 3679 cm^{-1} in the SEMES is attributed to the OH stretching of the sorbed water. This sorbed water vibration band suggests that the surface property of SEMES changed from hydrophobic to hydrophilic [96]. The existence of the epoxy ring in the SEMES was shown by the presence of C—O stretching absorption band in the area of 988–830 cm^{-1}.

The strong vibration (absorbance) peak at 1614 cm^{-1} corresponds to the existence of sulfonate group due to S═O stretching which is also an indication of the presence of esters [95, 97]. These results clearly indicate that the substance synthetized is a sodium epoxidized methyl ester sulfonate. For better understanding the structural arrangement of the surfactants investigated in this study, commercial anionic, SDS, and cationic, CTAB surfactants were also characterized using the same procedure. The FTIR spectra of pure SDS showed similar pattern with the synthetized SEMES, but the percentage of transmission were different as a

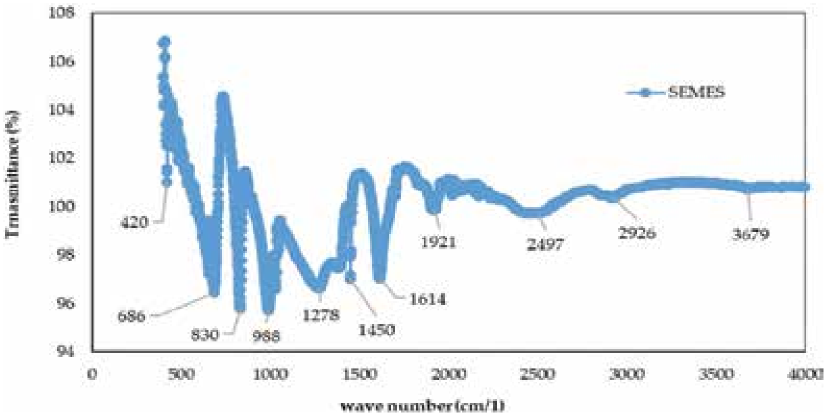


Figure 11. FTIR spectrum of SEMES.

result of the discrepancy in their relative molecular mass. This clearly indicates that the formulated surfactant SEMES is an anionic surfactant.

5. Conclusion

The CaO/Al_2O_3 employed as the catalyst to produce methyl esters used from the waste oil performed as expected, despite the presence of free fatty acids. The catalysts synthesized by the co-precipitation method exhibited high dispersion of the Ca and Al particles. The optimum reaction conditions for the production of methyl esters via simultaneous esterification and transesterification reaction of the waste pal oil were found to be: a reaction time of 4h at 65°C with a methanol:oil ratio of 9:1 and 4 wt% catalyst amount. A 60% CaO/40% Al_2O_3 ratio was found to be optimum for waste palm oil. The high esters yield obtained despite the low quality of the oils used demonstrated that the use of a bifunctional catalyst will provide an opportunity to lower the cost of production of the esters. Furthermore, the catalyst showed substantial chemical stability and could be used again for at least 8 times with minor losses in its catalytic activity.

It is evident that the saturated fatty acid contents of the methyl esters subjected to epoxidation reaction in the presence and absence of a solvent at 25, 30, and 50°C were reduced while promoting the desired conversion of the unsaturated fatty acid methyl esters to epoxy esters (with oxirane groups). A temperature of 30°C was found to be suitable for epoxidation of oleic acid with PFA (performic) for optimum oxirane levels and hydrolysis rate diminishment. The EFAME was consequently sulfonated to produce the sodium epoxidized methyl ester sulfonate (SEMES) surfactant, which was then compared with the synthetic SDS and CTAB surfactants. The identified FTIR spectrum of SEMES was similar to that of SDS which indicated that the formulated SEMES is an anionic surfactant. The same result has been reported [98]. The sulfonated surfactant has been evaluated in a separate study for performance in petroleum reservoir [15]. It was found to exhibit excellent characteristics comparable to commercial petroleum-based anionic surfactant.

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The Inclusion of Palm Oil Ash Biomass Waste in Concrete: A Literature Review

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Additional information is available at the end of the chapter

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Abstract

Oil palm ash (OPA) is a waste material produced by countries having a blooming palm oil industry. Recycling of oil palm ash is receiving increasing attention because of its huge potential in improving economic benefits and environmental awareness. Recently, it has been used as a partial replacement to cement in concrete, mortar and other cementitious materials. OPA is considered a new member of the supplementary cementing materials. Therefore, it is imperative to have a complete understanding of this material and its effects. In this chapter, a thorough literature review involving OPA will be presented. The physical and chemical properties of OPA will be listed as well as its effect when used as a partial cement replacement on the fresh state, mechanical and durability properties of a number of cementitious products. Capitalising such waste products in the production of concrete will not only benefit the recycling chain process but also produce a green product which enables the reduction of cement quantities used and also produce an energy-efficient building material.

Keywords: biomass waste, concrete, cement replacement, properties

1. Introduction

The surge in fossil fuel prices and the fear of future supply shortages alongside the increasing awareness of greenhouse gas emissions increased the shift towards the search for alternative fuels. These alternative fuels are conditioned to be technically feasible, environmentally friendly, competitive from an economic perspective and readily available [1]. Vegetable oils, which are from plant origin, are considered to be an alternative to fossil fuels. The alternative fuel is named as bio-diesel. Bio-diesel is biodegradable, non-toxic and has low CO_2 emission profiles in comparison to conventional fossil diesel. Using bio-diesel will allow a balance to occur between agricultural economic development and the environment [2]. Various plants have been identified as a raw stock for the production of bio-diesel such as rapeseed and soybeans in the United Sates and palm oil and jatropha in the Asian region [3]. However, among these resources of bio-diesel, palm oil is considered to be the cheapest and has the highest oil yield per hectare of plantation [1].

Today, Malaysia is the world's largest producer and exporter of palm oil, and its palm oil industry is an important contributor to the country's gross domestic product (GDP) [4]. Before the bio-diesel boom, 90% of the oil was used in food-related commodities with the remaining 10% being used as a raw material in soap production [5]. However, after realising the potential of palm oil in producing bio-diesel, the Malaysian palm oil industry grew from a shy 400 hectares in 1920 [6] to 4.17 million hectares in 2006 and nearly 4.5 million tonnes in 2008 [7]. In 2008, about 17.7 million tonnes of crude palm oil have been produced from the 410 palm oil mills in Malaysia reaching 41% of the world's palm oil production [8].

As a result to the thriving Malaysian palm oil industry, the amount of biomass produced will increase. A single hectare of palm oil plantation can generate up to 70 tonnes of biomass residues [9]. As a rough estimate, 1 kg of palm oil results in 4 kg of biomass produced alongside it [7]. About 90 million metric tonnes of biomass is produced in Malaysia annually [10]. This biomass residue consists of empty fruit bunch, fibre, shell, wet shell, palm kernel, fronds and trunks. Each oil palm tree fruit bunch produces about 21% palm oil, 6–7% palm kernel oil, 14–15% fibre, 6–7% shell and 23% empty fruit bunch [11].

It has been a common practice for palm oil mills to burn their biomass instead of using conventional fossil fuels for heating up their boilers and generate steam [1, 5]. According to Shuit et al. [9], more than 300 palm oil mills are operated by self-generated electricity using palm oil biomass in Malaysia. In addition, the generated electricity is not only used for their internal use in crude palm oil extraction but also provided the surrounding remote areas with electricity. Due to the abundant amounts of biomass produced, Malaysia has the potential to utilise these quantities in power generation. Using such alternative fuels to partially or fully replace fossil fuels used in all Malaysian industries to generate energy will result in a significant drop in CO_2 emissions, achieving the vision to be a developed country without degrading the environment and promoting the utilisation of renewable energy in power generation.

However, the process of burning palm oil biomass will result in a new type of waste. This waste is called oil palm ash (OPA) which is causing numerous problems to the environment. OPA quantities are expected to increase in quantities due to the increasing demand for energy and the booming palm oil industry.

2. Oil palm ash (OPA)

It was mentioned earlier in the previous chapter that OPA is the result of incinerating palm oil biomass to generate necessary energy for the palm oil mill. Incineration of biomass occurs at temperatures ranging from 800 to over 1000°C. OPA is produced at a rate of 5% by weight of burned biomass [12]. In this section, the physical and chemical properties of OPA will be discussed thoroughly. In addition, the effects of OPA integration on the properties of concrete, mortar and paste will be discussed.

2.1. Physical properties of OPA

When lower temperatures are used to incinerate the palm oil biomass, a black to dark grey OPA is produced due to the high amounts of unburned carbon [13]. Higher incineration temperatures will reduce the amounts of unburned carbon, thus producing OPA with a lighter colour and improved characteristics [14]. Therefore, every OPA is unique to its mill and there is no OPA similar to another. When received from the source, OPA is a coarse-sized particle which is at the same time porous in structure. In order to change its physical characteristics, OPA is usually ground. The grinding process not only will increase the fineness of the OPA particles but will also increase its specific gravity [15]. Grinding of OPA is done through the use of a modified Los Angeles machine [12, 13] or by ball mill [12, 16, 17]. **Table 1** lists a number of physical properties for OPA used in different studies.

2.2. Chemical properties of OPA

Due to the different production processes, every OPA is unique in its chemical composition. No OPA is chemically similar to another OPA from another source. OPAS used in different studies were compliant to a chemical composition of a Class N pozzolan [15, 19], Class C pozzolan [20] and a Class F pozzolan [21]. However, when insufficient incineration temperatures are used, impurities such as unburned shell and fibre and unburned carbon exist. Therefore, extra processing procedures are needed to enhance the properties of OPA before using it in concrete.

The usual procedure for processing OPA starts with sieving. The sieving process discards any large unburned fibre or shell. To increase OPA's pozzolanic reactivity, the sieved OPA will undergo the process of grinding. As stated earlier, grinding the OPA will create a finer substance possessing a heavier specific gravity. OPA is usually ground until a median particle size of 10 μm is achieved [14]. When the OPA is of poor quality, the grinding process will not change the

Author(s)	Unground OPA			Ground OPA		
	Specific gravity	Retained on 45-μm sieve (%)	Median particle size (μm)	Specific gravity	Retained on 45-μm sieve (%)	Median particle size (μm)
Sata et al. [12]	1.97	41.2	62.5	2.33	1.5	10.1
Tangchirapat et al. [17]	1.89	94.4	183.0	2.43	1.0	7.4
Tangchirapat et al. [15]	1.97	41.2	65.6	2.33	1.5	10.1
Megat Johari et al. [18]	2.42	—	15.76	2.50	—	2.99

Table 1. Physical properties of OPA used in different studies (Al-Mulali et al. [14]).

chemical characteristics of the OPA drastically. Therefore, the fine OPA is usually burned in an electric furnace at a temperature of 500°C for at least an hour to remove any carbon content [22]. **Table 2** lists different OPA chemical compositions utilised in a number of studies.

When compared to fly ash, OPA is known to have a higher percentage of organic residue, a higher alkali content and a larger particle size [25]. Coarse OPA is proven to be of low pozzolanic reactivity when no reduction in strength occurred. This is achieved after a curing period of 1 year is used and 10% of cement used in the production of concrete was replaced by OPA sieved through 150-μm sieve [25]. Increasing the pozzolanic reactivity of OPA is achieved through the grinding process to produce a finer particle sized ash [12]. When OPA with three different median particle sizes is used as a partial cement replacement in conventional concrete, the finest OPA with a median particle size of 7.4 μm showed a higher compressive strength than the control mix at a replacement level of 20–30% by weight of cement [17]. Mortars with cement partially replaced by coarse (55 μm), medium (25 μm) and fine (7 μm) OPA showed the same behaviour [26]. Mortar with fine OPA partially replacing cement shows superior strength in comparison to the control mortar and mortars containing the medium and coarse OPA.

In high-strength concrete, mixes containing fine OPA as a partial cement replacement exhibited the same behaviour. High-strength concrete mixes incorporating 20% of fine OPA (d_{50} = 10 μm) as a partial cement replacement showed a higher compressive strength and an increased resistance to chloride penetration, acid and sulphate attack [27]. High-strength concrete containing 20% fine OPA (d_{50} = 10.1 μm) achieved a compressive strength of 70 N/mm^2 at the age of 90 days proving that fine OPA is a good mineral admixture [15].

In blended cement pastes, the effect of OPA fineness and pozzolanic reaction is studied by Kroehong et al. [16]. Ground OPAs with a particle size of 15 ± 1 and 2 ± 1 μm along with ground river sand were used to partially replace cement at levels of 10–40% by weight of cementing materials. At the age of 90 days, blended cement pastes containing 10–30% of 2-μm OPA exhibited higher compressive strengths than that exhibited by the control paste at a percentage of 105–111%. This increase was reasoned to the high pozzolanic reactivity of the 2-μm OPA.

Author(s)	**Oxides present in OPA (%)**									
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**SO_3**	**SUM**	**LOI**
Sata et al. [12]	65.3	2.60	2.00	6.40	3.10	5.70	0.30	0.50	69.9	10.10
Tangchirapat et al. [17]	57.71	4.56	3.30	6.55	4.23	8.27	0.50	0.25	65.57	10.52
Chindaprasirt et al. [23]	63.6	1.60	1.40	7.60	3.90	6.90	0.10	0.20	66.6	9.60
Altwair et al. [24]	66.91	6.44	5.72	5.56	3.13	5.20	0.19	0.33	79.07	2.30
Megat Johari et al. [23]	65.01	5.72	4.41	8.19	4.58	6.48	0.07	0.33	75.14	2.53

Table 2. OPA chemical compositions used in different studies.

2.3. The effect of OPA incorporation on the properties of concrete

In the following sections, the effect of OPA's incorporation on the properties of concrete, mortar, cement paste, high-strength concrete and aerated concrete will be discussed thoroughly.

2.3.1. Workability

In general, increasing OPA content in concrete reduces its workability. Fresh concrete with 50% of its cement replaced by coarse OPA (passing through a 150-μm sieve) achieved a slump reading of 120 mm which is lower than the 150 mm exhibited by the control mix [25]. When using the compacting factor, concrete with a 50% coarse OPA replacement showed a compacting factor reading of 0.93 which was lower than the 0.99 exhibited by the control mix [28].

Using the slump test and the amount of superplasticizer used to obtain a spread between 175 and 225 mm, high-strength concrete with increasing amounts of OPA exhibited less spread and used more superplasticizer to achieve the required spread [29]. The authors reasoned the increase in superplasticizer dose to the high porous nature of the OPA particles resulting in the absorption of a higher water quantity. Reduced workability of high-strength concrete with 20% by weight of cement is replaced by fine OPA is reasoned to the increased surface area of the OPA particles due to their grinding [27].

The increased water demand for OPA concrete to achieve a required workability limit is due to the shape and nature of the OPA particles themselves. OPA particles are known for their angularity, irregularity and their porous nature [18, 30, 31], and as a result, demanding an increased amount of water for their lubrication and by that attaining similar workability as their control mixes. Chindaprasirt et al. [30] discovered this aspect when comparing the OPA particles to those of fly ash which required less water due to their spherical shape and solid nature.

Sieved through a 300-μm sieve, OPA was used to replace cement at levels of 5, 10 and 15% by weight in conventional concrete. These OPA concrete mixes were compared to concrete with 10% replacement levels of fly ash and quarry dust also sieved through 300-μm sieve. Ahmad et al. [20] found that even with a dose of superplasticizer, OPA concrete mixes showed reduced slump readings and low compacting factors than those of the control and the fly ash mixes. The same observation is made in concrete with 50, 60 and 70% OPA replacement levels (35% retained on 45-μm sieve) and a superplasticizer dose of 2% by weight of binding material [31].

2.3.2. Setting times

The initial and final setting times of concrete incorporating OPA as a cement replacement are investigated by a number of researchers. In general, OPA concretes showed prolonged initial and final setting times [14]. Concrete containing OPA (sieved through a 150-μm sieve) as a cement replacement exhibited a delay in both initial and final setting times; however, they were within the limits stated by ASTM 150 [25]. The retardation of initial and final setting times increased with increasing OPA replacement levels [28].

The particle size of OPA plays a role in defining the setting times [17]. The authors found that concrete with 40% of its cement replaced by coarse OPA (d_{50} = 183 μm) exhibited an initial setting time of 390 min and a final setting time of 740 min. The authors reasoned these prolonged initial and final setting times to a number of factors. These factors are reduced cement quantity and the large and porous unground OPA particles that increase the water binder ratio used in the mix. However, the authors stated that increasing the fineness of OPA decreased the setting times, making them closer to those exhibited by the control mix. High-strength concrete mixes with fine OPA (d_{50} = 2 μm) replacement levels show prolonged setting times to those exhibited by the control mix [18]. The authors reasoned this retardation to the pozzolanic reaction which is slower than cement hydration.

2.3.3. Compressive strength

Numerous studies investigated the effect of OPA incorporation as a cement replacement on the strength of concrete, mortar and cement paste. Increasing OPA content in concrete decreases the compressive strength [14]. Concrete with OPA (sieved through a 150-μm sieve) at replacement levels of 0–50% by weight of cement experienced a drop in compressive strength with increasing OPA content [25, 28]. Compressive strength reduction was less observed at the age of 365 days in comparison to that at 28 days due to the pozzolanic activity of the OPA. The researchers recommended an optimum OPA replacement level of 10% by weight of cement because the reduction in compressive strength is found to be 1% at the age of 1 year.

Increasing the fineness of OPA increases its pozzolanic reactivity, hence increasing the compressive strength of concrete. Chindaprasirt et al. [30] concluded that a 20% replacement level of OPA (d_{50} = 8 μm) possessed a slightly higher compressive strength than the control mix. Increasing the fineness of OPA further makes it possible to increase the replacement level used in the concrete and achieve a higher compressive strength. Concrete samples containing OPA with a median particle size of 7.4 μm at a replacement level of 30% managed to possess 99% of the control mix's strength at 90 days [17]. Fine OPA replacing 50% of cement in concrete showed double the compressive strength of concrete having half of their cement replaced by raw OPA [32].

Even when using different water cement ratios in concrete (0.5, 0.55 and 0.6), samples containing a 10% fine OPA (2% retained on a 45-μm sieve) exhibit higher compressive strengths at all water cement ratios at 14 days of age than its corresponding control mixes [29]. Fine OPA (d_{50} = 10. 7 μm) at a replacement level of 20% enhanced the compressive strength of concrete with recycled aggregate in comparison to the same concrete samples without OPA [33]. High-strength concrete samples containing 20% cement replacement by fine OPA (d_{50} = 10 μm) exhibited higher compressive strengths than both the control mix and the mix containing 5% silica fume at the same age [12]. In another study, high-strength concrete samples containing OPA (d_{50} = 10.1 μm) at a replacement level of 30% exhibit higher compressive strengths than those of mixes containing Type I and Type V Portland cements at the same age [15].

Ultrafine OPA (d_{50} = 2 μm) is capable of replacing cement at a level of 60% and achieve a higher compressive strength than that exhibited by the control mix at 28 days [18]. The increase in compressive strength is due to the pozzolanic reaction between the high silica oxide content of OPA and calcium hydroxide emitted by the cement hydration. This pozzolanic reaction will produce extra amounts of calcium silicate hydrates (C-S-H); hence, an increase in compressive strength is experienced [15, 18, 27, 29].

Increasing OPA content reduces the compressive strength of aerated concrete [35]. However, it is still possible to replace cement by OPA at levels ranging from 10 to 35% without effecting the compressive strength of aerated concrete [14]. Aerated concrete sample containing fine OPA (Class F pozzolan) at a replacement level of 20% exhibits compressive strengths higher than that of the control aerated concrete mix at the same age [34]. Foamed concrete mixes containing 10 and 20% sand replacements by OPA sieved through a 600-μm sieve showed increased compressive strengths than that exhibited by the control mix due to the increase in density [31]. **Table 3** summarises the studies that investigated the effect of OPA replacement on the compressive strength.

2.3.4. Tensile strength and modulus of elasticity

High-strength concrete samples containing 10 and 20% replacement levels of fine OPA (d_{50} = 10.1 μm) exhibit higher splitting tensile strengths than their corresponding control mix at 90 days of age [29]. The authors reasoned this increase to the high fineness of OPA and its pozzolanic reaction with cement, creating increased CSH compounds. Even though a fine OPA was used, higher replacement levels of cement by OPA (50% by weight of cement) exhibit lower tensile splitting strengths than the control mix [32]. Higher tensile splitting strengths are exhibited by foamed concrete samples containing OPA (passing through a 600-μm sieve) replacing sand at 10 and 20% than those of the control mix [31].

High-strength concrete samples containing 20% of fine OPA (d_{50} = 10.1 μm) exhibited similar modulus of elasticity readings as that of the control mix [12, 29]. Concrete samples containing fine OPA (10.1 μm) at cement replacement levels of 10 and 25% by weight of cement exhibit higher modulus of elasticity readings than that of the control mix. However, concrete samples containing coarse OPA (d_{50} = 19.9 μm) exhibit lower modulus of elasticity readings than the control mix [38].

In aerated concrete samples using fine OPA (1% retained on 45-μm sieve), samples containing 20% replacement of cement by OPA exhibited higher modulus of elasticity readings than the control mix [21]. The authors reasoned this increase to the pozzolanic reaction between the fine OPA particles and the calcium hydroxide emitted by cement hydration, creating a refined and stiffer microstructure. The modulus of elasticity readings of concrete samples containing recycled aggregate and a 20% fine OPA replacement level was lower than that of the control mix and was similar to those exhibited by a concrete sample with recycled aggregate and 100% cement [33].

2.3.5. Flexural strength

Limited studies have endeavoured on studying the effects of OPA incorporation into concrete on its flexural strength. High-strength concrete samples containing OPA as cement replacements exhibit a lower flexural strength than those exhibited by the control mix [40]. However, the author states that the samples containing a 30% fine OPA replacement level exhibit flexural strengths near to that of the control mix. On the other hand, Lim et al. [31] states that foamed concrete mixes having their sand replaced by 10 and 20% of OPA (sieved through a 600-μm sieve) exhibit higher flexural strengths than those exhibited by the control mix.

Author(s)	Particle size tested (μm)	Replacement levels of OPA investigated	Tested median	Standard	Recommended particle size/replacement level
Tay [25] Tay and Show [28]	Passing through a 150-μm sieve	10–50% by weight of cement	Concrete	BS 1881	10%
Sata et al. [12]	10.0	10–30% by weight of cement	High-strength concrete	100 × 200-mm cylinders	20%
Abdullah et al. [35]	1% retained on 45-μm sieve	10–50% by weight of cement	Aerated concrete	BS1881:116 (70.6 mm^3)	10–30%
Jaturapitakkul et al. [36]	183.0, 15.9, and 7.4	10–40% by weight of cement	Concrete	100 × 200-mm cylinders	7.4 μm to 20%
Sata et al. [29]	10.1 μm	10–30% by weight of cement	High-strength concrete	100 × 200-mm cylinders	20%
Chindaprasirt et al. [30]	10.2 μm	20, 40, and 55% by weight of cement	Concrete	100 × 200-mm cylinders	20%
Tangchirapat et al. [17]	183.0, 15.9, and 7.4	10–40% by weight of cement	Concrete	100 × 200-mm cylinders	15.9 μm to 10% 7.4 μm to 20%
Chindaprasirt et al. [23]	1–3% retained on 45-μm sieve	20 and 40% by weight of cement	Mortar	ASTM C39	20%
Rukzon and Chindaprasirt [26]	55.0, 20.0, and 7.4 μm	20 and 40% by weight of cement	Mortar	ASTM C109 (50mm^3)	7.4 μm to 20%
Tangchirapat et al. [15]	10.1 μm	10–30% by weight of cement	High-strength concrete	100 × 200-mm cylinders	20%
Sata et al. [37]	9.2 μm	10–30% by weight of cement	Concrete	ASTM C39	10%
Hussin et al. [21]	1% retained on a 45-μm sieve	20% by weight of cement	Aerated concrete	BS 1881:116	20%
Tangchirapat and Jaturapitakkul [38]	19.9 and 10.1	10–30% by weight of cement	Concrete	100 × 200-mm cylinders	19.9 μm to 20% 10.1 μm to 30%
Megat Johari et al. [18]	2.06 μm	20, 40, and 60% by weight of cement	High-strength concrete	BSEN 12390–3	40%
Sata et al. [39]	13 μm	10–40% by weight of cement	Mortar	ASTM C109	10–20%
Lim et al. [31]	Passing through a 600-μm sieve	10 and 20% by weight of sand	Foamed concrete	BSEN 12390–3	10–20%

Table 3. Summary of studies investigated the effect of OPA incorporation on compressive strength.

In another study conducted by Altwair et al. [24], engineering cementitious composites (ECCs) are tested for their flexural behaviour. These ECCs are designed to exhibit enhanced ductility and toughness; therefore, they use higher amounts of cementing materials and have their coarse aggregates eliminated from their design. The ECCs in this study used different amounts of added fine OPA 0, 0.4, 0.8 and 1.2 by weight of cement and used different water to binder ratios of 0.33, 0.36 and 0.38. The OPA that the authors use in this study was sieved through a 300-μm sieve, then ground using a ball mill and afterwards heat-treated at 450°C for 90 min to eliminate any glassy phase crystallisation and agglomeration of the OPA particles. They state that an ECC mix containing OPA at 0.4 by weight of cement and water to binder ratio of 0.36 exhibits the highest flexural strength among the conducted ECC mixes. In addition, a decrease in flexural strengths is exhibited with increasing OPA content and increasing water to binder ratio. Furthermore, ECC mixes containing OPA at 0.4 and 0.8 by weight of cement and water to binder ratio of 0.33 exhibit higher flexural strengths than the control mix at 90 days of age.

2.3.6. Drying shrinkage

Concrete samples containing cement replacements by OPA (sieved through a 150-μm) sieve show higher drying shrinkage readings than those exhibited by the control mix [25]. In addition, drying shrinkage is proportional to the increase in OPA content. Concrete samples with 50% of its cement replaced by OPA (sieved through a 45-μm sieve) exhibit a drying shrinkage reading higher by 21% than that of the control mix at the age of 90 days [32]. The authors reason this increase in drying shrinkage to the variation in moisture loss rate caused by different porosity and pore distribution.

Different sized OPA particles exhibit different readings of drying shrinkage [38]. At the age of 6 months, concrete samples having 30% of its cement replaced by coarse OPA exhibit slightly lower drying shrinkage than the control mix. On the other hand, concrete samples containing fine OPA (d_{50} = 10.1 μm) at the same replacement level of 30% exhibit lower drying shrinkage readings than both the control mix and the mixes with coarse OPA. Tangchirapat and Jaturapitakkul [38] and Tangchirapat et al. [15] reason this reduction in drying shrinkage to the pozzolanic reaction and the packing effect of the fine OPA particles, hence, transforming the large pores into smaller pores and as a result reducing the moisture loss.

Added fine OPA (1% retained on a 45-μm sieve) to aerated concrete at an addition percentage of 20% by weight of cement reduced the drying shrinkage [21]. Drying shrinkage readings of aerated concrete samples containing OPA exhibit lesser drying shrinkage readings than the plain aerated concrete samples. The authors reason this reduction in drying shrinkage to the more compact paste caused by the pozzolanic activity of the fine OPA and to its packing effect. **Table 4** summarises the studies that tested the effect of OPA on drying shrinkage.

2.3.7. Heat evolution

Using fine OPA as a cement replacement delays the time for the concrete to reach its peak temperature [29]. Concrete specimens containing 30% fine OPA cement replacement is capable of causing a 15% reduction in peak temperature in comparison to the control mix [12, 21, 41]. Fine OPA and heat-treated fine OPA exhibit different behaviours when it comes to heat evolution [42]. Cement pastes containing fine-treated OPA emit a higher heat evolution temperature than the control paste. The researchers reason this raised temperature to the high pozzolanic activity of the treated fine OPA. On the other hand, fine OPA pastes emit lower

Author (s)	OPA particle size (μm)	Replacement level investigated	Median	Effect	Recommended replacement
Tay [25]	100% passing through 150-μm sieve	10–50% by weight of cement	Concrete	Drying shrinkage increased with OPA replacement level	10% replacement slightly increased the shrinkage strain but it does not adversely affect the change in volume of concrete
Tangchirapat et al. [15]	10.1 μm	10–30% by weight of cement	High-strength concrete	Decrease in drying shrinkage with increase in OPA level	30% showed a lower drying shrinkage strain than the control mix
Abdul Awal and Nguong [32]	100% passing through 45-μm sieve	50% by weight of cement	Concrete	OPA concrete samples showed a higher drying shrinkage than the control mix	—
Tangchirapat and Jaturapitakkul [38]	19.9 and 10.1 μm	10–30% by weight of cement	Concrete	Coarse OPA up to 30% exhibited similar shrinkage to that of the control mix.	10–30% fine OPA exhibited a lower drying shrinkage than the control mix
Hussien et al. [21]	99% passing through 45-μm sieve	20% by weight of cement	Aerated concrete	OPA aerated concrete exhibited less drying shrinkage strains than the control mix	20%

Table 4. Effect of OPA incorporation on drying shrinkage readings.

temperatures compared to that of the control paste. This is reasoned to the low pozzolanic activity of the fine OPA in comparison to the treated fine OPA. The reduced pozzolanic activity is due to the decreased content of glassy phases within the particles of fine OPA in comparison to that of the fine-treated OPA.

2.3.8. Porosity, permeability and water absorption

Concrete samples containing OPA (sieved through a 150-μm sieve) show the tendency in absorbing more water with an increasing OPA content [25, 28]. Higher readings of water absorption are exhibited by concrete samples containing OPA as cement replacements in comparison to those exhibited by the control mix. The authors reason this increase in water absorption to the porous nature of concrete containing OPA. However, high-strength concrete containing fine OPA (10.1 μm) at a cement replacement level of 10% exhibits less water absorption readings than that of the control mix [43]. The authors reason this reduction in water absorption to a refined pore structure which results in a concrete sample with a reduced porosity.

High-strength concrete samples containing fine OPA (d_{50} = 8 μm) replacement levels of 20, 40 and 55% are tested for their water permeability by Chindaprasirt et al. [30]. At the ages of 28 and 90 days, high-strength concrete samples incorporating fine OPA at replacement levels of 20 and 40% by weight of cement exhibit less permeability readings than that of the control mix. In addition, samples containing fine OPA replacement levels show lower permeability readings, even though requiring higher water to binder ratios. The researchers recommend a 20%

replacement level of fine OPA as an outcome of their study. In another study, a 30% replacement level of cement by fine OPA (d_{50} = 10.1 μm) is recommended in achieving impermeable high-strength concrete [15]. The reduced permeability is attributed to the pozzolanic reaction and to the packing effect of fine OPA particles which results in filling the voids and increasing the density of the mix [30].

Concrete samples containing fine and coarse OPA replacement levels show a different behaviour when testing their permeability. Concrete samples containing coarse OPA as partial cement replacements are more permeable than the control mix at an earlier age but lower at later ages [38]. The higher permeability readings are attributed to the increased water to binder ratio to achieve the same workability as that of the control mix.

In contrast to coarse OPA, concrete samples containing fine OPA replacement levels are less permeable than the control mix. Concrete samples containing recycled aggregate and fine OPA replacement level of 20% by weight of cement show that they are less permeable than the control mix [33]. High-strength concrete samples containing partial cement replacements at levels of 20, 40 and 60% by weight of cement by ultrafine OPA (d_{50} = 2.06 μm) are tested for their absorption, permeability and porosity [18]. The authors state that the incorporation of ultrafine OPA reduced the porosity of high-strength concrete, reduced its water absorption and reduced the water permeability at the age of 28 days.

2.3.9. Carbonation

Mortars containing OPA having 3° of fineness at replacement levels of 20 and 40% by weight of cement are tested for their carbonation ingress depth [26]. The fineness of OPA particles are coarse OPA (70% retained on a 45-μm sieve), medium OPA (15% retained on the 45-μm sieve) and fine OPA (3% retained on the 45-μm sieve). The carbonation ingress depth is conducted according to RILEM's CPC18, and readings are taken at the ages of 3, 7, 14, 28 and 60 days of age. In general, OPA mortars show an increase in carbonation depth in comparison to the control mortar. However, the behaviour of OPA mortars differs according to the fineness of OPA. Mortar samples containing fine OPA show less increase in carbonation ingress depth with increasing age than mortars containing medium sized and coarse OPA. The authors reason this decrease to the better dispersion and to the filler effect of fine OPA despite its higher pozzolanic activity. This made the mortars with finer OPA incorporations denser and better to resist carbonation.

2.3.10. Chloride penetration and corrosion resistance

High-strength, high-workability concrete containing 10–30% OPA replacement levels by weight of cement are tested for their chloride penetration resistance and corrosion resistance [43]. The OPA used in this study has a median particle size of 20 μm. The chloride penetration test is conducted in accordance with ASTM 1202. Results for the chloride penetration show that chloride penetration decreases with an increasing OPA content. The authors reason this decrease in chloride penetration to the separation of large pores to the increase in nucleation sites caused by the increase in pozzolanic reaction products in the cement paste. The study states that replacing cement by fine OPA at a level of 30% by weight of cement shows increased resistance to corrosion. The authors reason this increase to the high pozzolanic reactivity of the fine OPA and to the reduced amount of calcium hydroxide in the paste. Although the 30% replacement level is effective in increasing chloride and corrosion resistance, the researchers recommend a 20% replacement level of cement by fine OPA. This is due to the increased quantity of superplasticizer required for the 30% OPA replacement mix to achieve the required workability, hence making the mix more expensive.

However, a 60% cement replacement by ultrafine OPA (d_{50} = 2.06 μm) in high-strength concrete is more effective in resisting corrosion [18]. The 60% cement replacement by ultrafine OPA reduces the total charge passed in comparison to that of the control mix by 84%.

2.3.11. Sulphate resistance and alkali silica reaction

Concrete bars containing fine OPA cement replacements are exposed to a 5% solution of magnesium sulphate ($MgSo_4$) for 24 months. Results show that fine OPA concrete bars exhibit less expansion when exposed to the sulphate solution [36]. Finer OPA replacements not only cause the reduction of calcium hydroxide ($Ca(OH)_2$) in the concrete but also reduce the voids between the aggregate and hydration products, creating a denser concrete. No adverse effect was found on the concrete expansion or on the compressive strength when replacing 20% of cement by fine OPA [15, 17]. High-strength concrete bars containing cement replacements of both 45- and 10-μm OPA are tested for their sulphate resistance and compressive strength loss [27]. The authors state that concrete bars containing 10-μm OPA show more resistance to sulphate attack and less reduction in compressive strength than those exhibited by the control and 45-μm concrete bars. The high sulphate resistance is attributed to the high pozzolanic reactivity of the finer OPA particles which in return reduces the $Ca(OH)_2$ and reduces the amount of voids in the mix making it denser, hence, more resistant to sulphate attack. Concrete samples made from recycled aggregate show a higher resistance to sulphate attack when 20% of their cement is replaced by fine OPA [33]. The higher resistance in this case is also attributed to the reduced amounts of $Ca(OH)_2$ and tricalcium aluminate (C_3A) when cement is replaced by fine OPA, hence reducing gypsum formation and ettringite re-crystallisation.

Mortar bars containing OPA having a fineness of 519 m^2/kg replacing cement levels of 10, 30 and 50% by weight of cement experience less expansion due to the alkali silica reaction (ASR) [19]. Increased suppressing of the ASR is observed with increasing OPA content. Abdul Awal and Hussin [19] reason this increased suppressing of the ASR to the pozzolanic reaction occurring between OPA's high amounts of silica with the alkalis existing in the concrete, hence limiting the amounts of alkalis reacting with aggregate.

3. Conclusion

OPA is a relatively new pozzolanic material that has been introduced in partially replacing sand or cement in manufacturing concrete, mortar, aerated concrete and high-strength concrete. The studies discussed showed that OPA needed further processing in order for it to work as a pozzolan. The further processing includes grinding to increase the fineness of OPA and heat treatment to decrease the amounts of carbon within its particles. Although enhancing the properties of OPA is beneficial, these enhancing processes do apply increased cost. In addition, the problem with OPA is its increased demand of water when mixing. Therefore, controlling the water demand by applying superplasticizer is a good method in reducing its water demand, hence enhancing its properties. Researchers go further in the use of OPA and state that it is compulsory to use water-reducing agents when using OPA as the supplementary cementing material.

This chapter reviews the potential use of OPA as a supplementary cementing material for concrete production. The review emphasises the effects of POFA on the fresh, hardened and durability properties of concrete. Capitalising such waste products in the production of concrete will not only benefit the recycling chain process but also produce a green product which enables the reduction of cement quantities used and also produce an energy-efficient building material. This is in line with the United Nation's Sustainable Development Goals.

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Mixture Proportioning for Oil Palm Kernel Shell

Mohamed Gibigaye and Gildas Fructueux Godonou

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Abstract

Oil palm kernel shell (OPKS) is an organic lightweight aggregate (LWA) used as coarse aggregate in tropical countries for concrete in low-cost buildings. Concrete mixture proportioning is used to calculate the quantities of different constituents required to achieve different properties. For LWA concrete with mineral aggregate, there exist mix design methods that follow rigorous sequence of steps that consider performance specifications. However, no such method exists for concrete using organic coarse aggregate, namely, OPKS. The methods that exist for OPKS concrete that satisfy technical specifications for structural lightweight concrete (LWC) are based on trial and error or empirical methods. With trial and error method, it is not always possible to predict the value of specific properties of the concrete; however, engineers are mainly concerned with obtaining specific properties when proportioning a concrete mixture. The present topic presents a structured method for trial mix proportioning of structural LWC using OPKS as coarse aggregate. Based on the principle of the absolute volume method in ACI 213, the method is presented, following the below headings: (1) properties of constituents of OPKS concrete; (2) mix design procedure; and (3) results and discussion. Technicians in tropical oil-palm-producing countries for low-cost buildings can use the presented method.

Keywords: lightweight concrete, mix proportioning, compressive strength, oil palm kernel shell, Benin

1. Introduction

The oil palm sector in the Republic of Benin is experiencing a revival since the last 10 years with a production estimated to be more than 505,000 tons in 2015 [1]. This production, according to the Ministry in charge of agriculture, is expected to increase to reach 800,000 tons by 2030. From the industrial and artisanal transformation of this product, we obtain among others, oil palm kernel shells (OPKSs), considered as vegetable waste. In areas of production, traditionally near rural populations, OPKS is often used in the building of houses with and without multiple storeys. The OPKSs are used as coarse aggregate for the concrete of structural elements (**Figure 1**). To date, it is permissible to note the apparent good record of service of most of these buildings, constructed more than 30 years back. However, despite the wide availability of OPKSs, the lack of reliable technical information behind OPKS concrete making has led to reluctance by conventional professionals. For the moment, in Republic of Benin as in other oil-palm-producing countries, these materials have little commercial value, despite their technical qualities: (1) they have a relatively low weight and are naturally sized; (2) they are hard enough to break and are of organic origin; and (3) once embedded in the cement matrix of concrete, they do not have any toxic effects on the concrete because they are imputrescible [2]. Moreover, in some of the production areas, the OPKSs are recovered and burned in the cement industry under conditions that do not necessarily satisfy the requirements relating to good management of air pollution. As in Benin, OPKSs are available in large quantities in almost all tropical countries and the problem of managing OPKSs is posed almost in the same way. In such countries as Malaysia and Nigeria, several studies have been undertaken in the past 30 years with success in studying the mix design of structural lightweight concrete using OPKSs as aggregate [2–9]. Most mix design methods for OPKS concrete that satisfy the requirements of technical specifications for structural lightweight concrete were based on trial and error or on empirical methods because the methods based on the proven structured methods for normal and lightweight structural concrete with mineral aggregates had failed. With the trial and error method, it is not always possible to predict the value of specific properties of the concrete, whereas an engineer is mainly concerned with obtaining these specific properties in the process of proportioning a concrete mixture. To lead to that, one of the ways consists of the determination of ranges of values for the ratios of water/cement, cement/aggregates, coarse aggregate/fine aggregate, as well for the cement content that can permit to get the targeted specifications. Some results are available [10], but it is still necessary to work to further refine the range of values of the coarse/fine aggregate ratio in the process of designing structural lightweight concrete using OPKSs as coarse aggregate.

In the present study, a trial mix is proposed for a structural lightweight concrete using OPKSs of Benin as coarse aggregate, based on the principle of absolute volume methodology of ACI 213.

Figure 1. An example of a one-storeyed house in Missérété, constructed in 2014 with the use of OPKS concrete for the supporting elements. (a) Overview of the ongoing building. (b) Zoom on the columns of the main facade, showing on their surface the oil palm kernel shells in the cement matrix.

This approach is conducive to recommending mix proportions of concrete that allow its use for structural elements in low- and moderate-cost buildings in tropical countries and in earthquake-prone areas.

2. Properties of constituents of OPKS concrete

OPKS concrete (OPKSC) is a judicious mix of cement, sand, OPKSs, and water. As the mechanical properties of OPKSC are largely influenced by the physical properties of OPKS, in the present chapter, the emphasis is on the study of the properties of OPKS. OPKSs used as coarse aggregate in OPKSC are one of the wastes produced during the process of obtaining palm oil. For that six stages are necessary: sterilization, threshing, pressing, depericarping, separation of kernel and shell, and clarification [11]. For the present study, the OPKSs used were collected from an artisanal mill at Missérété 6°35′43.4″N; 2°35′26.9″E and were freshly discarded (**Figure 2**).

They were thoroughly rinsed with potable water and dried in the sun for 4 h, in order to remove impurities, present on the shells. Then, they had been stored in containers. After the pretreatment, OPKS aggregate needs to be treated before using in concrete [12]. Various treatment processes are mentioned in the literature to remove the impurities (dust and oil coating) from aggregates [13–18].

In this study, the treatment method used consists of the following:

- Put 30 kg of OPKS in an aqueous solution of potassium hydroxide with a mass concentration of 7.4 g/l for 2 h.
- Wash the shells with potable water in the sun, until the shells surface became dry.

Figure 2. OPKS waiting for a transaction at Missérété.

Figure 3. Different size of Oil Palm Kernel Shell for the concrete mixing.

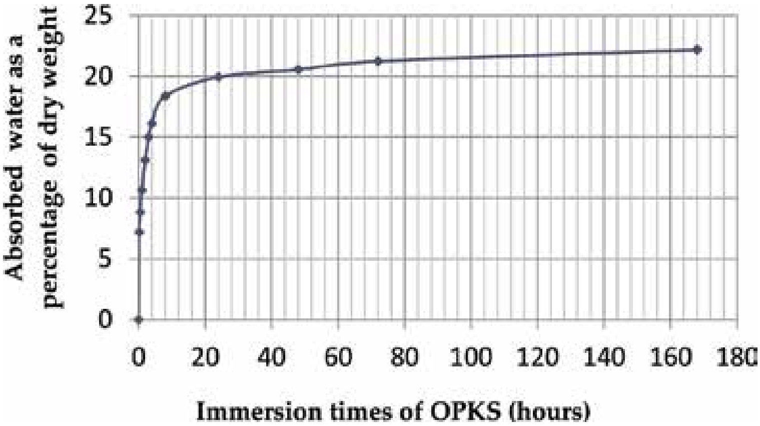

Figure 4. Curve of water absorption of the used OPKS.

Figure 5. Draining of OPKSC after imbibition to obtain saturated surface dry (SSD) status.

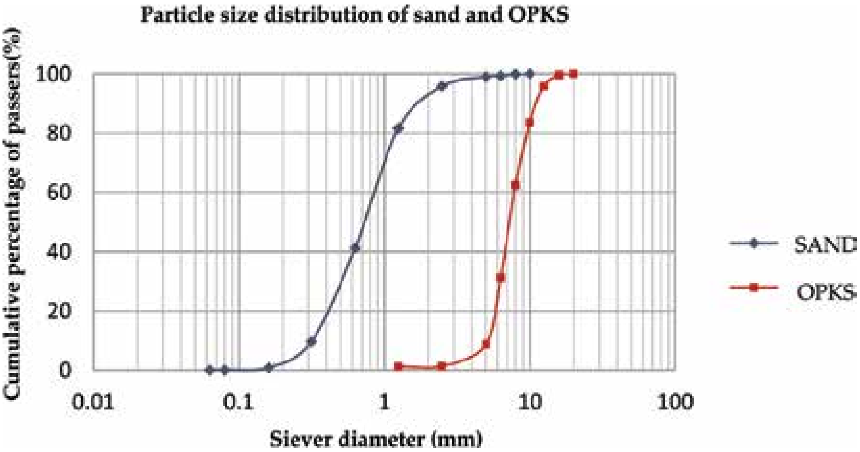

Figure 6. Particle size distribution of sand and OPKS.

Properties	Constituents of OPKS concrete from Benin		Constituents of OPKS concrete used elsewhere [10]	
AGGREGATES (SAND = Fine, OPKS=Coarse)				
	Sand	OPKS	Sand	OPKS
Specific gravity	2.59	1.31	2.60	1.17
Loose bulk density (kg/m^3)	1410	530	—	500-600
Water absorption, 24 h, (%)	—	19.93	—	23.32
Fineness modulus	2,4	—	2.56	—
Aggregate abrasion value (Los Angeles),%	—	5.02	—	4.80
Type of cement	CEM II 32.5		CEM I 42.5	

Table 1. Physical properties of constituents of OPKS concrete.

Most of the shells were within the thickness range of 2.00–6.00 mm. The shape of the OPKS aggregate varies irregularly as flaky shaped, angular, or polygonal as shown in **Figure 3**. The surface texture of the shell was fairly smooth for both concave and convex faces. The broken edges were rough and spiky. To take into account the fact that the shells absorb water (**Figure 4**), we used them in saturated surface dry condition as shown in **Figure 5**. Particle size distribution for OPKS and sand are shown in **Figure 6**. The other measured physical properties of OPKS were compared with those obtained by previous authors and are shown in **Table 1**.

3. Mix design procedure for OPKS concrete

3.1. Trial mixture proportions

The lightweight concrete (LWC) mix design is usually established by trial mixes [19]. In the preliminary investigation of OPKS concrete mix proportion, the procedure followed was the method for lightweight concrete proposed by Georges Dreux [20]. As mentioned in **Table 2**, the obtained cylindrical compressive strength was far below the targeted designed strength, and what that means is that the method is not appropriate for the mixing of structural lightweight concrete using OPKS.

According to [21], the best approach to making a first trial mixture of lightweight concrete, which has given properties and uses a particular aggregate from a lightweight aggregate source, is to use proportions previously established for a similar concrete using aggregate from the same aggregate source. Based on the similarity of the physical properties of the constituents of OPKS concrete (**Table 1**), in a second approach, the mix proportions proposed by Mannan [3] was used. The obtained results were presented in **Table 3**. The 28-day cylindrical compressive strength of 23.50 MPa obtained is greater than the 17 MPa required by ACI [22]. This shows that the said method of mix proportioning is suitable for mix design of structural lightweight concrete, using OPKS from Benin, and therefore can be recommended. Though effective, the method proposed by Mannan is a trial and error method. It does not give the flexibility to vary the mix ratio in order to change the technical specifications of the concrete in the event of need.

3.2. Experimental method of mix proportioning

According to ACI 213 [23], the absolute volume method considers that the volume of fresh concrete, produced by any combination of materials, is considered equal to the sum of the absolute volumes of cementitious materials, aggregate, net water, and entrapped air. The approach proposed by ACI 213 is based on the use of the indications of the ACI 211 [24], which is a method of mix proportioning, often used for concrete of normal weight aggregates. Mannan [3] has proven that this approach does not give good results for the mix design of structural lightweight OPKS aggregate. In this study, we agree to use the principle defined by said method, through its definition, that is to say:

$$V_{OKPS} + V_{Sand} + V_{Cement} + V_{Water} + V_{Air} = 1 \tag{1}$$

Using the specific gravity, the formula (Eq. (1)) can be rewritten:

$$\frac{C}{\rho_C} + \frac{S}{\rho_S} + \frac{W}{\rho_W} + \frac{OPKS}{\rho_{OPKS}} + V_{Air} = 1 \tag{2}$$

By applying $\frac{W}{C} = k_W$ and $\frac{OPKS}{S} = k_{OPKS}$ we have:

$$C\left(\frac{1}{\rho_C} + \frac{k_W}{\rho_W}\right) + S\left(\frac{1}{\rho_S} + \frac{k_{OPKS}}{\rho_{OPKS}}\right) + V_{Air} = 1$$

$$S = \frac{(1 - V_{Air}) - C\left(\frac{1}{\rho_C} + \frac{k_W}{\rho_W}\right)}{\left(\frac{1}{\rho_S} + \frac{k_{OPKS}}{\rho_{OPKS}}\right)} \tag{3}$$

				28-Day compressive strength (N/mm²)	
Mix order	**OPKS/Sand Ratio (by absolute volume)**	**Mix proportion C:S:OPKS**	**Demoulded density (kg/m³) (NF EN 12350-6)**	**Obtained strength (EN12390-3)**	**Targeted design strength**
A1	2.1	1:1.05:1.21	1570.59	4.67	25.00
A2	1.6	1:1.26:1.09	1766.52	7.27	25.00
A3	1.0	1:1.64:0.89	1826.65	8.11	25.00
A4	0.8	1:1.82:0.79	1881.30	9.25	25.00
A5	0.6	1:2.04:0.67	1893.16	10.65	25.00

Table 2. Mix design for OPKS concrete according to Dreux [OPKS aggregates: saturated surface dry (SSD) conditions, bulk density = 0.53, specific gravity = 1.43; cement: CPJ 35 (type CEM II, 32.5), Density = 3.10, genuine class = 450 bar, content = 530 kg/m³; sand: Bulk density = 1.41, specific gravity = 2.63; w/c ratio = 0.48; wished slump = 5 cm; mix proportion by weight, C = cement, S = sand, OPKS = oil palm kernel shell].

	Proportion by weight of cement (cement = 480 kg/m³), w/c = 0.41			**Demoulded density (kg/m³)**	**Fresh property (slump, mm)**	**28-Day compressive strength (N/mm2)**
	Cement	**Sand**	**OPKS**			
B1	1.00	1.71	0.77	1890–1905	7	24.20[a]
B2	1.00	1.71	0.77	1889–1941	9	23.50[b]

[a] Compressive strength obtained by Mannan [3].

[b] Compressive strength obtained by authors.

Table 3. Mix design for OPKS concrete according to [3].

where S denotes the sand content in kg/m^3 of concrete, V_{Air} denotes the entrapped air content in $litres/m^3$ of concrete, C denotes the cement content in kg/m^3 of concrete, ρ_C denotes the density (specific gravity) of the cement in kg/m^3 of concrete, ρ_S denotes the mean particle density (specific gravity) of the sand in kg/m^3 of concrete, and ρ_{OPKS} denotes the mean particle density (specific gravity) of the OPKS in kg/m^3 of concrete.

As the specific gravity of all constituents of the mix were known (see Section 2), the entrapped air volume V_{Air} and the ratio k_W were fixed, taking into account the values obtained by most of previous authors [10, 25]. Thus, the only unknown quantities in the formula (Eq. (3)) were the cement content, C, and the k_{OPKS} ratio. Knowing that, according to Basri et al. [26], the cement contents range from 285 to 510 kg/m³; we agreed in this study to vary the cement content classes from 400 to 550 kg/m³ with a step of 50 kg/m³. For each class of cement, we varied the k_{OPKS} ratio from 0.50 to 0.75. Indeed, according to the practice of traditional use of OPKS concrete in Benin, the average value of this ratio is 0.6 for the mix proportion of structural lightweight concrete. The obtained results were presented in **Table 4**.

Mix order	Cement content	OPKS/Sand ratio	Mix proportion	Demoulded density	Fresh property	Average Cylindrical 28-day Compressive strength
	(kg/m^3)		C:S:OPKS	(kg/m^3)	(Slump, mm)	(N/mm^2), 28-day
		0.45	—	—	—	—
C1		0.50	1:2.10:1.05	1872.63	8.5	8.35
C2	400	0.55	1:2.00:1.10	1875.44	7.92	6.14
C3		0.60	1:1.91:1.15	1838.74	6.23	8.91
C4		0.65	1:1.83:1.19	1829.82	5.1	11.22
C5		0.70	1:1.75:1.23	1811.33	4.7	12.03
C6		0.75	1:1.68:1.26	1789.50	3.86	10.70
		0.40	—	—	—	—
		0.45	—	—	—	—
C7	450	0.50	1:1.76:0.88	1859.40	34.50	10.80
C8		0.55	1:1.67:0.92	1876.81	30.35	13.54
C9		0.60	1:1.60:0.96	1840.09	26.98	15.19
C10		0.65	1:1.53:0.99	1843.79	22.01	18.63
C11		0.70	1:1.47:1.03	1790.92	16.38	9.58
C12		0.75	1:1.41:1.06	1759.35	16.25	9.44
		0.40	—	—	—	—
C13		0.45	1:1.56:0.70	1895.35	47.07	12.38
C14	500	0.50	1:1.48:0.74	1887.08	42.36	18.27
C15		0.55	1:1.41:0.78	1901.31	51.12	12.21
C16		0.60	1:1.35:0.81	1879.85	52.67	12.09
C17		0.65	1:1.29:0.84	1849.70	48.16	13.50
C18		0.70	1:1.24:0.86	1798.10	27.07	10.03
		0.75	—	—	—	—
C19	550	0.40	1:1.40:0.56	1920.86	86.84	14.91
C20		0.45	1:1.32:0.60	1857.09	125.01	15.36
C21		0.50	1:1.26:0.63	1892.48	80.4	17.54
C22		0.55	1:1.20:0.66	1893.12	80.60	12.28
C23		0.60	1:1.14:0.69	1866.81	77.15	12.21
C24		0.65	1:1.09:0.71	1851.51	83.09	12.21
		0.70	—	—	—	—
		0.75	—	—	—	—

Table 4. Mix design for OPKS concrete based on the variation of the OPKS/Sand ratio and the cement content [w/c=0.45; Stage of OPKS=saturated surface dry; Mix proportion by weight].

4. Results and discussion

4.1. Workability

The workability increased with increasing cement content and sand content but not for all cement classes. The cement contents of 400 and 450 kg/m^3 gave for each OPKS/sand ratio, more than 70% in weight for the solid part of the concrete mix, and in the same moment, for cement contents of at least 500 kg/m^3, the said quantity was lower than 70%. For 400 and 450 kg/m^3 of concrete, the workability decreases with the increase in the quantity of OPKSs, that is to say, more the quantity of OPKSs is, the lower is the workability. This is due to the increase of the specific surface because of the increase in the quantity of OPKSs, thus requiring more water to make the specimens workable. This trend was mentioned elsewhere [5].

Slump values for cement content of 450, 500, and 550 kg/m^3 were included mostly in the range of recommended values for structural lightweight concrete according to ACI 211. 2–98 [24], that is to say, 25.4–101.6 mm. The low value of the workability (slump less than 10 mm) for the cement content of 400 kg/m^3 could be because the quantity of mortar that penetrates the cavities and the pores of OPKSs no longer permits to have the needed quantity of cement paste, which allows for good workability. On the other hand, for cement contents higher than 450 kg/m^3, the variation of the slump value versus OPKS/sand ratio, does not follow the logic of the growth of the slump value according to the decrease of the OPKS quantity as proven also by [5, 27].

Therefore, the optimal cement content relative to the workability would be 450 kg/m^3, and the recommendable range values of OPKS/sand ratio could be in the range of 0.50–0.65 by weight.

Thus, to obtain the minimum recommendable values of slump for various types of constructions according to Table 3.1 of [24], the mix ratios designated by C7, C8, C9, and C10 in **Table 4** could be the suitable ones. Note that the ratio of water/cement was 0.45.

4.2. Density

In this investigation, we determined the 28-day air-dry density of the specimens, which were kept in ambient laboratory conditions (RH of 74–88%; temp. of 27 ± 2°C). The results were shown in **Table 4**. Note that all densities obtained are less than 2000 kg/m^3, which allows saying that all the mix proportions were those for lightweight concretes. From **Table 4**, it can be seen that, in each cement content class, the density decreases as the proportion of shells increases, with a maximum value of almost 1880 kg/m^3 for cement content of 400 and 450 kg/m^3. Mixtures with cement content equal to or higher than 500 kg/m^3 had a maximum density of more than 1900 kg/m^3, which is above the maximum value of the density for structural lightweight concrete, according to Mindess [16]. Thus, it appears that except the sand, the cement content is also a parameter influencing the density of OPKS concrete. Taking into account the results of workability (Section 4.1) and the maximum value of 1900 kg/m^3, we could recommend the mix proportions of C7, C8, C9, and C10, with cement content of 450 kg/m^3 and w/c = 0.45 to achieve a density which corresponds to the requirements of structural lightweight concrete.

4.3. Compressive strength

From the results presented in **Table 4**, it can be noted that for every class of cement content, the 28-day cylindrical compressive strength increased to attain a maximum value, before it decreased, depending on the quantity of shells in the concrete mix. The cement content of 400 kg/m^3 showed a maximum of 28-day cylindrical compressive strength of 11.22 MPa for OPKS/sand ratio equal to 0.65, corresponding to almost 27% of OPKS in the rigid part of the concrete. For 450 kg/m3, we recorded the greatest value of the 28-day cylindrical compressive strength of 18.63 MPa, corresponding to 447.36 kg of OPKS in 1 m^3 of concrete. This content is in the rangeof values (290–450 kg) for OPKS in structural lightweight concrete, as reported by [25]. The value of 18.63 MPa is higher than the specified cylindrical compressive strength of 17 MPa given by ACI. Relative to cement contents of 500 and 550 kg/m^3, the maximum values of the 28-day cylindrical compressive strength were, respectively 18.27 and 17.54 MPa, and the corresponding OPKS/sand ratio was 0.5, which corresponds to almost 20% of OPKS in the rigid part of the concrete.

The developing of the compressive strength of the concrete with cement content less than 500 kg/m^3 was influenced by the amount of OPKS in the concrete mix, with a maximum value of up to 27% of the rigid part of the concrete. For these cement contents, the compressive strength is controlled by the strength of the shells [28]. During the compressive strength test, it is observed that the cement matrix failed first, which is to say that, the cracks path passed around OPKS aggregates. For cement contents of 500 and 550 kg/m^3, the compressive strength was influenced by the strength of the cement matrix and contrary to 400 and 450 kg/m^3, the cracks path passed through the shells of the concrete.

Thus, to produce economically structural lightweight concrete using OPKS as coarse aggregate and taking into account the recommended mix proportions for good workability and acceptable density, the mix ratios of C9 and C10 could be suggested. They could give the possibility to an engineer to fix efficiently the targeted values of specific properties in the mix proportioning of lightweight concrete, using OPKS as coarse aggregate.

4.4. OPKS concrete mixing proportioning process

Taking into account the results obtained earlier, we could recommend a general mixture proportioning procedure as follows [9]:

1. Establish the specific properties of the lightweight OPKSC for structural elements in low-cost buildings: slump [24], density [10], and 28-day compressive strength [29].
2. Determine the physical properties of constituents of concrete based on the applicable codes. For sand, we consider specific gravity, loose bulk density, fineness of modulus, and grading curve. For OPKS, we consider specific gravity, loose bulk density, water absorption after 24 h, aggregate abrasion value, and grading curve.
3. Choose the water/cement ratio based on the targeted 28-day compressive strength using the data from previous authors [10], as presented in **Table 5**.

Author (year) as cited by [10]	Mix proportion	Water/cement	28-day compressive strength (MPa)
Abdullah (1984)	1:2:0.6	0.40	20.50
Okafor (1988)	1:1.70:2.08	0.48	23.00
Okpala (1990)	1:1:2	0.50	22.30
	1:2:4	0.50	18.90
Teo and Lew (2006)	1:1.12:0.80	0.41	22.00

Range for water/cement ratio is from 0.40 to 0.50.

Table 5. Water/cement ratio for compressive strength (≥ 15 MPa), recommended by ACI and British code for structural LWC, obtained from the data of previous authors as reported by [10], for concrete without admixture.

4. Determine the cement content [10] in the range of 400 to 550 kg/m^3 based on the slump value and the 28-day compressive strength.
5. Determine the OPKS/sand ratio depending on the targeted slump value and the 28-day compressive strength.
6. Determine the air content ratio [12] in the range from 4.8 to 5.1
7. Calculate the sand content for 1 m^3 of concrete, based on the principles of the absolute volume method of ACI 213:

$$S = \frac{(1 - V_{Air}) - C(1/\rho_C + k_W/\rho_W)}{(1/\rho_S + k_{OPKS}/\rho_{OPKS})}$$

8. Determine the OPKS content for 1 m^3 of concrete, using the OPKS/sand ratio and sand content determined earlier.
9. Make a test mixture with sufficient volume to perform the "slump test" coming to 0.008 m^3, that is to say 8 l. If the slump is smaller than the one specified above, then increase the amount of cement and water between 5% and 15%, while respecting the ratio w/c as indicated earlier. If the slump is larger than indicated in the data, then increase the amount of sand and OPKSs by 5–15% without changing the ratio of OPKS/sand.

   If despite all the operator does not obtain the results, then review the calculations and obtain precisely again the characteristics of the materials constituting the concrete.
10. Calculate the final mix proportion

5. Conclusion

The mix proportions of C:S:OPKS in weight of 1:1.60:0.96 and 1:1.53:0.99 with cement content of 450 kg/m^3 and $w/c = 0.45$ had resulted in obtaining appropriate values for workability ($\geq 20mm$), density ($1800 \leq d \leq 1900kg/m^3$), and cylindrical compressive strength ($\geq 15MPa$), recommended by ACI and British Code for structural lightweight concrete. This study, as part of efforts to develop a structured method of proportioning of eco-friendly composite, demonstrates the possibility of linking mix proportions to properties of lightweight OPKS concrete and therefore makes the use of locally available materials in developing countries more feasible.

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Conflict of interest

There is no conflict of interest in this submission.

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Section 4

Dietary Applications of Palm Oil

Chemical Characteristics and Nutritional Properties of Hybrid Palm Oils

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Additional information is available at the end of the chapter

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Abstract

Nutritional guidelines and environmental issues are adversely affecting palm oil's image among consumers. However, hybrid palm oils are currently receiving increasing attention because of their interesting chemical characteristics and nutritional properties. Interspecific hybridization *Elaeis oleifera* × *E. guineensis* (O×G) has been originally exploited with the main aim of developing disease-resistant varieties. However, available literature data contribute to reinforcing the idea that interspecific hybrid O×G palm oil could be a potential substitute for other vegetable oils rich in monounsaturated fatty acids (i.e., high oleic sunflower and safflower oils). The chapter aims to review current knowledge on various aspects of hybrid palm oil chemical composition (fatty acids, triacylglycerols, partial glycerides, unsaponifiable matter components) and their changes during fruit ripening. The nutritional attributes of hybrid palm oils are compared with the ones of conventional African palm oils.

Keywords: interspecific hybrid palm, palm oil, ripening, *Elaeis oleifera*, tocotrienols, positional analysis, fatty acids, triacylglycerols

1. Introduction

Fruits of palms (drupes) belonging to the genus *Elaeis* have been exploiting to produce edible oils for 5000 years. "Palm oil" is obtained from the reddish pulp (mesocarp) of the fruits, mainly those of the African palm (*Elaeis guineensis* Jacq.) (EG) and, to a considerably small amount, those of the palm native in central and northern South America (*Elaeis oleifera* [H.B.K.] Cortés) (EO), also known as "caiaué." "Palm kernel oil" derives from the kernel inside the shell (endocarp) [1]. The

African palm grows spontaneously or in cultivated fields in tropical regions of Africa, Southeast Asia, and South and Central America, whereas the American oil palm only occurs in spontaneous populations from the south of Mexico to Amazon areas in Brazil and Colombia. High productivity, perennial nature of the plant, and low cost of oil production make the palm oil obtained from *E. guineensis* (henceforth referred to as "palm oil") the most produced and marketed vegetable oil worldwide. A total of 66.9×10^6 t of palm oil and 7.8×10^6 t of palm kernel oil were produced in 2017; Malaysia and Indonesia are the most important producers, with 57×10^6 t in all, corresponding to 85% of the world production [2].

Palm oil is a typical multipurpose vegetable oil; it is used in food products (cooking oils, margarine and other spreads, crisps, baked food, food additives, confectionary, dairy and dairy replacements, prepared foods, snacks), in food for livestock and household pets (as fat supplement), and in several non-food productions (biodiesel, oleochemicals, cosmetics and textiles). The wide range of applications for mesocarp oil is due to its fatty acid (FA) composition. Palm oil has approximately equal amounts of saturated (SFA) and unsaturated fatty acids (UFA), while the mesocarp oil from EO is much more unsaturated [3–6].

Despite its technological characteristics, public perception of palm oil is getting worse and worse; new evidence concerning the presence of process contaminants [7] and environmental issues [8] have been added to the well-known health impact of high dietary intake of SFA. Palm oil is considered "the worst" edible oil in France, in French Belgium and in Italy, as regard to both people's health and environmental impact, whereas in the extra-European countries (USA, UK, Canada, Australia, China, Saudi Arabia) the negative opinion on palm oil is really low [9]. Campaigning against palm oil has been quite tenacious in Italy; in the last 3 years, several petitions have been promoted by online magazines (Il FattoAlimentare), consumer associations (AltroConsumo), and farmer associations (Coldiretti); even a parliamentary motion to ban palm oil from canteens has been proposed. This induced some important brands (Misura, Mulino Bianco) and retailers (Coop, Esselunga) to meet the consumer demand by introducing foodstuffs without palm oil.

In such a climate, interspecific hybrid between the cultivated oil palm EG and its wild relative EO (O×G) is receiving increasing attention by researchers and stakeholders. The O×G hybrid provides a crude oil that contains significantly higher amount of oleic acid (O) and lower percentages of palmitic (P) and stearic (S) acid than conventional African palm oil. Hardon [10, 11] first provided data on crossability, cytogenetics, fertility, growth, yield, and FA composition of F1 hybrids O×G, with the objective of developing varieties resistant to diseases [12]; in fact, hybrid expresses less severe symptoms and a slower progression of "bud rot" disease than EG. Besides, hybrid is significantly less preferred by *Rhynchophorus palmarum* than African oil palm [13]. O×G hybrids inherit from the American parent other characters of interest, such as slower vertical stem growth [14], which could result in reduced harvesting costs.

Only in recent years, a wide range of characteristics of O×G interspecific hybrids has been thoroughly studied and described: yield and morphology [15–19]; phenological stages [20]; genome size [21, 22]; sensitivity to water stress [23, 24]; physiological and biochemical response to aluminum toxicity [25]; nutritional status [26]; seed germination [27]; fruit abscission process [28]; and mycorrhization process [29]. Even a comparative characterization of the physiological and biochemical performance of seedlings of O×G hybrids grown in hydroponics was carried out [30]. Nevertheless, very few studies have been conducted on the composition of the mesocarp oil. The chapter aims to review current knowledge about the various aspects of hybrid palm oil chemical composition: FAs, triacylglycerols (TAGs), partial glycerides, and unsaponifiable matter components. Available data on the composition of the hybrid palm oil during ripening are also summarized. Eventually, the nutritional attributes of hybrid palm oils are discussed in view of recently published papers about the consumption of crude oils from O×G hybrids.

2. Quality parameters

A set of quality parameters (free acidity, unsaponifiable content, water content, and insoluble matter content) gives an overall assessment of the whole amount of non-glyceridic constituents, which is relevant in determining the commercial value of raw fatty substances. In crude oils obtained by pressing pulp of hybrids palm drupes, unsaponifiable matter accounts for about 1 g/100 g oil, without any significant difference due to harvest time [31, 32]; water content ranges from 0.20 to 0.73 g/100 g oil; and insoluble matter content lies in the range 0.09–0.20 g/100 g oil [31]. The free fatty acid (FFA) content ranges between 0.35 (as g/100 g oil, determined by GC areas) and 2.91 (as palmitic acid %, determined by titration) [31–33]. Higher FFA contents (9.7–36.7%, as palmitic acid) were ascribed to improper handling of raw material [34]. In fact, mesocarp lipase (triacylglycerol acyl hydrolase, EC 3.1.1.3) has been associated with the membranes of oleosomes (lipid bodies) and is activated when any kind of damage occurs to fruits, during harvest, transportation, and storage. Due to lipase activity lower than EG, interspecific O×G hybrids are considered as promising crosses with better stability of the drupes after harvest, if they have been properly handled before oil extraction [35].

As regard to the oxidative state, hydroperoxides have not been detected by conventional titrimetry (determination of peroxide number) in samples of freshly pressed oils [3], thus confirming the stability toward oxidation of crude palm oils [36]. Nevertheless, induction times measured at 100°C are spread over a wide range (5.7–17.2 hours) [3]: these inconsistencies could be related to differences in the qualitative and quantitative composition of components with antioxidant properties (tocols, polyphenols).

3. Acylglycerols

Edible vegetable oils mainly consist of TAGs; however, partial glycerides, namely diacylglycerols (DAGs) and monoacylglycerols (MAGs), are always present and their origin could be traced to both biosynthetic and lipolytic processes, the latter being of enzymatic or chemical nature.

Hardon [10] first quantified the amounts of MAG (0.88%) and DAG (5.55%) in F1 hybrids. Recently, a more detailed data have become available; 1(3)-P, 1(3)-O, and 1(3)-L were detected in the range 70–300 mg/100 g oil, with no significant differences related to ripening stage; small quantities of the corresponding 2-MAGs have also been identified. DAG types identified are the α,β- (1,2- + 2,3- racemic mixture) and 1,3-isomers of PP, PS, PO, PL, SO, OO, OL, and LL. The most represented are PO and OO isomers, which globally account for 58–66% of total DAGs, 43–78% of α,β-DAGs, and 62–80% of 1,3-DAGs, in agreement with the of different TAG species [3, 31]. The presence of 1,3-DAGs is not "natural", as they are neither biosynthetic nor lipolytic intermediates; yet their presence may be due to both non-specific (chemical) lipolysis of TAGs and rearrangement of natural α,β-DAGs to the thermodynamically stable 1,3-isomers [3]. Hence, the presence of 1,3-DAGs is associated with mediocre quality of raw materials and unsuitable conditions during extraction and storage of oil. The biosynthesis of DAGs in fruit mesocarps accelerates during the period of maximum oil accumulation (18–22 weeks after anthesis, WAA). A decrease of relative abundance of PP and a corresponding increase of PO and OO were also observed [31]; this finding was consistent with results about changes in TAG composition during ripening described by the same authors.

3.1. Fatty acid composition

Two main FAs, O and P, account for about 80% of total FAs in hybrid palm oil and their ratio typically lies in the range 1.5–1.9 (**Table 1**), while in African palm oil O/P ratio is close to one and in EO oleic acid is the main FA (36.4–61.7%) and P is the second most represented one (21.0–37.0%) [3, 4]. Several authors have pointed out the wide range of oil composition from EO, reflecting the wider genetic diversity of EO than EG [4, 37]. Oleic acid comes with *cis*-vaccenic acid (C18:1Δ11) in an amount equal to about 0.7–1% of total FAs [3, 4]. Besides FAs listed in **Table 1**, other saturated (C8:0, C10:0, C24:0) and ω9 unsaturated (C22:1Δ13, C24:1Δ15) FAs were identified, which globally account for 0.2% of total FAs [3].

Despite the importance of determining the optimal harvest time for fruit bunches, only a very limited number of studies have been focused on the FA changes during fruit ripening. In cold pressed oils from fruits harvested between 18 and 24 WAA, a significant decrease of P (from 40.3 ± 0.3% to 32.2 ± 0.3%) and S (from 3.8 ± 0.1% to 2.7 ± 0.1%) and a corresponding increase in the relative percentage of O (from 49.7 ± 0.4% to 57.0 ± 0.4%) and L (from 4.1 ± 0.1% to 5.6 ± 0.0%) were observed [31]. Other researchers [33] detected an opposite behavior (an increase of P from 28.1 ± 2.3% to 31.3 ± 1.9% and a decrease of O from 56.4 ± 2.4% to 51.8 ± 2.1%), but in a different ripening period (phenological stages from 806 to 809, which roughly corresponds to 24–27 WAA).

As a rule, the FA composition of oils from F1 O×G interspecific hybrids is intermediate between those of their parents [3, 4, 38], while FAs in the F1 × F1 (i.e. the F2 generation) exhibit the composition of F1 [38]. This behavior has been attributed to a codominant and additive heredity in hybrid palms. The differences in FA composition between oils from African and hybrid palms should be related to the expression of genes encoding β-ketoacyl-ACP synthase (KAS) II, which is specifically used for chain lengthening of C16:0 to C18:0, and stearoyl/palmitoyl-ACP Δ^9-desaturase. Hereditariness and expression of genes linked to FAs and TAGs biosynthesis were explored by several authors [1, 6, 39–41]. Different quantitative trait loci (QTLs) for iodine value (index of total unsaturation) and FAs (C14:0, C16:0, C16:1, C18:0, C18:1, C18:2) have been identified, and a few structural genes encoding the enzymes involved in the *de novo* synthesis of FAs and in the TAG assembly (e.g., acyl-ACP thioesterases, acyl-CoA synthetase, diacylglycerol acyltransferase) have been localized in those genomic intervals. It is interesting to notice

Reference	**[10]**	**[34]**	**[42]**	**[38]^{a}**	**[5]**	**[44]**	**[3]**	**[33]**	**[31]**	**[6]**	**[6]**	**[4]**
Samples origin	Congo, Malaysia, Colombia	Nigeria, Colombia	Nigeria	Malaysia	Malaysia	Malaysia	Colombia	Colombia	Colombia	Malaysia	Malaysia	Costa Rica
Hybrid	F1	F1	BC1 (with EG)	F1; BC1 (with EG and EO); F2	F1	F1; BC1 (with EG)	F1	F1	F1	F1	BC2 (with EG)	BC3 (with EG); BC3 × EO
Oil extraction system		pressure	pressure				pressure	pressure	pressure			solvent
N. of samples	3	7	14		126		3	21^{b}	12^{c}	85	111	2
Fatty acid												
C12:0 (La)	0.01–0.1	tr		tr			0.5–1.7		0.4–0.5			
C14:0 (M)	0.47–0.9	0.4–0.9	0.3–0.9	0.4–0.8	0.1–0.5	0.5–1.6	0.5–0.9		0.4–0.4	0.14–0.55	0.14–0.75	0.9–0.9
C15:0							tr		0.1–0.1			
C16:0 (P)	27.3–32.5	29.3–35.5	28.9–38.6	36.2–41.4	22.4–44.7	32.2–43.1	27.7–29.5	28.1–31.3	32.2–40.3	22.25–34.33	24.73–41.69	37.0–43.5
C16:1Δ9				tr		0.1–0.3	0.3–0.4		0.3–0.5	0.20–0.83	0.07–0.34	0.2–0.2
C17:0							0.1–0.2		0.1–0.4			
C17:1							tr		0.1–0.1			
C18:0 (S)	3.4–6.1	3.0–4.6	3.3–5.9	0.4–1.5	1.4–4.9	3.2–4.1	2.6–3.1	2.3–2.7	2.7–3.8	1.50–3.10	2.11–9.43	4.0–4.3
C18:1 (O)	48.0–52.5	50.2–53.4	44.9–56.0		36.9–60.1	34.4–51.8	53.5–55.2	51.8–56.4	49.7–57.0	48.20–61.45	37.58–54.48	38.7–43.4
C18:2Δ9,12 (L)	11.3–11.8	10.3–13.9	9.3–11.5	6.5–9.3	8.2–16.8	10.8–16.5	10.7–11.5	9.4–10.4	4.1–5.6	10.45–15.15	8.15–17.65	10.7–12.7
C20:0 (A)	0.0–0.11			tr – 0.1			0.2–0.3		0.3–0.4			
C18:3 Δ9,12,15 (Ln)	0.4–1.3			0.1–0.7		0.5–0.5	0.4–0.4		0.1–0.2	0.40–0.65	0..00–0.53	0.3–0.4
C20:1 Δ11							0.2–0.2		0.1–0.2			

Reference	[10]	[34]	[42]	[38][a]	[5]	[44]	[3]	[33]	[31]	[6]	[6]	[4]
C22:0									0.1–0.1			
ΣSFA							33.2–34.1	31.5–34.7	36.6–46.1			42.4–49.1
ΣMUFA							53.8–55.8		50.6–57.6			39.8–44.5
ΣPUFA							11.1–11.9		4.2–5.8			11.1–13.1
ΣSFA/ ΣUFA							0.50–0.52		0.58–0.84			0.7–1

[a] mol %.

[b] Samples collected between the phenological stages 806 and 809.

[c] Samples collected between 18 and 24 weeks after anthesis (WAA).

BCn = back-cross. Cm:nΔx: m = number of carbon atoms, n = number of double bonds, x = position of double bonds. tr. = trace. C18:1 = sum of oleic and *cis*-vaccenic acids. SFA = saturated fatty acids. MUFA = monounsaturated fatty acids. PUFA = polyunsaturated fatty acids.

Table 1. FA composition (% w/w) of O×G interspecific hybrid palm oil.

that, while most of the FAs and total unsaturation indicate additive or co-dominance effects, L seems to be an exception; in fact, the percentage of this essential FA does not undergo significant changes between African palm and O×G hybrids [3, 4, 38, 42]. In this case, EG seems to be dominant and dictates the level of L in the hybrid.

While great emphasis in breeding has been given to the mesocarp oil, less attention has been focused on the composition of kernel oils from EG, EO and their hybrids. Medium chain FAs characterize the composition of *Elaeis* kernel oils. Lauric acid (La) represents the most abundant FA, followed by myristic acid (M) and O; these three FAs account for 75–80% of total FAs. Besides, *cis*-vaccenic acid was only present at trace levels in kernel oil (~0.1%) [4]. Unlike the mesocarp oils, the kernel oils of the hybrids do not display an intermediate composition between their American and West African parents (**Table 2**); hybrids and back-crosses show a composition close to the one of EG kernel oil [5, 34, 43].

3.2. Composition and structure of triacylglycerols

A TAG type is defined by its three constitutive FAs. Data on the FA composition of individual TAG molecular species can be achieved through the combination of the separation properties

Reference	**[5, 43]**	**[5, 43]**	**[34]**	**[4]**
Samples origin	Malaysia	Malaysia	Nigeria, Colombia	Costa Rica
Hybrid	F1	BC1 (with EO)	F1	BC3 (with EG); BC3 × EO
Oil extraction system	Solvent	Solvent	Solvent	Solvent
N. of samples	12	5	6	2
C6:0	0.2–0.2	0.2	tr	
C8:0	3.2–3.4	4.0	1.3–3.2	1.2–2.3
C10:0	2.7–2.9	3.5	1.8–3.2	1.1–2.2
C12:0 (La)	44.4–46.8	50.0	40.6–49.0	35.0–42.3
C14:0 (M)	18.1–18.6	16.5	17.4–22.1	19.6–24.7
C16:0 (P)	7.9–8.8	7.8	8.0–9.5	9.1–10.2
C18:0 (S)	2.1–2.2	2.2	1.5–2.5	2.4–3.5
C18:1 (O)	14.8–16.3	13.1	14.1–18.5	17.2–19.1
C18:2Δ9,12 (L)	3.2–3.4	2.4	1.0–4.5	4.4. – 4.7
ΣSFA				75.9–78.2
ΣMUFA				17.5–19.3
ΣPUFA				4.4–4.7
ΣSFA/ ΣUFA				3.2–3.7

BCn = back-cross. Cm:nΔx: m = number of carbon atoms, n = number of double bonds, x = position of double bonds. tr. = trace. C18:1 = sum of oleic and *cis*-vaccenic acids. SFA = saturated fatty acids. MUFA = monounsaturated fatty acids. PUFA = polyunsaturated fatty acids.

Table 2. FA composition (% w/w) of O×G interspecific hybrid palm kernel oil.

of instrumental chromatographic techniques, both in liquid [45, 46] and gas [3] phase, and the powerful of mass spectrometers, as detection system.

Mozzon et al. [3, 31] identified 23 TAG molecular species (**Table 3**), by direct GC-MS analysis of oils. Other 14 TAG molecular species characterized by the presence of medium chain SFAs (8:0, 10:0, 12:0, and 14:0), which globally accounted for about 0.7% of oil samples, have been identified after TLC fractionation of oil. These are the TSTAGs 32:0 (LaLa8:0), 34:0 (LaLa10:0), 36:0 (LaLaLa), 38:0 (LaLaM), 40:0 (LaMM+LaLaP), 42:0 (LaMP), 44:0 (LaPP+MMP), and the DSTAGs 42:1 (LaLaO), 44:1 (LaMO). TAG structures with three (LaLaLa) and two (LaLaM, LaLaP, LaLaO) lauryl groups constitute 69.4–72.0% of medium chain TAGs.

No qualitative differences between TAG species of O×G hybrid palm oil and its African parent have been detected. From a quantitative viewpoint, most (about 80%) of total TAGs are made up of both saturated (16:0, 18:0) and unsaturated (18:1, 18:2) FAs (DSTAG + MSTAG). Lower percentages of MPP, PPP, MOP, PPS, PPO, PPL, POS, and higher contents of OOO (2.5 times), OOL (three times), POO, PLO, SOA (from 0.1–0.2% to 0.9–1.2%) than African parent were observed in oil samples from O×G hybrid. Grouped data reflect the discoveries summarized above: oil samples from the hybrid are characterized by higher contents of MSTAGs (47.5–51.0% vs 36.7–37.1%) and TUTAGs (15.5–15.6% vs 5.2–5.4%) than EG [3]. Despite similar FA compositions, other authors [33, 35] observed different TAG profiles, namely lower percentages of POO and PPO, and higher percentages of PPL, PLO, OOL, PLL + POLn.

The pattern of TAGs of mesocarp oils, according to the number of acyl carbon atoms (CN), follows a typical unimodal distribution with an apex at CN 52 for the hybrid palm oil, at CN 50–52 in African palm oil, and at CN 52–54 in EO oils [3, 5]. In kernel oils of EG and its interspecific hybrids (F1 hybrids, back-crosses), the major TAG groups range from CN 36–38 (the most represented) to CN 44 (**Table 3**), whereas in EO kernel oils they range from C36 to C54. A bimodal distribution with maxima at CN 38 and C 48 characterizes the TAG profile of EO kernel lipids [5, 43].

Pancreatic lipase degradation of TAGs was extensively applied in the TAGs structure studies [47–49]. Experimental data reveal an asymmetric structure of the hybrid palm oil TAGs, thus suggesting that the length of carbon chain and the number of double bonds could constitute discriminating factors in the acylation steps. SFAs (C16:0, C18:0) are acylated mainly in positions sn-1,3, while unsaturated fatty acids (C18:1Δ9, C18:2Δ9,12) are preferably acylated in position sn-2 [3, 38]. The conservation of FAs regiodistribution in TAGs of O×G hybrid with respect to its African parent could indicate that hybridization cannot affect the general pattern of stereospecific acylation of glycerol [3].

Trends in FAs availability during ripening (18–24 WAA) mainly affect TSTAGs and TUTAGs: total TSTAG relative percentage halves from 3.6 ± 0.1 to 1.8 ± 0.1, whereas ΣTUTAG increased from 16.9 ± 0.1% to 18.9 ± 0.3%, mainly because of the increase of OOO and decrease in PPP. As saturated and unsaturated FAs have opposite trends during ripening, ΣDSTAG and ΣMSTAG overall changes are very inconspicuous, although they are statistically significant. No significant differences have been observed for medium chain TAGs [31].

Reference		[5]	[33]	[35]	[3]	[31]	[5, 43]	[5, 43]
		Mesocarp oil					Kernel oil	
Samples origin		Malaysia	Colombia	Colombia	Colombia	Colombia	Malaysia	Malaysia
Hybrid		F1	F1	F1	F1	F1	F1	BC1 (with EO)
Oil extraction system			Pressure	Pressure	Pressure	Pressure		
N. of samples		38	21[a]	3[b]	3[c]	12[d]	12	5
TAG m:n	TAG ABC							
ΣC28							0.1–0.2	0.1
ΣC30							0.4–0.7	0.7
ΣC32							2.9–3.9	4.7
ΣC34							4.8–6.0	7.1
ΣC36							17.9–19.6	24.5
ΣC38							17.2–18.0	18.9
ΣC40							10.9–11.3	10.3
ΣC42							9.9–10.6	9.1
ΣC44							8.0–8.8	6.7
46:0	MPP				0.1 ± 0.0	0.1–0.5		
46:1	MMO + LaPO				0.3 ± 0.2	tr – 0.3		
ΣC46		0.0–1.1					6.3–7.2	5.1
48:0	PPP		0.0–0.6		1.3 ± 1.3	1.5–2.8		
48:1	MOP				0.8 ± 0.0	0.4–0.6		
48:2	MLP		0.0–0.7	0.4 ± 0.0	0.2 ± 0.1	tr - 0.1		
ΣC48		0.9–8.9					7.1–8.0	6.0
50:0	PPS		0.0–0.2	n.d.	0.4 ± 0.3	0.2–0.6		

Reference		[5]	[33]	[35]	[3]	[31]	[5, 43]	[5, 43]
		Mesocarp oil					Kernel oil	
50:1	PPO		10.4–15.3	17.0 ± 2.4	20.4 ± 0.2	20.3–21.1		
50:2	PPL		5.6–9.4	9.4 ± 0.9	5.5 ± 0.2	2.5–3.2		
50:2	MOO				0.5 ± 0.1	0.3–0.5		
ΣC50		11.1–25.5					3.3–3.9	2.3
52:0	PSS				tr	tr		
52:1	POS		1.5–1.8	2.8 ± 0.5	3.3 ± 0.2	2.8–3.8		
52:2	PLS				1.6 ± 0.3	1.7–2.0		
52:2	POO		21.9–24.8	23.4 ± 0.7	32.6 ± 2.4	33.1–35.8		
52:3	PLO		17.8–20.2	17.7 ± 0.8	11.2 ± 0.2	7.4–8.9		
52:4	PLL + POLn		7.4–9.4	6.7 ± 0.6	2.0 ± 0.0	1.1–1.9		
ΣC52		43.5–50.5					2.9–3.3	1.9
54:1	SSO		0.2–0.4	n.d.	0.3 ± 0.0	0.3–0.4		
54:2	SOO		1.1–2.5	1.8 ± 0.3	2.6 ± 0.1	2.3–3.5		
54:3	SLO				0.7 ± 0.7	1.4–1.5		
54:3	OOO		8.5–12.8	7.6 ± 1.0	10.7 ± 0.2	12.2–14.2		
54:4	OOL		8.5–11.3	7.6 ± 0.6	4.7 ± 0.1	4.6–5.2		
54:5	OLL		3.9–5.0	3.2 ± 0.3	0.2 ± 0.1	tr - 0.3		
ΣC54		21.8–44.7					3.0–3.5	2.6
56:1	SOA				1.1 ± 0.1	0.9–1.1		
56:2	AOO				0.1 ± 0.0	0.1–0.1		
ΣC56		0.0–0.6						
	ΣTSTAG				1.6 ± 1.6	1.8–3.6		

Reference	[5]	[33]	[35]	[3]	[31]	[5, 43]	[5, 43]
	Mesocarp oil					Kernel oil	
ΣDSTAG				33.3 ± 0.3	29.8–31.5		
ΣMSTAG				49.6 ± 1.8	47.7–49.5		
ΣTUTAG				15.5 ± 0.1	16.9–18.9		

[a] Samples collected between the phenological stages 806 and 809.

[b] Phenological stage 807.

[c] 24 weeks after anthesis (WAA).

[d] Samples collected between 18 and 24 WAA. BCn = back-cross. m:n = acyl carbon number:double bonds number. In TAG species composition (TAG ABC), the order of the abbreviations, e.g. PLO, does not mean the binding position of each FA. FAs like in **Table 1**. tr = trace values (< 0.1%). n.d. = not detected. TAG types listed in **Table 3** have been grouped according to the type of FA bonded to the glycerol moiety as TSTAG, trisaturated TAGs (MPP, PPP, PPS, PSS); DSTAG, disaturated TAGs (MMO + LaPO, MOP, MLP, PPO, PPL, POS, PLS, SSO, SOA); MSTAG, monosaturated TAGs (MOO, POO, PLO, PLL + POLn, SOO, SLO, AOO); TUTAG, triunsaturated TAGs (OOO, OOL, OLL).

Table 3. Triacylglycerol (TAG) composition (% w/w) of O×G interspecific hybrid mesocarp oil and kernel oil.

4. Unsaponifiable matter

A full characterization of the unsaponifiable matter (UM) of the hybrid palm oil is required to assess its potential as a source of health-promoting bioactive compounds. However, only few specific studies have been conducted about the composition of UM of the O×G hybrid oil (**Table 4**).

Reference	**[10]**	**[44]**	**[33]**	**[32]**	**[31]**
Samples origin	Congo, Malaysia, Colombia	Malaysia	Colombia	Colombia	Colombia
Hybrid	F1	F1; BC1 (with EG)	F1	F1	F1
Oil extraction system			pressure	cold pressed	cold pressed
N. of samples	3		21[a]	3[b]	12[c]
Squalene				247.4 ± 3.3	20.3–83.1
4-desmethylsterols					
Cholesterol		3–5%		10.0 ± 2.6/1.8 ± 0.4%	7,8–10.2/3.5–5.4%
Campesterol		20–22%		93.1 ± 23.4/19.3 ± 1.2%	18,8–47.6/11.8–16.3%
Ergosterol				11.0 ± 3.4/1.9 ± 0.3%	
Stigmasterol		13–19%		62.8 ± 10.8/13.1 ± 0.6%	25,8–45.2/15.3–16.3%
Δ^7-campesterol				1.7 ± 0.7/0.5 ± 0.3%	2,3–3.6/0.8–1.9%
β-sitosterol		58–61%		275.6 ± 57.4/59.3 ± 1.0%	98,2–180.9/61.5–62.4%
Δ^5-avenasterol				8.8 ± 1.3/1.9 ± 0.2%	1,6–3.9/0.9–1.4%
$\Delta^{5,24}$-stigmastadienol				2.1 ± 1.4/0.5 ± 0.2%	2,3–3.6/1.1–1.9%
Fucosterol				5.6 ± 2.9/1.1 ± 0.6%	
Other unidentified sterols				2.1 ± 1.4/0.5 ± 0.2%	
Total 4-desmethylsterols		700–1400	469–1417	472.7 ± 102.8	158.7–293.8
Isoprenoid alcohols					
Phytol				120.7 ± 26.1	127.5–175.0
3,7,11,15-tetramethyl-2,6-hexadien-1-ol				11.3 ± 2.1	
3,7,11,15-tetramethyl-2,6,10-hexatrien-1-ol				7.7 ± 1.5	
Geranylgeraniol				129.0 ± 31.7	31.3–76.3
Isoprenoid alcohol (X_1)				tr	

Reference	[10]	[44]	[33]	[32]	[31]
Isoprenoid alcohol (X_2)				tr	
Total Isoprenoid alcohols				269.3 ± 60.0	160.7–251.3
***n*-Alkanols (Ak)**					
n-octadecanol				5.3 ± 2.1	
n-docosanol				1.8 ± 1.3	0.5–1.4
n-tetracosanol				1.2 ± 0.5	0.4–1.2
n-hexacosanol				2.7 ± 0.2	0.4–2.5
n-octacosanol				7.3 ± 0.8	3.0–5.2
n-nonacosanol				tr	
n-triacontanol				15.6 ± 1.6	7.2–12.9
n-hentriacontanol				0.7 ± 1.2	
n-dotriacontanol				18.1 ± 6.5	6.9–13.1
n-tritriacontanol				0.7 ± 1.2	
n-tetratriacontanol				8.2 ± 7.6	2.2–37.4
Total *n*-Alkanols				61.7 ± 17.0	24.9–37.4
4-methylsterols					
gramisterol					
obtusifoliol					2.7–5.2
citrostadienol					4.2–9.8
Total 4-methylsterols				12.7 ± 1.5	6.9–14.9
4,4-dimethylsterols					
Cycloartenol					14.6–24.9
24-methylene-cycloartanol					2.0–3.4
Isoarborinol					2.0–3.9
Unknown					
9,19-cyclopropanesterol					0.8–1.6
Total 4,4-dimethylsterols				74.0 ± 12.3	20.0–33.7
Tocols					
α-tocopherol		11–24%		27.1 ± 7.4/10.0 ± 0.2%	1.5–7.4
β- tocopherol				tr/0.3 ± 0.3%	
γ- tocopherol				tr/0.3 ± 0.4%	
α-tocotrienol		22–31%		44.7 ± 13.7/15.0 ± 1.9%	
β-tocotrienol				3.7 ± 1.2/1.4 ± 0.4%	
γ-tocotrienol		42–51%		148.1 ± 23.3/59.7 ± 1.1%	9.4–18.9

Reference	[10]	[44]	[33]	[32]	[31]
δ-tocotrienol		5–9%		31.8 ± 4.2/11.7 ± 0.8%	
α-tocomonoenol				4.0 ± 1.7/1.6 ± 0.3%	
Total Tocols		600–1000	452–2189	259.3 ± 48.4	10.9–26.2
Other (Hc + carotenoids)	1070–1800	800–2400	514–1375	10389.3 ± 1004.9	

Hc = hydrocarbons.

[a] Samples collected at phenological stages 806–809.

[b] Ripe fruit (24 WAA).

[c] Samples collected between 18 and 24 WAA.

Table 4. Literature data on composition of the unsaponifiable fraction of O×G interspecific hybrid palm oil. Data are provided as mg/Kg oil unless % is indicated. Percentages refer to within class of unsaponifiable components.

Carotenoids are responsible for the color of the oils obtained from mesocarp of palm fruits. A wide range (500–10,000 mg/Kg oil) of their level in hybrid palm oils was reported in literature [3, 10, 33, 44]. Eleven types of carotenes have been identified (α-, β-, ζ-, γ-, and δ-carotene, phytoene, phytofluene, neurosporene, α- and β-zeacarotene, and lycopene), with no qualitative variations among EO, EG and their hybrids. β-carotene is the most represented (52–60% of total carotenes), followed by α-carotene (33–36% of total carotenes). Major quantitative differences are related to lycopene, whose levels account for 1–8% of total carotenes in EG whereas in EO and O×G hybrids lycopene percentages are less than 0.1% [44]. Squalene ranges from 20 to 250 mg/Kg oil [31, 32]. African palm oil was characterized by higher contents of carotenes [44] and squalene [32] than O×G interspecific hybrid oil.

More than 40 alcoholic compounds, belonging to six classes (4-desmethylsterols, 4,4-dimethylsterols, isoprenoid alcohols, n-alkanols and tocols) have been identified in screw pressed crude palm oil obtained from interspecific hybrids. Desmethylsterols and isoprenoid alcohols are the most represented classes, accounting for 79–85% of total alcohols, followed by *n*-alkanols (4–8% of total alcohols), 4,4-dimethylsterols (5–6%), tocols (3–4%), and 4-methylsterols (1–3%) [32].

Quantitative data expressed in mg/kg oil show a trend of progressive accumulation of squalene, desmethylsterols, isoprenoid alcohols, tocols, and 4,4-dimethylsterols in crude hybrid palm oil during ripening, whereas *n*-alkanols and 4-methylsterols show apparently stable levels in total lipids, which can be attributed to the increase in their amounts at the same time TAGs were synthesized [32, 33].

4.1. 4-desmethylsterols

The content of phytosterols in hybrid palm oil ranges from 160 to 1400 mg/kg oil [31–33, 44]. Δ^5-sterols represent 97% of total sterols in hybrid palm oil. The identified molecules are "campesterol" (campesterol +22,23-dihydrobrassicasterol), stigmasterol, β-sitosterol, Δ^5-avenasterol, $\Delta^{5,24}$-stigmastadienol, fucosterol, and clerosterol; ergosterol (ergosta-5,7,22-trien-3β-ol) was tentatively identified, whereas Δ^7-campesterol (ergosta-7-en-3β-ol) is the only Δ^7-sterol clearly identified in hybrid palm oil. β-sitosterol is the most represented phytosterol (58–62% of total sterols), followed by campesterol (12–22%) and stigmasterol (13–19%). Cholesterol is a significant component of sterol fraction, accounting for 2–5% of total sterols

[31, 32, 45]. As described above, an increase in total sterols content of oil samples occurs during ripening, whereas no significant variations in the composition of the desmethylsterol fraction were observed [31].

4.2. 4,4-dimethylsterols

Very little information is available on the occurrence of 4,4-dimethylsterols (or triterpenic alcohols, or triterpenols) in hybrid palm oil. Three 9,19-cyclopropanesterol have been identified: cycloartenol, 24-methylenecycloartanol, and a third triterpenol characterized by a mass spectrum very similar to 24-methylenecycloartanol, compatible with cyclobranol or cyclolaudenol. The structure of isoarborinol was tentatively attributed by Mozzon et al. [32] to a fourth triterpenol. The content of 4,4-dimethylsterols ranges between 20 and 85 mg/Kg g oil (corresponding to 0.6% of total unsaponifiable matter), with no significant differences between African and hybrid palm oils. The composition of the triterpenol fraction does not show significant variations between the African and hybrid palm oils, as well; cycloartenol (70–75% of total triterpenols), and 24-methylenecycloartanol (14–20%) are the two most represented components [31, 32]. Oil levels of 4,4-dimethylsterols increase from 200 mg/Kg at 18 WAA (beginning of inolition) to 340 mg/Kg at 24 WAA (maximum of inolition) [31].

4.3. 4-methylsterols

Citrostadienol was the main 4-methylsterol in hybrid palm oil, followed by obtusifoliol (4,14-dimethylergosta-8,24(28)-dien-3-ol). Gramisterol (24-methylenelophenol) was also identified. The content of 4-methylsterols ranges 7–15 mg/Kg g oil (corresponding to 0.1–0.2% of total unsaponifiable matter), with no significant differences between African and hybrid oils. The composition of the 4-methylsterols fraction does not show significant variations between the African and hybrid palm oils too; cytrostadienol ranged from 44.5 to 50.3% of total 4-methylsterols, obtusifoliol from 14.3 to 31.5%, and gramisterol from 24.0 to 35.4%. Total content of 4-methylsterols does not significantly change during ripening [31, 32].

4.4. Aliphatic alcohols

A complete series of aliphatic alcohols of even number of carbon atoms from 18 to 34 was identified in mesocarp oil from hybrid palm fruits. Odd carbon number alkanols C29, C31, and C33 were also identified [31, 32]. *n*-alkanols level ranges 25–80 mg/Kg oil, without significant differences between African and hybrid palm oil. The pattern of *n*-alkanols, according to the number of carbon atoms, follows a typical unimodal distribution with a maximum abundance of alcohol C32, in both EG and hybrid oil types [32]. Ripening stage affects aliphatic alcohol fraction neither from a qualitative nor from quantitative viewpoint [31].

After 4-desmethylsterols, isoprenoid alcohols (terpenols) are the most represented class of alcoholic components of unsaponifiable matter of hybrid pal oil. A series of terpenols with 20 carbon atoms and 1 (phytol), 2, 3, and 4 (geranylgeraniol) double bonds has been identified. Hybrid palm oil is characterized by higher (160–330 mg/Kg), although not statistically significant, contents of isoprenoid alcohols, and by a higher phytol/geranylgeraniol ratio than EG mesocarp oil [32].

4.5. Tocols

At least seven different tocols were identified in mesocarp oil from hybrid palm fruits [31, 32, 44]: 5,7,8-trimethyl (α isomer) tocol and tocotrienol, 5,8-dimethyl (β isomer) tocol and tocotrienol, 7,8-dimethyl (γ isomer) tocol and tocotrienol, and 8-monomethyl (δ isomer) tocotrienol. The whole amount of tocols in hybrid palm oils greatly varies between 10 and 2200 mg/Kg [31–33, 44]. Experimental data about tocols composition of hybrid palm oils [32, 44] report a range of 10–24% for α-tocopherol, 42–60% for γ-tocotrienol, 15–31% for α-tocotrienol, and 5–12% for δ-tocotrienol. A trend of increase in total tocols content was observed during fruit ripening [31, 33].

5. Hybrid palm oil and health

Several drawbacks contribute to negatively affect the reputation of conventional palm oil among consumers. Involvement of dietary SFAs, mainly P, in the serum lipids profile and in the development of obesity, metabolic syndrome, type 2 diabetes and cancer were thoroughly discussed and confirmed [50]. Besides, it is estimated that only a quarter of palm oil worldwide is used as a crude oil. In EU and USA fatty substances from palm drupes are mostly used in their odorless and pale-yellow forms resulting from refining processes. Refining aims to remove volatile (off-odors, water) and non-volatile (FFA, phospholipids, pigments) oil components other than TAGs. The process causes not only a strong reduction of nutritionally valuable components (antioxidants, such as tocols and polyphenols) but also generates new toxicant. Since late 2000s, non-volatile chloropropanols (3-monochloropropane-1,2-diol, 3-MCPD; 2-monochloropropane-1,3-diol, 2-MCPD), glycidol, and their esters with FAs have been receiving increasing attention. Due to the elevated temperatures reached, the deodorization step is the most important contributor to the generation of those toxicants. Among the most consumed edible fatty substances, palm oil has the highest levels of MCPD and glycidol esters (**Table 5**). On the basis of available data, the European Food Safety Authority (EFSA) have concluded that estimated exposure of the younger aged groups of population to 3-MCPD could substantially exceed the tolerable daily intake (TDI) [7].

	3-MCPD	**2-MCPD**	**Glycidol**
Palm oil	2912	1565	3955
Sunflower oil	503	233	650
Rapeseed oil	232	109	166
Olive oil	48	86	15
Soybean	394	167	171
Palm kernel oil	624	270	421

Table 5. Occurrence (mean values, μg/Kg) of 3-MCPD, 2-MCPD and glycidol (from esters) in edible fats and oils during the period 2012–2015. Data referred to five edible oils most consumed in EU (globally 90% of total edible oil consumption); palm kernel oil as comparison (data from [11]).

Hence, the use of unrefined vegetable oils can both avoid the exposure to toxicants originating during processing and provide significant levels of substances (antioxidants) that are able to protect from negative effects of free radicals and reactive oxygen species. Indeed, EVOO is the most famous (among edible fats/oils) source of nutritionally valuable bioactive compounds (polyphenols) and, for the latest decades, a great amount of literature has been producing on the role of EVOO antioxidants in the prevention of chronic and degenerative diseases (cardiovascular diseases, obesity, type 2 diabetes, inflammatory processes, cancer, aging). Recently, tocotrienols have gained attention for their higher biological effectiveness than tocopherols, as antioxidant and anticancer agents. Crude palm oil obtained from O×G interspecific hybrid contains high amount of tocotrienols and carotenoids, together with a more favorable SFA/UFA ratio than the traditional African palm oil. Recently, phenolics of crude hybrid palm oil and their evolution during ripening were studied [51]: total amount of phenolic substances ranges between 190 and 260 mg GAE/kg oil and a decreasing trend during ripening has been observed. Those levels are comparable to phenolic amounts in EVOO and several molecules that already have been identified in EVOO have been found in hybrid palm oil as well (protocatechuic acid, protocatechualdehyde, *p*-salicylic acid, vanillic acid, syringic acid, syringaldehyde, ferulic acid).

Lucci and co-workers [52] found that consumption of crude palm oil from interspecific hybrids has a favorable effect on plasma lipids pattern (total cholesterol, low-density lipoprotein cholesterol, and high-density lipoprotein cholesterol) and that this effect is not statistically different from dietary EVOO. Recently, Ojeda et al. [53] explored the impact of daily crude oil consumption (25 mL/day for 3 months) on plasma/serum antioxidant capacity (trolox equivalent antioxidant capacity, TEAC, and oxygen radical absorbance capacity, ORAC, assays) and total phenolic content in adults aged 50–77; they also compared the effect of hybrid palm oil and EVOO supplementations. Palm oil significantly increases the total phenolic content and the antioxidant capacity of human plasma (measured by both ORAC and TEAC methods); furthermore, no significant differences have been found between crude palm oil and EVOO groups for the measured parameters. Due to those interesting discoveries, it has been suggested to consider crude palm oil from interspecific hybrid as the "tropical equivalent of olive oil".

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Chapter 10

Effects of Dietary Palm Oil on the Whole-Body Mineral Composition of African Catfish, *Heterobranchus longifilis* (Teleostei, Clariidae)

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Additional information is available at the end of the chapter

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Abstract

A 50-day feeding trial was carried out to determine the effect of the graded incorporation of crude palm oil on the whole-body mineral composition of African catfish juveniles *Heterobranchus longifilis*. Six diets were formulated to contain from 3–21% crude palm oil (CPO). Whole-body macromineral composition represented by calcium (Ca), potassium (K), sodium (Na), phosphorus (P) and magnesium (Mg) showed significant variations ($p < 0.05$) with the different dietary palm oil levels. The same trend was observed in whole-body micromineral composition in iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu). Regardless of the micromineral, the increase in the body was related with increasing dietary palm oil levels between 3 and 9%. In summary, the results of this study suggest that an incorporation of palm oil into the fish diet modifies the mineral body composition without major effects on health and nutritional quality of fish.

Keywords: *Heterobranchus longifilis*, palm oil, feeding, whole-body mineral composition, nutritional quality

1. Introduction

Fish plays an important role in human nutrition. It represents an important source of proteins and lipids. In terms of nutrition, fish provides high-value proteins and long-chain (omega-3) polyunsaturated fatty acids that are beneficial to human health [1]. According to the Food and Agriculture Organization (FAO) of the United Nations [2], world consumption of fish per capita has increased from 5.2 kg in 1961 to 20 kg in 2014. In sub-Saharan Africa, fish represents on average 22% of dietary animal protein [3]. Fish consumption is therefore constantly increasing in relation to the growth of world population.

Currently, aquaculture is the main activity likely to meet the need for fish due to the reduction of capture fisheries and the depletion of natural stocks associated with overfishing. Among the factors of production, food represents more than 50% and constitutes one of the major constraints to the development of aquaculture. To maintain aquaculture yields at a satisfactory level, the intensification of production with significant use of compound feed is achieved [4]. In aquafeeds, fish meal and fish oil represent the main ingredients because of their good nutritional quality. Fish oil provides dietary lipids that are an important source of essential fatty acids for growth, health and reproduction [5]. However, the availability of fish oil remains limited by higher price and the decline in fisheries' catches [6]. The use of alternative dietary oil sources such as vegetable oils is being considered and their ability to meet the nutritional requirements of fish has been studied for some years [7].

Among the vegetable oils, palm oil is the one whose world production has increased rapidly in recent years [5, 8]. The oil palm tree (*Elaeis guineensis*) from which crude palm oil (CPO) is extracted is native to West Africa. Palm oil is the richest natural source of the antioxidants ß-carotene and vitamin E. In addition, CPO contains 48.8% of saturated fats, especially 16:0, 37% of monounsaturated fats, mainly 18:1 n-9, and has low concentrations of polyunsaturated fats (9.1% n−6 and 0.2% n−3) with 9.1% linoleic acid [8]. Several studies using palm oil-based diets showed an improvement of growth performance [8–11]. Dietary lipids play important roles of the fish diet as a source of energy and have a sparing action on dietary protein [12]. However, high dietary lipid intake can affect carcass composition and reduce the utilization of other nutrients [13].

Minerals are among the nutrients that fish need to live. Minerals are essential constituents of skeletal structures and play an important role in the maintenance of osmotic pressure. Minerals serve as essential components of many enzymes, vitamins, hormones and respiratory pigments or as cofactors in metabolism, catalysts and enzyme activators.

Fish can satisfy their mineral needs by absorbing minerals dissolved in water or through the diet [14]. Biological factors such as trophic levels, dietary habits and nutritional status, dietary factors such as diet composition, availability and nutrient interactions and environmental factors such as water mineral concentration and temperature of the rearing system can affect dietary levels of minerals and trace elements in fish [14]. The aim of this study was to evaluate the effect of graded incorporation of crude palm oil on the mineral composition of African catfish *Heterobranchus longifilis*, fingerlings.

2. Materials and methods

2.1. Fish and experimental design

This study was conducted at the hatchery of the Oceanological Research Center in Abidjan, Côte d'Ivoire. The fingerlings of *H. longifilis* used during the experiment had an average weight of 0.80 ± 0.7 g. Before the start of the trial, the fish were stored in glass tanks and acclimated to the experimental conditions for a 2-week period during which they were fed with a control diet (CD). After this step the fish were randomly distributed in the glass (50 L) containing 30 fish. The flow of water in the glass tank was ensured at all times by an electric motor pump allowing a flow of 1.5 liter/min. The filtration was carried out by settling and water renewal of 30% was performed daily. During the experimental period the water temperature, pH and dissolved oxygen were considered favorable in fish culture tanks according to Boyd [15].

2.2. Experimental diets and methods

A control diet (containing no crude palm) and six experimental diets in which different palm oil levels were used were incorporated, and control diets were prepared using a 2 mm diameter pellet press and dried at 37°C. During the experiment, the diets were stored at 20°C. The composition and proximate composition of all diets are given in **Table 1** and mineral composition in **Table 2**. The diet was fed ad libitum, twice daily during 50 days. At the end of the experiment, all fish from the same tank were killed, weighed and individually measured and stored in the freezer at −20°C for the further analysis of whole-body composition.

2.3. Proximate analysis

The proximate composition of the experimental diets was determined according to the AOAC standard methods [16]. Gross energy (GE) contents of diets were calculated from the lipid and protein contents using the equivalents of 38.9 $KJ.g^{-1}$ crude fats, 22.2 $KJ.g^{-1}$ crude protein and 17.2 $KJ.g^{-1}$ carbohydrate (NFE) [17].

The mineral compositions were determined by atomic absorption spectrophotometry for calcium (Ca), phosphorus (P), potassium (K), sodium (Na), magnesium (Mg), iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu) according to the AOAC standard methods [16].

2.4. Statistical analysis

All data were subjected to analysis of variance (ANOVA) using Statistica, statistical software for Windows (release 7.1). Comparisons among treatment means were carried out by a one-way analysis of variance followed by Duncan's test (0.05) [18]. Standard deviation (±SD) was calculated to identify the range of means.

2.5. Results and discussion

Lipids represent an essential component in the diet as they are a major source of energy and essential fatty acids [13]. However, an excess of dietary fat can affect the composition of the carcass due to increased lipid deposits and reduce the use of other nutrients [13]. On the other hand, dietary factor as feeding habits and nutritional status of fish can affect mineral and trace elements in fish. Minerals are inorganic elements that fish need for their different development stage, which they usually obtain through diet and water [19, 20]. In terms of minerals, dietary requirements in several fish distinguish two groups: macrominerals such as Ca, K, Mg, Na and P and microminerals such as Cu, Fe, I, Mn, Se and Zn, and several response

	Experimental diets						
	DC	**D1**	**D2**	**D3**	**D4**	**D5**	**D6**
Palm oil inclusion level	0%	3%	5%	7%	9%	15%	21%
Ingredients (g/100 g)							
Fish meal	30.00	30.00	30.00	30.00	30.00	30.00	30.00
Soybean meal	19.00	19.00	19.50	20.00	21.00	22.50	24.50
Cottonseed meal	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Maize meal	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Wheat bran	29.00	26.00	23.50	21.00	18.00	10.50	2.50
Cassava starch	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Crude palm oil	00.00	3.00	5.00	7.00	9.00	15.00	21.00
Mineral mixture[1]	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Vitamin mixture[2]	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Proximate analysis							
Crude protein (%)	36.41	36.09	36.06	36.00	36.13	36.00	36.04
Crude lipid (%)	5.76	8.60	10.49	12.38	14.27	19.95	25.62
Ash (%)	8.94	8.89	8.88	8.87	8.88	8.85	8.84
Crude fiber (%)	3.73	3.63	3.58	3.52	3.48	3.31	3.15
NFE (%)	43.81	41.41	39.62	37.82	35.84	30.46	24.88
Digestible energy (kJg^{-1})[3]	13.97	14.71	15.21	15.71	16.22	17.73	19.25

NFE: Nitrogen free extract.

[1] Composition for 1 kg of premix: Vitamin A 1.760000 IU, Vitamin D3 880,000, IU Vitamin E 22.000 mg, Vitamin B1 4400 mg, Vitamin B2 5280 mg, Vitamin B6 4400 mg, Vitamin B1236 mg, Vitamin C 151000 mg, (Vitamin K) 4400 mg, Vitamin PP 35200 mg, folic acid 880 mg, choline chloride 220,000 mg, Pantothenic acid D-14080 mg.

[2] Composition for 1 kg of premix: cobalt 20 mg, Iron 17,600 mg, Iodine 2000 mg, Copper 1600 mg, Zinc 60.000 mg, Manganese 10000 mg, Selenium 40 mg.

Table 1. Formulation and composition of the experimental diets (% dry weight).

criteria have been used to determine mineral requirements in different fish species [14]. In this study, the effect of the gradual incorporation of oil palm in the diet of juveniles *H. longifilis* was investigated.

The mineral proximate composition of the experimental diets in **Table 1** showed that, for the same mineral element, the contents were different according to the diets. As regards macrominerals, it should be noted that dietary Ca contents ranged from 72.8 to 231.3 g.kg^{-1}, with the highest level found in control diet and the lowest in diet D4. These calcium contents are widely higher compared to the dietary calcium requirements of channel catfish that were between 5 and 20 g.kg^{-1} [13]. P contents in diet ranged from 5.5 to 8.6 g.kg^{-1} and were in accordance with the fish P requirements which ranged from 0.5 to 0.9% of the diet [21]. Ca and P are

	Experimental diets						
	CD	**D1**	**D2**	**D3**	**D4**	**D5**	**D6**
Palm oil inclusion level	0%	3%	5%	7%	9%	15%	21%
Mineral composition							
Ca ($g.kg^{-1}$)	231.34	136.8	105.42	108.68	140.47	72.82	140.88
P ($g.kg^{-1}$)	8.66	5.83	12.00	5.50	8.16	6.00	6.16
K ($g.kg^{-1}$)	66.02	78.95	100.25	86.18	82.54	33.56	68.9
Na ($g.kg^{-1}$)	82.36	75.39	78.31	99.41	61.56	45.36	59.09
Mg ($g.kg^{-1}$)	2.43	1.40	2.44	2.23	2.41	2.21	2.51
Fe ($mg.kg^{-1}$)	647.97	225.5	560.25	542.7	680.13	949.14	590.51
Zn ($mg.kg^{-1}$)	940.02	51.00	267.01	440.01	855.02	609.01	950.02
Mn ($mg.kg^{-1}$)	651.38	37.83	218.84	309.98	568.05	320.73	667.51

Table 2. Mineral composition of experimental diets (dry weight basis).

the two structural components that play an important role in the body of fish. Ca is involved in bone formation, muscle contraction and enzymatic activation and is also involved in bone development and fish growth [19, 21]. Phosphorus is the most important mineral element in fish. Because of the limited contribution from the aquatic environment, the fish is obliged to satisfy the needs through diet. A phosphorus deficiency results in decreased skeletal growth and bone deformation [21, 22]. The other macrominerals determined in the diets were K, Na and Mg. The diets showed fairly variable contents of K with a higher value (100.2 g.kg^{-}1) in diet D2 and the lowest (33.5 g.kg^{--1}) in diet D5. Dietary Na and Mg contents did not vary considerably and ranged from 45.3–99.4 and 1.4–2.5 g.kg^{-}1.

The microminerals analyzed in the experimental diets were Fe, Zn and Mn. Here too, it appeared that the contents were variable from one diet to another. Dietary Fe contents ranged from 225.5 to 949.1 mg.kg^{-1} with the higher level obtained in diet D5 and the lowest in diet D1. Zn contents were between 51.0 and 950.0 mg.kg^{-}1 when Mn contents ranged from 37.8 to 667.5 mg.kg^{-}1. For these last two minerals, the highest levels are obtained in the D6 diet and the lowest in the D1 diet. The minimal and maximal requirements for fish reported in other studies were: Fe (65–493 mg.kg^{-}1), Zn (36–330 mg.kg^{-}1) and Mn (4.4–226 mg.kg^{-}1) [19].The values recorded in this study were in excess than dietary requirements mentioned for fish.

Whole-body macromineral composition of fish is presented in **Figure 1**. Body composition in calcium (Ca), potassium (k), sodium (Na), phosphorus (P) and magnesium (Mg) showed significant variations ($p < 0.05$) with the different dietary palm oil levels. The Ca content of whole body increased with increasing dietary palm oil levels at 5 and 9%. The highest value of Ca (168.49 ± 8.01 g.kg^{-1}) was recorded in fish fed with diet containing 9% of palm oil. Incorporation of palm oil at 3, 5, 7, 15 and 21% in diet increased fish whole-body K content and the highest value (98.54 ± 1.30 g.kg^{-1}) was obtained in the flesh fish fed with 9% dietary palm oil level. The same trend was observed for whole-body Na content, with the marked increase (87.50 ± 0.73 g.kg^{-1}) in fish fed with the diet containing 9% of palm oil. Change in dietary palm oil levels had significantly affected P on whole-body content of fish. Whole-body P content decreased with increasing palm oil levels in the diet, with the lowest value (6.68 ± 0.34) recorded in fish fed diet containing a 15% palm oil level. These values are generally higher than those reported by other works. For instance, Anthony Jesu Prabhu et al. [14] reported for Rainbow trout and Common carp the following values: for Ca, 5.2 ± 1.2 and 7.1 ± 0.8 g.kg^{-1}; Mg: 0.3 ± 0.2 and 0.25 ± 0.05 g.kg^{-1}; P: 4.8 ± 1 and 4.9 ± 0.7 g.kg^{-1}. In another study, Bogard et al. [23] obtained in Common carp Ca: 0.37 g.kg^{-1}, Mg: 0.26 g.kg^{-1} and P: 1.8 g.kg^{-1}.

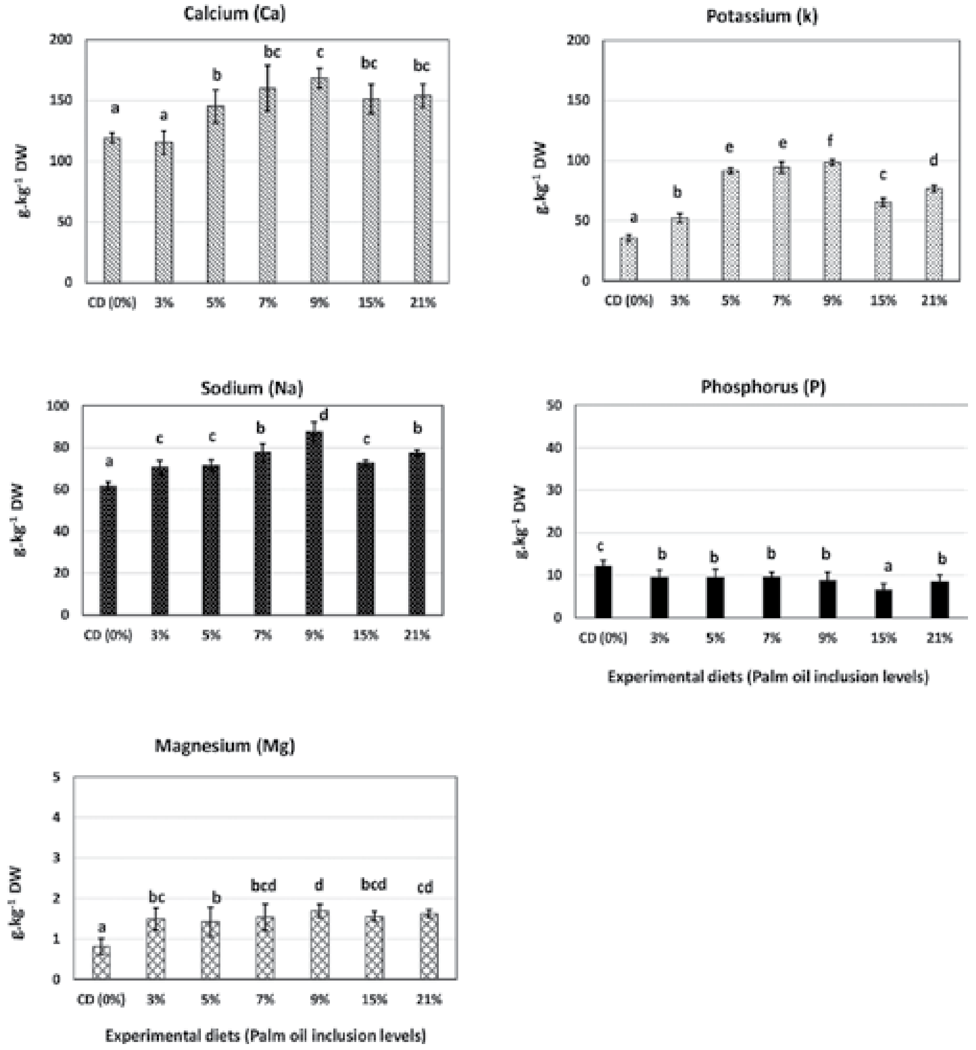

Figure 1. Whole-body Ca, k, Na, P, and Mg contents (wet weight basis) of *H. longifilis* fed graded levels of dietary palm oil for 50 days.

Fish whole-body micromineral composition in iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu) was significantly affected ($P < 0.05$) by dietary palm oil levels, with different variations according to the mineral (**Figure 2**). Regardless of the mineral, the increase in the body was related with increasing dietary palm oil levels between 3 and 9% and the highest value was obtained in fish fed diet containing a 9% palm oil level. The highest value was: body Fe with 536.88 ± 38.74 ppm and that of Zn, Mn and Cu were 246.43 ± 4.09 , 48.24 ± 4.07 and 22.63 ± 0.91 $mg.kg^{-1}$, respectively.

Despite the variations described above, the whole-body mineral composition of *H. longifilis* was generally increased with increasing dietary palm oil levels. In this study, the diets were formulated to contain from 3 to 21% crude palm oil with dietary lipid levels ranging from 8 to 25%. Wang et al. [24] reported that crude lipid contents in the whole body and muscles were not significantly influenced by the dietary lipid source. It may be thought that the effect of palm oil on body composition may be related to lipid metabolism. Several studies in fish have reported that dietary lipid sources could regulate gene expression. Qui et al. [25] reported that dietary lipid source could influence hepatic fatty acid synthetic gene expression, gene expression related to fatty acid β-oxidation and lipid deposition in the muscle and liver.

It appears in the light of various works that fish whole-body mineral contents are highly variable from one species to another and often for the same species. This may be partly attributable to sampling variability and methodological differences in analysis and fish species.

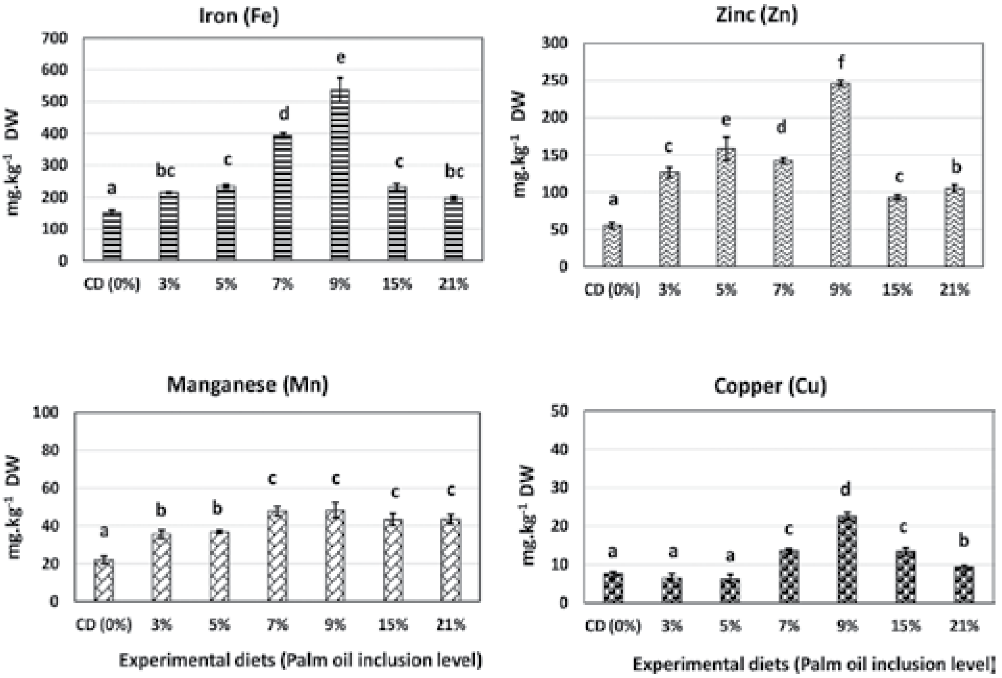

Figure 2. Whole-body Fe, Zn, Mn, and Cu contents (wet weight basis) of *H. longifilis* fed graded levels of dietary palm oil for 50 days.

However, the results obtained in this study are within the range of fish reported elsewhere [26]. Indeed, good results have been reported on the use of palm oil in the diets of several catfishes: *H. longifilis* [11, 27], *Mystus nemurus* [28] and *Clarias gariepinus* [9, 10, 29]. Other studies have also shown that inclusion of palm oil in the diet of tilapia did not affect hematology and organoleptic properties [30].

Although it has been proven that substantial quantities of palm oil can be used as energy substitutes in fish diets without negative effects on growth performance [11, 12, 28, 30, 31] it is important to determine the dietary level for optimal use that does not affect growth, whole-body composition and nutritional quality of fish. In Nile tilapia *Oreochromis niloticus*, [32] reported that 6% of dietary palm oil improved growth performance and fish recorded the highest level of whole-body docosahexaenoic acid (DHA). In view of the different studies on the incorporation of vegetable oils in fish feed, it appeared that palm oil, due to its fatty acid composition, is one of the best lipid sources that can be replaced by fish oil in aquafeed [5].

3. Conclusion

The results of this study showed that the incorporation of palm oil in the diet of juveniles of *H. longifilis* affected their whole-body mineral composition. Increasing the level of dietary palm oil from 3–9% resulted in increased whole-body macrominerals and micromineral contents. Previous studies have shown that dietary palm oil improved fish growth and feed utilization. This study suggests that palm oil modifies the whole-body mineral composition without major effects on health and nutritional quality of fish, confirming the interest of this oil as an ingredient for fish feed. Due to its nutritional value and relative low cost, palm oil is an interesting source of lipid to promote in the aquafeed manufacture for sustainable and profitable aquaculture.

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Palm oil production is one of the most developed and noteworthy industries in the world, leading to rapid economic growth in countries where the industry has been established. Currently, palm oil is the world's leader in the vegetable oil industry with a yearly production and consumption of approximately 45.3 million tons, which almost covers 60% of the global trade of vegetable oils in the international market. Along these lines, it is expected that the global demand for palm oil will be doubled by 2020. The book focuses on various aspects of palm oil production, primarily, the environmental aspects, its application as an animal feed, chemical and nutritional properties of the oil, and technical aspects of enhancing the efficacy of production.

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