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Transformative Approaches to Produce PHAs from Waste Streams: A Brief Review

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ABSTRACT

Throughout their existence, plastics made from petroleum have been associated with increasing environmental problems, such as pollution, accumulation in terrestrial and marine environments, and the release of greenhouse gases. To address the present environmental concerns, creating and producing eco-friendly polymers has received much attention in the industrial and research communities over the past ten years. The current review focuses on one of the beneficial products obtained after the waste treatment. The biodegradable polymer, Polyhydroxyalkanoates (PHAs), is synthesized from the variable organic materials collected during the waste aerobic and anaerobic treatment. PHAs with short-chain-length (*scl*-PHA) and medium-chain-length (*mcl*-PHA) are commonly synthesized with different bacterial strains as a factor to determine the chain length. Researchers studied various methods to find the optimum parameters and yield of PHAs while considering the cost. It can be concluded that pH 7 and 60 °C are the optimum conditions for bacteria pretreatment to obtain a high conversion of PHAs.

Furthermore, one of the potential wastes, Palm Oil Mill Effluent (POME) obtained from palm oil production, was highlighted since Malaysia is the world's second-largest palm oil industrial player. The abundance of POME becomes highly toxic effluent and causes water pollution. Hence, POME can be manipulated to play an important role as one of the feedstocks for PHAs. This renewable PHAs biopolymer can solve the plastic degradation and the pollution caused by conventional polymers. The continuing improvement of PHAs was extensively examined to fulfill the world PHAs market demand.

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INTRODUCTION

Polyhydroxyalkanoates (PHAs) are thermoplastic or elastomeric, and their sufficiently high molecular mass provides them with properties similar to those of conventional petrochemical polymers. Bacterial species have produced different PHAs and copolymers (Anjum et al., 2016; Hashim et al., 2024). PHA production is impacted by temperature swings, osmolarity, pH changes, high pressure, and microbial growth inhibitors (Obruca et al., 2021). Under conditions of nutrient limitation (e.g., nitrogen, phosphorus, oxygen, and magnesium) and ample carbon supply, most known PHA-producing bacteria exhibit improved polymer formation (Vicente et al., 2023). However, some bacterial species may manufacture PHA without being restricted by nutrients. When faced with nutritional restrictions, intracellular bacteria normally create PHAs and store them as carbon and energy in specialized sub-cellular organelles called carbonosomes (Tanamool et al., 2013). Polyhydroxybutyrate (PHB) synthesis in bacteria is typically stimulated by limiting dietary factors such as phosphate (P) and nitrogen (N) limits or the availability of an excess carbon (C) supply. The content and quality of PHAs are determined by the culture employed, the bacteria's growth circumstances, and the amount of carbon source provided.

PHAs comprise a variety of monomers, making it difficult to determine the specific qualities of the substance. Meanwhile, carbon-rich sources such as carbohydrates and fatty acids are used in commercial PHAs manufacturing. PHAs can be produced and stored by bacteria during the growth phase, including recombinant *Escherichia coli*, a mutant strain of *Azotobacter vinelandii*, and *Alcaligenes lactus* (Kumar et al., 2020). Approximately 92 bacterial species can manufacture PHAs in both aerobic and anaerobic environments. According to a study, PHAs provide a biological benefit for producers when subjected to oxidative and osmotic pressure and cold temperatures (Sehgal & Gupta, 2020). *Ralstonia eutropha* H16 is regarded as the model organism in PHA production research (Reinecke & Steinbüchel, 2009). Because *Pseudomonas* species are adaptable and can generate polymers from various carbon sources, they have also been extensively researched for their potential in manufacturing PHAs.

There are currently two primary techniques for making PHA from bacteria. The primary mode of production used in commercial and industrial settings is the pure culture mode. A single strain or engineered bacterium with high PHA synthesis capacity is employed to make PHA. The production of PHA products is still quite expensive due to the tight aseptic environment conditions and high-purity carbon source substrate required for the pure culture mode (Sabapathy et al., 2020). Compared to conventional petrochemical polymers, PHA's economic viability has been significantly diminished by its high production costs, which also restrict the broad range of applications for PHA products. Another technique uses mixed microbial communities (MMCs) as the biological carrier for PHA production. To avoid adulterating pure cultured microorganisms with other hybrid bacteria that could ruin the PHA production ability, it is imperative to carefully sterilize the fermentation facilities, operational environment, and substrates while using the pure culture mode. PHA synthesis can be conducted in a more open environment since the MMC-PHA production mode has a larger microbial diversity that withstands environmental effects than the pure culture mode (Zhou et al., 2023). Specifically, the MMC-PHA production process reduces the high energy cost by not requiring an aseptic operating environment or rigorous substrate sterilization. Additionally, low-value and readily accessible organic wastes such as crude glycerol and volatile fatty acids were used as carbon source substrates to manufacture MMC-PHA. As a result, the production method for MMC-PHA is more affordable, sustainable, and favorable to the environment.

To make PHAs production more cost-effective, this challenge has recently been handled using waste feedstock as a carbon source, mixed cultures for fermentation, and aqueous two-phase systems for purification and recovery. Obtaining a useful product from waste is advantageous at any time. Furthermore, industrial and agricultural wastes produce enormous difficulties (Hashim et al., 2021; Hassan et al., 2022)by accumulating and disrupting the ecosystem. Palm oil wastes, agro-based wastes, animal wastes, molasses, maize steep liquor whey, rice and wheat bran, and other wastes are powerful substrates for synthesizing

PHAs. Mixed culture, on the other hand, lowers the cost of equipment and the number of control measures required while maximizing substrate utilization. This article reviews the different wastes as sources in synthesizing the PHAs. The findings of the optimum conditions in aerobic and anaerobic methods from another research were discussed. In addition, the importance of the PHAs and their future potential were also discussed.

SYNTHESIZING THE PHAs

Basic Molecule of PHAs

Biotechnological methods are used to manufacture PHAs, which have numerous inherent restrictions on the production scale for upstream and downstream processes. Each stage of production incurs costs (Otoni et al., 2021). Important queries are as follows:

i. What type of PHA will be generated, and what final chemical and physical characteristics are anticipated?
ii. What will serve as the carbon source to produce PHAs?
iii. How can we accumulate the most PHAs? Which microbial producers have the greatest potential?
iv. Is the transition from batch production methods to continuous processes industrially feasible?
v. How may the need for an aseptic atmosphere be reduced?
vi. Which agricultural waste and surplus garbage can be used as carbon sources, and what pretreatments or derivatization are necessary for these substrates?

In bacteria, PHAs are known to be deposited intracellularly as a carbon and energy source. Lemoigne discovered PHA in *Bacillus megaterium* for the first time in 1926 (Lemoigne, 1926). PHAs and copolymers are suitable for medicinal and industrial uses due to their biodegradability and biocompatibility. PHAs are an essential source of material for packaging due to their hydrophobicity, vapor barrier, insulation, and thermoplasticity (Reshmy et al., 2021). The food industry has access to PHA-derived jars, throwaway cups, trays, containers, and foam-based packaging equipment. Pharmaceutical carriers, tissue engineering, heart valves, surgical sutures, medical implants, artificial skin, artificial organ reconstruction, chemotherapeutics, antibacterial, anti-cancer, memory enhancers, and biocontrol agents in aquaculture are just a few of the medicinal applications for PHAs (Kalia et al., 2021). PHAs have been proposed as a potential material for medical devices because of their strong mechanical characteristics, biodegradability, and biocompatibility with human bones and tissues. Among the devices are orthopedic pins, tacks and rivets, screws and staples, stents, suture fasteners, surgical mesh, meniscal repair devices, adhesion barriers, repair patches, and articular cartilage restoration are among the most potential devices. Moreover, PHAs have no detrimental effects on health, either short-term or long-term, when used in vivo (Rekhi et al., 2022). Furthermore, an additional benefit is their unchanged local pH value during degradation. PHAs come in various forms, with poly-hydroxybutyrate (PHB) and copolymer of hydroxyl butyrate and hydroxyvalerate (PHBV) being the most researched.

Reports of over 150 constituent repeat units have been used as PHA units along chains (Blunt et al., 2018; Shakirah et al., 2020). PHAs' monomer composition can be changed to produce polymers with specific physicochemical and mechanical characteristics (Muneer et al., 2020). The bioplastic products derived from PHA have comparable physico-chemical properties to conventional petrochemical plastics, including corrosion resistance. They also have complete biodegradability and great biocompatibility.

Researchers studying biopolymers have discovered that altering the monomer content of the PHA can change its mechanical and thermal characteristics. Its molecular weight, monomer type, and proportion are the primary factors influencing its diversity of properties. Additionally, the breakdown rate under different environmental conditions is highly correlated with the monomer composition of the PHA (Pagliano et al., 2017). Additionally, there is a strong correlation between the breakdown rate under different environmental circumstances and the monomer makeup of the PHA.

Structurally, PHA is a linear polyester composed of ester linkage linking hydroxyalkanoates (HA) monomers. The components of the PHA monomer and the ratios of each component primarily influence the mechanical and processing properties of PHAs. The two most widely used HA monomer types in MMC-PHA synthesis are hydroxyvalerate (HV) and hydroxybutyrate (HB). Homopolymer PHA, which includes PHB and PHV, is defined as PHA consisting of a single component type. On the other hand, PHA, like PHBV, is a type of copolymer composed of two or more components. These three polymers generate the most prevalent and straightforward PHA kinds in the MMC-PHA process. Due to their high brittleness and crystallinity, homopolymers, like PHB, have extremely great water resistance and hardness, but their low-temperature stability makes them unsuitable for ductile processing. To create specific monomers in pure culture, one can utilize transgenic engineering bacteria or specific PHA-producing bacteria in combination with the pure substrate. On the other hand, the biological process of producing MMC-PHA enriches the matching microbial population through natural ecological selection. Therefore, changing the process conditions in the MMC-PHA production process at this time is a more realistic way to manufacture specific PHA monomers based on the process development premise of ecological selection.

PHAs can be classified depending on their monomeric composition, as in Figure 1. There are three types of PHA: short-chain-length PHA (*scl*-PHA), which has 3–5 carbon atoms per monomer; medium-chain-length PHA (*mcl*-PHA), which has 6–14 carbon atoms; and long-chain-length PHA (*lcl*-PHA), which is a relatively uncommon subgroup and has >14 carbon atoms (Rodriguez-Contreras, 2019). The majority of bacteria either produce *scl*-PHAs with 3-hydroxybutyrate (3HB) units as the main monomer or *mcl*-PHAs with 3-hydroxyhexanoate (3HHx), 3-hydroxyoctanoate (3HO), 3-hydroxydecanoate (3HD), and 3-hydroxydodecanoate (3HHD) as the main monomers. The low 3HV or 4HB content *scl*-PHA's structural flaws, such as strong stereoregularity, a slow crystallization rate, the creation of large-size spherulites, and secondary crystallization (Wang et al., 2016), restrict its further use in the packaging, textile, and biomaterials industries. Methods including physical blending and chemical structure design in conjunction with processing conditions have been used to address the aforementioned issues, improving the mechanical qualities and application of *scl*-PHA. Meanwhile, *scl*-PHAs are crystalline and possess conventional thermoplastic qualities. *Mcl*-PHA resins resemble elastomers and latex-like materials with typically low glass transition (T_g) temperature and lower molecular mass if compared to *scl*-PHA (Bedade et al., 2021), which makes them soft, ductile materials (Hashim et al., 2024; Norazlina et al., 2015).

Cupriavidus necator is a typical strain for *scl*-PHAs production due to its adaptability, allowing it to acquire up to 90% of the dry cell weight (DCW) (Amstutz et al., 2019; Flores-Sánchez et al., 2017)polymer. *Pseudomonas sp.* is one of the main microbes that produce *mcl*-PHAs (Mozejko-Ciesielska et al., 2019; Silva et al., 2021). These bacteria have evolved into a productive cell factory for PHA production due to their adaptable metabolism and amazing tolerance to various carbon sources. The current focus areas are the design of *Pseudomonas* strains to increase their capacity to accumulate PHAs in the cell and alter their biosynthetic pathways to produce strains with altered compositions and improved properties.

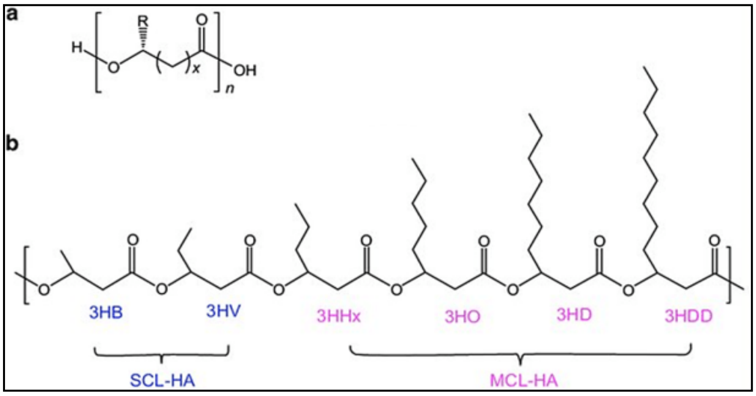


Fig. 1: (a) General molecular formula of PHAs. Typically, x=1–8, and n ranges from 100 to 1000 s. (b) Some commonly synthesized *scl*-PHA monomers and *mcl*-PHA monomers (Sudesh et al., 2000). *Note: 3HB: 3-hydroxybutyrate, 3HV: 3-hydroxyvalerate, 3HHx: 3-hydroxyhexanoate, 3HO: 3-hydroxyoctanoate, 3HD: 3-hydroxydecanoate, 3HDD: 3-hydroxydodecanoate*

Feedstocks and Methods Used to Synthesis PHAs

Industries generate tens of thousands of tons of PHAs each year. However, the high expense of PHA manufacture has made it difficult to expand its use to large-scale production. Alcântara et al. 2021 reviewed the methods of PHA production (Medeiros Garcia Alcântara et al., 2020). They concluded that the PHAs can be produced via three main routes: microbiological, enzymatic, and chemical. The authors examine all three methods, paying particular attention to the molecular properties of the resulting polymer, the cost of the raw materials and manufacturing procedures, and the availability of industrial technologies for large-scale production, with the ultimate objective of determining the potential scalability and current barriers towards commercialization.

For any potential large-scale production, the microbiological technique is preferred regarding process costs. PHA hydrolases are found in a wide variety of natural microorganisms. They can hydrolyze PHA into oligomers and monomers, which bacteria can use as nourishment for growth. While the enzymatic method seems to be the least likely of the three, the chemical route also presents an attractive possibility, especially in light of the accessibility of industrial technology for large-scale production. The cost of the finished product continues to be a significant barrier to the mass commercialization of PHAs bioplastics since it is still too high to be competitive with conventional plastics made from fossil fuels, even in the most convenient instance of the microbiological approach (Costa et al., 2019; Govil et al., 2020). As a result, current research is focused on finding suitable and affordable raw materials, such as waste streams from other industrial or construction activities.

PHAs were produced commercially via fermentation, aerobic dynamic feeding (ADF), and batch reactors. Several fed-batch, continuous, and semi-continuous bioreactor systems have been used, with varying degrees of success, to try and increase process productivity. The accumulation of other PHA types, without including precursors that interfere with microbial strains' metabolism, is only known to occur in a few numbers of bacteria (Montano-Herrera et al., 2017; Policastro et al., 2021). Utilizing extremophiles could reduce the need for process sterility, increasing the process's viability from an economic standpoint. The primary benefit of extremophiles is their capacity to grow and produce a wide range of metabolites, including but not limited to PHA, in environments that minimize or eliminate the possibility of process contamination by common mesophilic microflora, such as extremely high or low temperatures, high salinities, or extreme pH values (Novackova et al., 2022). Because extremophilic microorganisms are resistant to unfavorable microbial contamination, which can wipe out entire fermentation batches, biotechnological processes utilizing these microorganisms can function with fewer sterility requirements—in some cases, even without sterilizing the cultivation media or equipment. As such, it has a highly favorable effect on these processes' energy and economic balance. Furthermore, the cultivation process can be operated in a highly productive continuous or semi-continuous mode due to the technique's great tolerance against contamination. Thus, the use of extremophilic microbes in biotechnology is currently considered a recent trend and is referred to as the "next-generation industrial biotechnology" (NGIB) idea (Chen & Jiang, 2018).

Extracting carbon or nitrogen sources from waste substrates (such as food production leftovers) can reduce final costs and avoid the ethical problem of using agricultural resources for plastic manufacturing if quality control is integrated. Implementing CO_2 as the carbon source, like in the case of cyanobacterial PHA production, is another option to reduce costs and increase production capacity (Hub, 2021). Acetate is an intermediary molecule in the two-step fermentative process that brings them together. A natural and effective bacterial conversion of CO_2 and H_2 results in acetate. In addition, it is a promising substrate from which various other premium goods, including lipids and proteins, can be created in addition to bioplastics. Table 1 shows the different feedstocks in synthesizing PHAs.

Studies using VFAs as carbon sources have accounted for most of the papers on PHA production by MMCs. Certain investigations employed inexpensive surplus raw materials from agriculture and industry or organic waste streams, such as fermented molasses, crude glycerol, etc., as carbon sources for MMC-PHA synthesis. However, as VFAs are the building blocks of PHA biosynthesis, they are the most favored substrate in MMC-PHA synthesis. Three phases are obtained in the conventional MMC-PHA production process: (1) Anaerobic fermentation: This process converts complex biowaste resources into volatile fatty acids (VFAs); (2) MMC enrichment: Under conditions of unbalanced nutrition, dominant cultures with high PHA synthesis capacity from activated sludge or other sources would be enriched. (3) To achieve the highest possible level of PHA accumulation and subsequent recovery, incorporate the VFAs generated in the first stage into MMCs enriched in the second phase.

Table 1. PHA synthesized from different wastes and methods

Feedstock	**Method**	**Optimum results**	**Reference**
Sludge from wastewater treatment plant	VFA in an anaerobic process and PHA production in an aerobic process	RT of 4 days and a small WD of 25% at pH = 6 and around 30 ºC is preferable for a high VFA production rate (PR) of 1913 mgVFA/(L×d) and a stable VFA composition. A high PHA production of up to 28.4% of CDW was reached at lower substrate concentration, 20 ºC, neutral pH-value, and a 24 h cycle time	(Pittmann & Steinmetz, 2017)
Mixed refinery sludge	Aerobic granular reactors	Small-sized (0.71 ± 0.04 mm) *Micrococcus aloeverae* strain SG002 granules achieved 81.40 ± 0.2% hydrocarbon removal efficiency accumulating 0.47 ± 0.01 mg PHA/mg CDW due to *cocci* populated strong microbial structure. Changing organic loading (0.6–1.8 kg COD/m^3. day) and high C/N (8–24) stimulated the yield of 0.71 ± 0.04 mg PHA/mg CDW in the refinery granules. About 40–70% PHA was accumulated in the feast phase, mostly utilized for microbial metabolism in the famine phase. PHA yield per unit COD removal ranged between 0.38 to 0.89 mg PHA/mg COD	(Ghosh & Chakraborty, 2020)
Wastewater	ADF strategy for the sequential batch reactor (SBR) using microbubble aeration	Maximum PHA was obtained at 1.5 L/min (3.9 mg PHA /g of wet aerobic granules) for mixed aerobic granules of different sizes. For 1.5 L/min of aeration rate, more PHA-proas compared to only at 2 µm in 1.0 L/min aeration rate	(Wei & Kanadasan, 2019)
Waste paper	Anaerobic digestion	56.98 % PHA and 0.31 g/g yield obtained from VFAs concentration of 10 g/L, 5:1:4 ratio of acetic, propionic, and butyric acids (HAc:HPr:HBu) and $NaNO_3$ as nitrogen source	(Al Battashi et al., 2021)

Waste sludge	Aerobic dynamic substrate feeding with different heat pretreated sludge (60 °C, 80 °C, 100 °C, 120 °C)	At 60 °C pretreated waste sludge, the highest PHA production rate (0.23 mg COD/mg X·h) and the PHA conversion rate (0.46 mg COD/mg COD) with the utilization efficiency of COD, proteins, carbohydrate, and VFAs were 74.3%, 82.3%,47.2%,81.4%, respectively.	(Liao et al., 2018)
Sugarcane bagasse	Fermentation using *Ralstonia eutropha* and *Lysinibacillus sp.*	By the addition of CSL and SCGO, the co-culture produced maximum cell growth (DCW: 11.68 and 11.0 g/L), PHA accumulation (76% and 76%), and PHA titer (8.87 and 8.36 g/L).	(Saratale et al., 2022)
Organic leachates	Aerobic dynamic feeding	Low C/N ratios of 13.3 and 23.3 promoted PHA accumulation in PHB, reaching a maximum of 16.8% stored, decreasing on the SOUR from 1.67 to 0.42 mg O_2/g VSS.	(Sánchez Valencia et al., 2021)
Leaf wastes	Microorganism fermentation	Maximum bacterial growth at 35 ºC, pH=7, 48 hrs incubation, and 0.25% concentration of NaCl. *Bacillus subtilis* produced 0.26 g/l (40.625 %) of PHA.	(Zaki, 2018)
Industrial soil effluent	Fermentation using *Bacillus cereus* strain and optimization by CCD	PHB content of (1.42 ± 0.01) g/L and a maximum PHB yield of (40.3 ± 0.77) % was obtained at pH=7, 37ºC, and agitation speed was 120 rpm.	(Evangeline & Sridharan, 2019)
Waste vegetable oil	*Pseudomonas putida* in batch bioreactors	*P. putida* KT2440 strain produced 1.01 ($g·L^{-1}$) of PHA whereas the engineered Δ*tctA P. putida* strain synthesized 1.91 ($g·L^{-1}$) after 72 h cultivation on 20 ($g·L^{-1}$) of waste oil, resulting in a nearly 2-fold increment in the PHA volumetric productivity.	(Borrero-de Acuña et al., 2019)
Waste frying oil	*Halomonas* species cultivations	*H. hydrothermalis* could synthesize a copolymer of P(3HB-*co*-3HV). When valerate was utilized as a precursor, the 3HV fraction in the copolymer reached high values of 50.15 mol.%	(Pernicova et al., 2019)

Note: VFA – volatile fatty acids; WD – withdrawal; ADF – aerobic dynamic feeding; CDW – cell dry weight; RT – retention time; CSL – corn steep liquor; SCGO – spent coffee waste extracted oil; DCW – dry cell weight; SOUR – specific oxygen uptake rate; VSS – volatile Suspended Solid; CCD – central composite design; P(3HB-co-3HV) – 3-hydroxybutyrate and 3-hydroxyvalerate

POME AS A FEEDSTOCK OF PHAs

Palm Oil Mill Effluent (POME) is an oily effluent containing various suspended components created by palm oil processing mills (Shakirah et al., 2020). Palm oil mill effluent is a liquid waste from sterilizer condensate and cooling water. POME has a biochemical oxygen demand (BOD) and carbon-oxygen demand (COD) level that is 100 times higher than municipal sewage. POME is a non-toxic waste because no chemicals are used in the oil extraction. However, it has a high oxygen depletion capacity in aquatic systems due to its organic and nutritional content. Diverse sugars such as arabinose, xylose, glucose, galactose, and mannose contribute to the high organic matter (Azman et al., 2016). Oil-bearing cellulosic components from the fruits comprise most of the POME's suspended particles. Because no chemicals are used in the oil extraction process, the POME is a good source of nutrients for microorganisms (Ujang et al., 2010).

Figure 2 shows the steps in processing palm oil to produce refined, bleached, deodorized oil. POME comprises condensate and clarification sludge from two basic processes: sterilizing and clarifying. POME is made up of 95–96 % water, 0.6–0.7 % oil, and 4–5 % solids (Mumtaz et al., 2010), depending on the oil extraction procedure and the qualities of fresh fruit bunch (FFB) (including 2–4 % suspended solids, mainly debris from the fruit). Palm oil is produced without chemicals, making it a non-toxic waste. POME is a highly concentrated dark brown colloidal slurry containing water, oil, and fine cellulose materials discharged from the mill. The discharge temperature of POME is around 80–90 ºC due to heat input (during the sterilizing stage) and powerful mechanical processes. Regarding BOD and COD, POME is 100 times more harmful than residential sewage, with BOD and COD levels typically exceeding 25,000 mg/L and 50,000 mg/L, respectively (Kamyab et al., 2018; Loh et al., 2013; Trisakti et al., 2017). Aerobic and anaerobic processes produce the final discharge and organic fertilizer, respectively. The organic fertilizer can be used during the oil palm plantation (Bazilah et al., 2022; Loh et al., 2017; Yap et al., 2020).

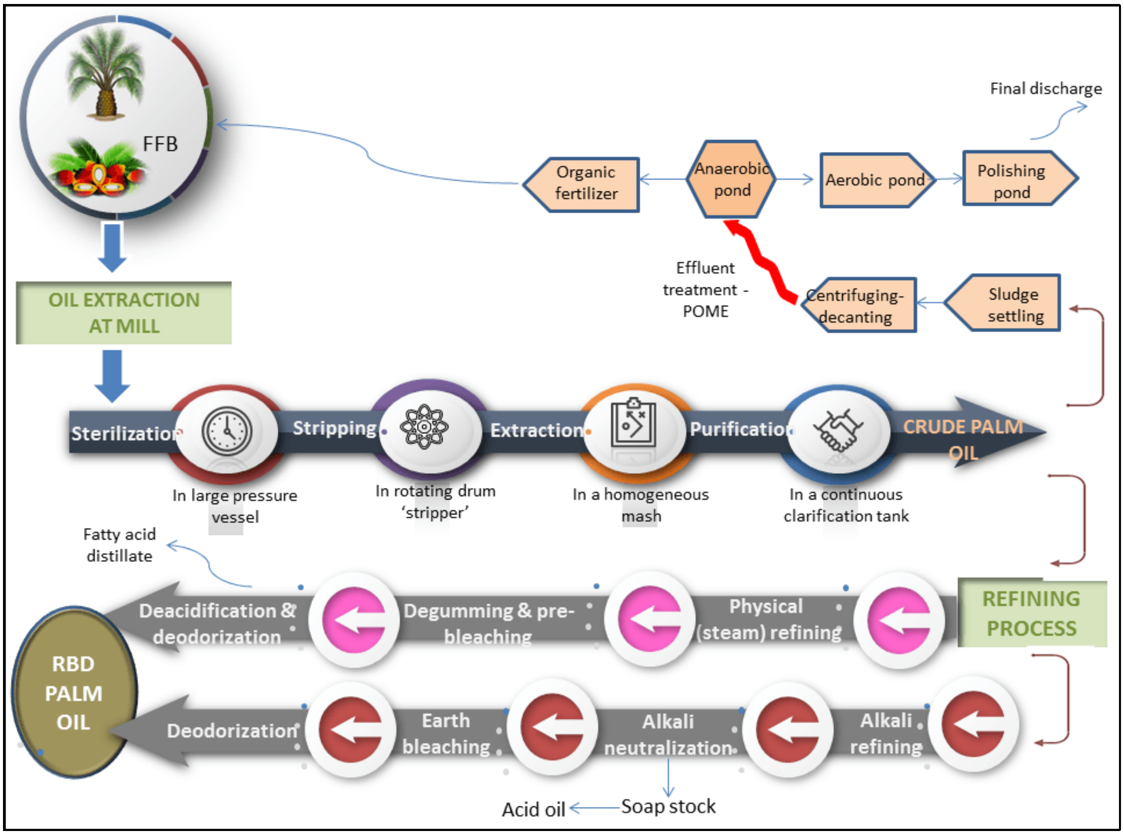


Fig. 2: Flow in palm oil process

POME treatment is a legal obligation that must be followed for a company to stay in business. Because of its high lipids, nitrogenous compounds, protein, and mineral content, most POME treatments result in biological handling. Anaerobic digestion, feedstock for biodiesel, and composting are the three major processes that palm oil producers prefer. Some producers employ treated POME on land application of compost creation to act as fertilizer for palm oil trees (Lokman et al., 2021)(Sheng et al., 2019), while others transform the POME produced from their plant into biodiesel using a dark fermentation process (Garritano et al., 2018; Low et al., 2021; Mahmod et al., 2022). Most manufacturers, however, prefer anaerobic digestion since it is less expensive and can lower BOD and COD. Because the anaerobic system is the most cost-effective biological technique for treating POME waste, several studies have attempted to improve it by modifying it or combining it with other treatments (Choong et al., 2018; Khadaroo et al., 2019; Zainal et al., 2020). POME can be a source of degradable organic matter processed into value-added products and fine chemicals. This organic content becomes the primary source of biogas, a combination of carbon dioxide (CO_2) and methane (CH_4). The anaerobic pond may create more CH_4 and have greater organic conversion efficiency than the open-digesting tank method (Loh et al., 2019). Organic acids produced during acid-phase anaerobic digestion of POME could be used as a carbon source for synthesizing PHAs.

POTENTIAL OF PHAs

PHAs may provide relief from the expanding oceans of plastic to which the commercial sector contributes, but what makes this solution so optimistic? PHA's extremely rapid biodegradation may be a disadvantage in particular applications. The aforementioned issues do not have a simple answer, but the fermentation process, downstream processing, and upscaling largely determine the pricing. Chemical modification during fermentation (copolymers) or after fermentation using post-polymerization, click-chemistry, or blending procedures might increase the thermal stability of PHAs during polymer processing. Enzymatic and chemical polymer modification techniques aim to alter the polyesters' structures and properties while maintaining their biodegradability. PHA structures can be chemically altered to produce modified polymers with predictable molecular weight and functionality differences. Chemical processes allow for integrating different functional groups to create useable, custom-made polymers with desired properties for specific applications and mass production of a homogenous product (Abdelmalek & Steinbüchel, 2022). PHAs can chemically change by several methods, including hydroxylation, epoxidation, carboxylation, and halogenation. These improved PHAs, through chemical modification, can serve as multipurpose materials. Research indicates that PHA materials' hydrophilic/hydrophobic balance was adjusted chemically. PHAs containing carboxylic groups in the side chains, like poly (3-hydroxyoctanoate-co-9-carboxy-3-hydroxydecanoate) and its derivatives, are the greatest candidates for hydrolysis (Timbart et al., 2007).

Additives, such as filler particles, can be used to modify the mechanical properties of PHB. Compared to pure PHB, fillers typically act as nucleants and cause the development of more spherulites of smaller size without noticeably or consistently changing the overall degree of crystallinity. Filler characteristics significantly influence PHB crystallization. Hence, further research should be done to understand how filler surface-polymer interactions affect PHB nucleation. Future experimental research must also consider the degree of crystallinity and the size distribution of spherulite. Due to differences in processing techniques, several additives, and changes in the fillers' surface characteristics, shape, and size, it is not easy to present an unambiguous trend in the system behavior without this information.

PHA polymers are subject to numerous research gaps and issues. PHAs have several benefits, such as bio-origin (processing by microorganisms), biocompatibility, biodegradability, and transforming toxic substances by microorganisms during fermentation (halogenated derivatives, CO_2). It also has special properties, like piezoelectricity and excellent barrier properties. Furthermore, no fossil resources are required to manufacture PHA polymers. When cyanobacteria generate them, CO_2 is absorbed and bonded in the polymer. Using CO_2, sunlight, and water, photosynthetic metabolism can create valuable goods. Prokaryotic organisms known as cyanobacteria, or blue-green algae, have drawn attention due to their possible role in promoting a sustainable economy. They can carry out oxygenic photosynthesis, which involves absorbing free energy from light from the sun to synthesize adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) (Gopi et al., 2014). Compared to chemoheterotrophs, cyanobacteria exhibit every benefit of a bacterial organism. Another feature of cyanobacteria is the ability to use solar energy and transform CO_2-rich, non-competitive carbon-based fuel into a desired output, like PHB (Carpine et al., 2020). The cyanobacterial system has two additional benefits: (i) it helps to absorb and utilize CO_2, reducing the pressure of its release of greenhouse gases into the atmosphere, and (ii) it does not compete with the agro-food market for resources (Gupta et al., 2013). Additionally, it is feasible to be independent of agricultural areas (cyanobacteria on the tops of buildings, at industrial sites, or in the ocean).

PHA polymers have distinct benefits for medical, cosmetics, pharmacy, and eco-agriculture applications. Industrial production reflects the demands of the marketplace. Penalties and legislation both affect market trends. Two primary production lines for PHAs might be predicted in this context:

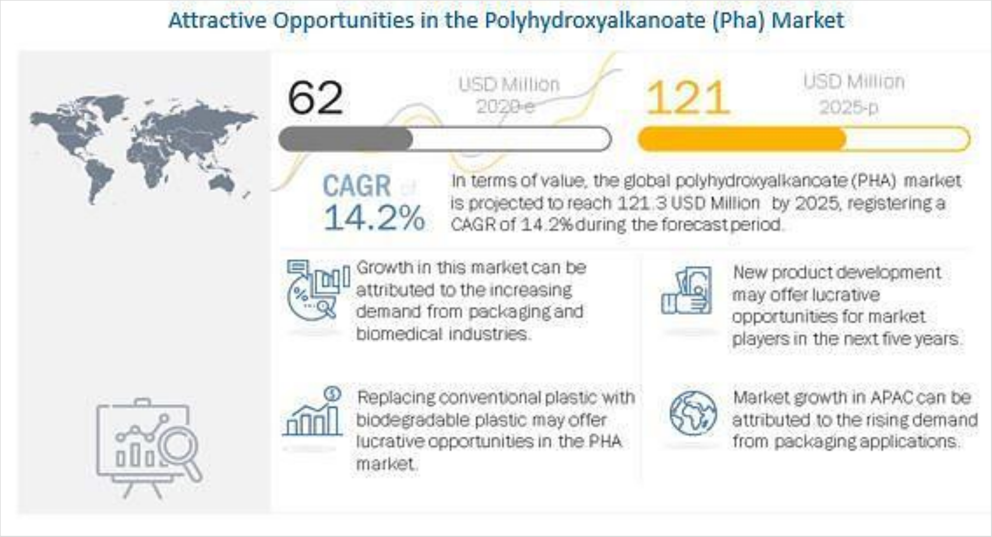
(i) High-end goods leverage the superior material properties of PHAs, such as their biocompatibility, flexibility, and strength, which are necessary as favorable qualities. These applications are often in specialized fields where the material's performance is crucial, justifying the higher cost. Examples include tissue engineering (pharmacy, medicine), drug delivery systems, and nanobiotechnology (medicine). PHA polymers have a great chance of replacing traditional plastics used as fillers and additives in cosmetics. A PHAs price premium over typical petroleum-based plastics may be acceptable.

(ii) For low-end items, the applications typically focus on products that require cost-effective materials and can tolerate lower performance standards. These applications often benefit from the biodegradability and biocompatibility of PHAs, even if the materials are more expensive than conventional plastics. These include materials for various sports entertainment items, such as airsoft balls and badminton shuttlecocks, bags for collecting organic waste, single-use packaging, mulching foils, and geotextiles.

In delivering the prominent application, PHA's production capacity is still in its infancy, resulting in a price significantly greater than that of traditional plastics. Creating a fermentation technology that allows for better production yields than 10 to 20 g PHAs per liter of media is the first step in lowering the price of PHAs. Second, the origin and cost of the ingredients, such as carbon source, should be changed to non-food chains' waste products (e.g., lignocellulosic biomass). Thirdly, PHA polymers' heat processing stability needs to be increased.

The PHA market has been divided into three categories based on the production process: methane fermentation, sugar fermentation, and vegetable oil fermentation. The quantity of carbohydrate sources in sugarcane, beet, molasses, and bagasse, which are quickly digested and transformed by bacteria to produce PHAs, is the primary factor driving the demand for PHAs in this market (CISION, 2021). Because there are so many sugar sources available, the market for sugar fermentation is expected to grow more rapidly than expected in the anticipated year.

The packaging industry needs to be more aggressive in embracing new environmentally friendly plastic alternatives and taking responsibility for products' end-of-life as the world moves toward Extended Producer Responsibility (EPR) regulations. According to estimates, the PHA market will be worth USD 62 million in 2020 and USD 121 million in 2025, with a CAGR of 14.2 % in that time, as shown in Fig. 3 (Market and Markets, 2021). The growing demands for PHA in many sectors, including packaging and food services, biomedicine, agriculture, and others, are the key drivers of the market. The PHA market will be driven by public awareness of the toxicity of petroleum-based plastics and environmentally friendly, sustainable bioplastics. In terms of volume and value, Europe is the world's largest market for PHA, followed by North America and Asia.



In terms of value, the global polyhydroxyalkanoate (PHA) market is projected to reach 121.3 USD Million by 2025, registering a CAGR of 14.2% during the forecast period.

Growth in this market can be attributed to the increasing demand from packaging and biomedical industries.

New product development may offer lucrative opportunities for market players in the next five years.

Replacing conventional plastic with biodegradable plastic may offer lucrative opportunities in the PHA market.

Market growth in APAC can be attributed to the rising demand from packaging applications.

Fig. 3. The opportunities of the PHA in the future (Market and Markets, 2021)

CONCLUSION

Polyhydroxyalkanoates (PHAs) are emerging as promising biopolymers synthesized from organic materials obtained during anaerobic waste treatment. This review examines the potential of Palm Oil Mill Effluent (POME) as an effective feedstock for producing PHAs, emphasizing its relevance to waste management and environmental sustainability. The valorization of POME, which is notorious for its high toxicity and contribution to water pollution, presents a sustainable strategy for mitigating its environmental impacts while facilitating the production of biodegradable plastics. Moreover, advancements in optimizing PHA production methodologies are crucial, with particular attention to cost efficiency and scalability, to address the increasing global demand for renewable biopolymers. The substitution of conventional plastics with PHAs may offer a significant reduction in plastic pollution, thereby supporting broader sustainable development goals. Ongoing research and innovation in this domain remain vital to realizing PHA production's enhanced economic and environmental advantages fully.

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AUTHOR’S CONTRIBUTION

Norazlina anchored the review and revised the article submission.

CONFLICT OF INTEREST STATEMENT

The author agrees that this research was conducted without any self-benefits or commercial or financial conflicts and declares the absence of conflicting interests with the funders.

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