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Opportunities for the development of cassava waste biorefineries for the production of polyhydroxyalkanoates in Sub-Saharan Africa

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ABSTRACT

The use of plastic materials is forecasted to double by 2030 in Africa. The increase in plastic demand presents an opportunity to develop biopolymers such as polyhydroxyalkanoates (PHA) instead of petroleum-based plastics. However, the high cost of PHA production is closely linked to feedstock price, which will hinder their deployment. On the other hand, the Sub-Saharan Africa (SSA) economy is heavily reliant on agriculture, with cassava being one of the most important crops. Cassava industries in SSA produce 146 Mtpa cassava, generating an estimated 40 Mtpa waste, of which 55% goes to landfill or is incinerated. The use of cassava waste as a carbon source for PHA production, therefore, represents an opportunity to decrease production costs of bioplastics while contributing to waste management solutions. This review critically analyses the potential for developing cassava waste biorefineries for the production of PHA in SSA, a region where the bioplastics industry is in a nascent stage. We conclude that cassava waste is an adequate resource for the production of bioplastics in the SSA region that can also contribute toward the reduction of GHG emissions whilst decreasing the dependence on fossil fuels. We identify cost reduction potential with PHA-overproducing strains or strains capable of utilizing substrates more efficiently and show the economic attractiveness of using waste biomass resources in a circular economy framing. Finally, we make recommendations on the next steps needed to pave the way for sustainable economic development, job creation and industrial activity in the SSA region using circular economy principles.

1. Introduction

Depletion of non-renewable resources and climate change are driving the development of bio-based processes and products using low-carbon-renewable biomass [1]. In 2019, 99% of plastics produced worldwide were obtained from non-renewable resources and the decomposition in landfills of petroleum-based plastic waste can take up to 1000 years [2]. It was estimated that between 1950 and 2015, 6300 Mt of plastic waste were generated [3]. Meanwhile, reductions in copper, gas and oil demand resulted in an economic slowdown in Sub-Saharan Africa (SSA) in 2015 after 15 years of growth. Although Africa relies significantly on wood for energy supply, there is also a high dependence on fossil fuels, with 80% of electricity produced in the continent coming from fossil fuels [4]. Sustainable technological and industrial development is needed in SSA to develop non-fossil-dependent sources of income [5]. In order to develop more sustainable production systems, the "circular economy" model is gaining interest [6] and biorefineries are proposed as production facilities that can potentially fulfil the implementation of such a model [1]. In 2016, biomass represented more than 63.3% of Europe's total renewable energy production [7] and around 10% of the global energy supply [8]. The use of food processing waste in biorefineries to produce value-added products can potentially provide a solution to waste management challenges while developing greener economic models [9]. The SSA economy is largely based on agriculture and its derived products and these activities result in large quantities of waste, presenting a major issue that can be seen as an opportunity for the waste to be used as feedstock in biorefineries [10].

Sugarcane, cassava, palm oil and jatropha are some of the most relevant crops with high production yields in SSA. In this review, we focus on cassava (*Manhiot esculenta*), which is an important source of farm income in SSA [11]. Around 169 Mt of cassava are produced in

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Africa annually [12] resulting in 40 Mt of cassava waste [13], and each ton of cassava pulp abandoned in landfills releases between 195 and 361 kg of CO_2 equivalent to the atmosphere [14]. Cassava waste includes peels, bagasse and wastewater; which have the potential for valorisation into products (i.e. starch, bioethanol and biofuel) in biorefineries [15]. There has been practically no consideration of this in the research literature to date.

Household and industrial use of plastic increased by an estimated 50% in the world between 2000 and 2019 [16] though this differs around the globe. While the global yearly average plastic consumption per capita in 2015 was 43 kg, in South Africa and Nigeria this figure was only 24.5 and 4.4 kg, respectively. African society is experiencing a change in living habits and urbanisation. SSA is the world's fastest urbanizing region, with urban areas expected to double their population in the next 25 years [17]. The production of polymers in SSA is scarce and the vast majority of plastic is imported [18]. Forecasts show that plastic imports in SSA will double by 2030 [18].

360 Mt of petroleum-based plastics are produced annually worldwide [19,20]. As illustrated in Fig. 1A, 9% of the global plastic waste is recycled, 12% incinerated and 79% landfilled [19]. If current production and waste management trends continue, roughly 12,000 Mt of plastic will be accumulated in landfills by 2050 [3]. Around 82 Mt of plastic waste was landfilled in Africa between 1990 and 2017 [18]. Therefore, the development of bio-based and bio-degradable polymers is a key priority [3], despite currently constitute only 1% of total plastic production. The remaining 99% are petroleum-based plastics such as polypropylene (PP) or polyethylene (PE). Bioplastic production shows an uneven geographic distribution. As depicted in Fig. 1B, most of the production capacities are located in Asia and Europe, followed by North America and South America. African production of bioplastics is negligible [19] hence, indicating an opportunity for exploitation. One of the most promising candidates for the sustainable development of environmentally-friendly plastics is the biodegradable polyester polyhydroxyalkanoate (PHA), which can be produced from renewable resources [21]. These biopolymers can be used in a wide range of applications such as commodity plastics for packaging, agricultural use and medical applications [22–26].

Biopolymers offer many environmental advantages over petroleum-based plastics e.g. recent studies report c.a. 80% reduction in global warming potential for production of 1 kg of PHA compared to the petrochemical alternative [24]. As a low-cost feedstock, cassava waste can help deliver cost-effective production, enabling the development of local circular economy systems in the SSA region by potentially including cassava-based products such as fertilizers during production.

This review, therefore, aims to determine the potential for the development of integrated cassava waste integrated biorefineries to produce PHA in SSA with several objectives: (i) To identify the most appropriate biorefinery configurations: second-generation biorefineries along with the current development in SSA are reviewed in section 2. (ii) To assess the sustainable feedstock and scale-up potential: cassava production and cassava waste generation are considered in the third section as well as the potential for cassava to become a major resource for biorefineries by examining the most relevant bioproducts produced to date from cassava waste. (iii) To identify development opportunities and barriers: in the fourth section, biopolymers (especially PHA) are reviewed and opportunities to produce PHA from cassava waste are discussed. (iv) To support market strategies and planning, the feasibility of implementing cassava waste biorefineries for biopolymers production is evaluated and discussed in the fifth section through a market analysis, techno-economic assessment, and life cycle analysis. (v) To integrate the above investigations to deliver a robust assessment of the future prospects of cassava waste biorefineries for biopolymers production in SSA, the above are synthesized in the sixth section.

2. Biorefineries

In the late 1990s, the concept of a biorefinery emerged as a result of increased awareness of climate change and fossil fuel scarcity [26]. The development of production facilities in less industrialized areas may entail additional benefits such as minimizing feedstock transportation as well as logistics and management considerations that may boost the local and regional economy [27]. Nevertheless, the replacement of petroleum with renewable feedstocks such as biomass requires changes in processing [6,28]. The integration of mature and emerging methods broadens the range of applications and products [29]. Section 2 analyses the use of waste crops in second-generation biorefineries and their development status with particular reference to SSA.

2.1. Biorefineries from waste biomass

Biorefineries are often categorized by the type of raw material used in the process: divided into first, second, third and fourth generation biorefineries [30] as depicted in Fig. 2.

This review focuses on the second-generation biorefineries since they use biomass waste and non-edible crops as feedstock [31]. This includes waste streams generated in a wide range of industries and environments such as agro-industry, agriculture, forestry and household activities [31]. This type of biorefinery presents some advantages over the other generation-biorefineries e.g. lower cost of raw materials and environmental benefit by valorising waste streams [29]. Various products such as biopolymers (i.e. PHA) [21] and chemicals (i.e. lactic acid, citric acid, hydroxymethylfurfural) [32] have been successfully produced following the 2nd generation biorefinery concept at laboratory scale.

Currently, the major industrial interest is focused on the development of second-generation biorefineries e.g. the AgriMax project, in Brazil, aims to establish a biorefining process using crops waste to produce new bio-compounds for the chemical, bio-plastic, packaging and agricultural sectors [33], and the OLEAF4VALUE project, in Spain,

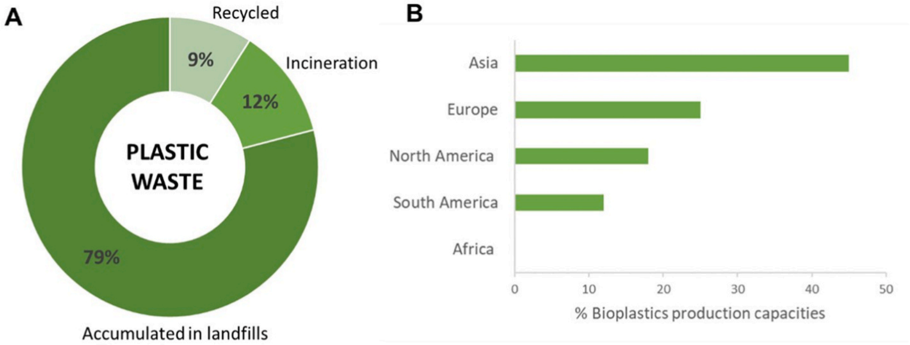

Fig. 1. (A) World waste plastic management in 2017 adapted from Ref. [3]; (B) Global production capacities of bioplastics in 2019 by continent, adapted from European Bioplastics (2019) [19].

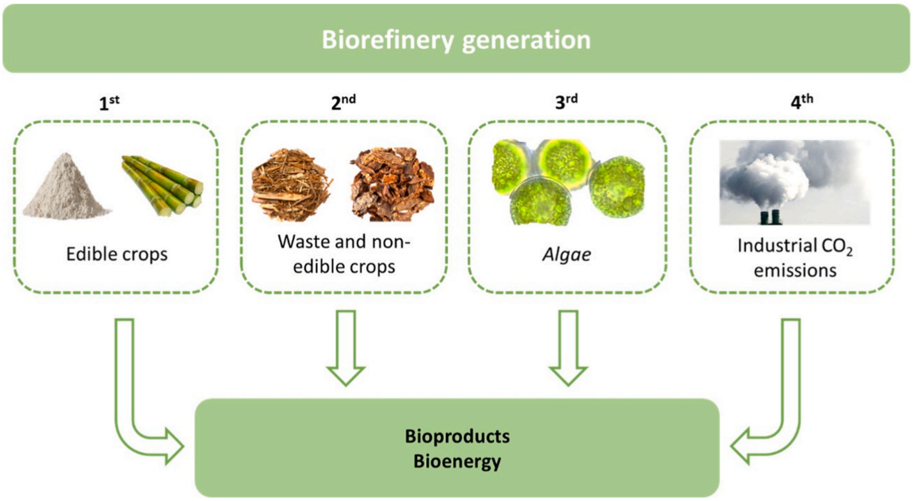

Fig. 2. Diagram depicting the types of biorefineries.

aims to isolate high value-added bioactive compounds from olive leaves, with high market potential in the food, feed, chemical and pharmaceutical sectors [34]. There are well-established industries that are mostly oriented to biofuels and bioenergy production. One example is Vivergo fuels (UK) [35], which produces ethanol from feed wheat. The production of other value-added products, such as bulk chemicals or biopolymers from waste biomass is still to be developed in the industrial landscape.

2.2. *Current developments of biorefineries in Sub-Saharan Africa*

Biorefineries offer environmental advantages over traditional refineries, and they are emerging in many areas of the world, such as North America, Europe, Australia and some areas of Asia. Biorefineries are also emerging in regions such as South America, but there has been very limited activity in Africa [36]. However, some countries in the continent have started developing strategies to promote their industrial implementation [10]. Ghana [37] and South Africa [38] are examples of countries that already published their own strategy to develop their bioeconomy through the exploitation of natural and renewable resources to contribute to economic growth and quality of life. *The bio-economy strategy* of South Africa states the potential of the development of biorefinery platforms for the co-production of a wide range of products and the benefits that this would entail to the country's economy [38].

In 2010 only 42% of the African population had access to power, and the increase in the oil price coupled with high population growth rates are hindering access to energy and basic goods [10]. With limited energy infrastructure, the development of biorefineries in SSA is mostly focused on biofuel production [15,16] since these offer a flexible and portable energy vector. Such development has the potential to alleviate fossil-fuel dependence in SSA as well as to promote infrastructure development. Additionally, biorefineries for biofuels can also help to boost the agricultural sector and thereby help tackle poverty [39].

Ghana is an example of a SSA country that has already made progress in this area since a government policy in 2010 that ordered a gradual replacement of petroleum-based fuels with biofuels [37]. Malawi developed a plan in 2006 where jatropha oil seeds are used as feedstock for biofuel production [40]. Various major cities in Malawi such as Lilongwe and Dwangwa have plants processing sugarcane molasses to obtain bioethanol [10] and there are biofuel production plants in Mozambique [41], Nigeria [10], Senegal [42] and Tanzania [43] and the use of bioresources for energy production in SSA countries is increasing e.g. 9–14% of South African energy needs were produced from biomass in 2016. However, the utilization of biomass for biofuel production is not always economically sustainable and added-value bioproducts can support this [44]. The choice of raw material must take into account the final product or combination of products, as well as the availability of feedstock and the main feedstocks used in the SSA region, which are cassava, sugarcane, molasses, jatropha and cashew [10]. However, the development of a biorefinery platform must also consider social and economic factors. Second-generation biorefineries are the preferred production plants in SSA due to the large cropped areas, resulting in large amounts of residues. The increasing global interest in moving away from petroleum-based chemicals could align well with the high availability of feedstocks in SSA if appropriate technologies are developed to enable co-production of other bioproducts [45], which provide income that supports economic profitability e.g. jatropha press cake after biodiesel production has been used to obtain coatings, paints, adhesives, ethanol, binders and fertilizers in various African countries [46]. The International Energy Agency (IEA) estimated the production cost of biodiesel to be around US$0.8/l and the market price around US$1.09/l [47] in 2018. By comparison, the biopolymer polyhydroxybutyrate (PHB) has an estimated cost of US$5–6.11/kg and some companies such as Newlight Technologies claim to be able to produce them in the range of US$2–3/kg [48]. These differentials significantly impact profitability and drive the rationale for integrated biorefineries rather than single-product strategies. Here, the co-production of high-value products within integrated biomass-processing facilities can potentially overcome some of the current economic challenges [38,49], since realizing higher sale values for small volume products can support the overall economic viability of the multi-product biorefinery system. Second-generation biorefineries could then be a potential waste management solution, improving the region's economy through the co-production of various bioproducts and energy [50].

3. Cassava production in Sub-Saharan Africa

Cassava (*Manihot esculenta*) is the fourth most important crop for starch production in tropical and subtropical countries, after rice, sugar and maize [51,52]. Its characteristics, such as endurance, resistance to disease and drought, and ability to grow in low-quality soils allow this crop to grow in different environments [53]. Cassava is a major food crop for more than 700 million people in the world, mostly in SSA and other developing countries such as Thailand, Vietnam and Indonesia. The vast majority of cassava production is located in Africa, Asia and South America, as shown in Fig. 3. In 2014, Africa was the top producer continent, with a 54.5% share of global production [54]. This crop offers a cheap source of carbohydrates in countries where most of the

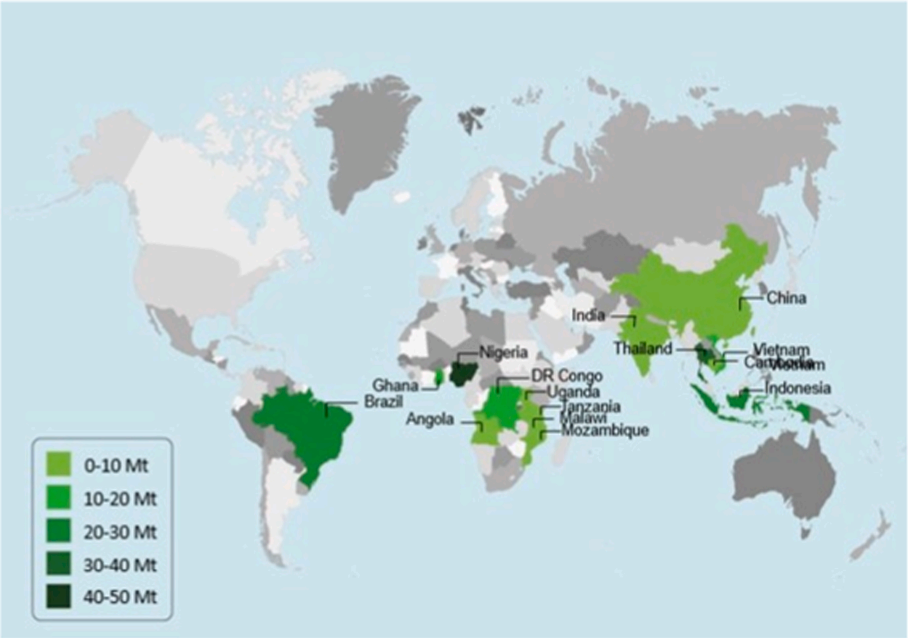

Fig. 3. Major cassava producer countries in 2014. Adapted from the joint FAO/IAEA division of nuclear techniques in food and agriculture report [57]. Mt: Million tons.

population face poverty and hunger. Moreover, cassava can be grown both, at small scale - where there is no need for mechanization and it is easy to harvest, allowing the growth in marginal areas with unfavourable weather conditions – and at large scale. Therefore, cassava properties make this crop very interesting and resistant to climate change, while promoting economic development in low and middle-income countries. Additionally, the development of local agro-industries for processing and trading cassava could decrease the need for imported crops and the associated high taxes. Therefore, this represents an opportunity to support local economies where cassava is yet underutilized due to the lack of technology to minimize post-harvest loss and the non-existent facilities to convert cassava residue into value-added products [51]. Water makes up 60% of the total cassava mass; while 90% of the dry material is starch, making this a cheap source of carbohydrates. The use of cassava in biorefineries as feedstock can result in value-added products and income generation [53], but implementation has been limited due to the lack of industrial and technological capacity. Nigeria is the largest cassava producer in SSA and a global leader. The production in 2013 reached c.a. 55 Mt, representing 20% of the worldwide production [55]. However, only 7% of global production is used to obtain products such as organic acids and flavour compounds [56].

Cassava crops also present significant waste management challenges: Waste generated after cassava harvesting and processing is usually left in the field or burnt, contributing to environmental pollution and human health hazards [54]. Understanding the different types of cassava waste is crucial in order to develop potential solutions. The main categories are: (i) peels from initial processing, (ii) fibrous by-products from crushing and sieving, (iii) settling starch residues and cassava processing bagasse and; (iv) wastewater [58]. There are six cassava production facilities in Nigeria that generate 1.5–3 t and 3–6 m^3 of solid and liquid waste respectively daily, respectively, from a supply of 6–8 t of cassava tubers. This results in approximately 40 Mt of cassava waste being generated in Africa annually [13]. Such waste is rich in organic compounds and can be potentially valorised and used as feedstock in biorefineries to produce fuels and chemicals [45]. If all the cassava waste generated in Africa in a year was to be converted into fuels, approximately 10^{14} kJ of energy could be produced annually, which would be enough to provide electric energy to Ghana for more than a year [59]. Cassava production has increased by an average of 2.2% per year in the last few decades, and the trend is expected to continue in the future, with the associated waste arising [55]. The development of cassava waste biorefineries in SSA, therefore, has the potential to help mitigate the environmental issues associated with waste disposal whilst promoting job creation and industrial activity [56].

3.1. *Cassava waste valorisation into value-added products*

The main types of cassava waste (peels, fibrous by-products, starch residues and wastewater) have a similar composition to the fresh crop: 90% starch, which has approximately 20% unbranched amylose and 80% of branched amylopectin, representing a carbohydrate-rich feedstock [53]. To use carbohydrate-rich feedstocks as a carbon source in biorefineries the starch granules must be first released, and then transformed into value-added products [58], such as organic acids [60], ethanol [61], flavour and aroma compounds [57], methane [62], biogas [63],and biopolymers [53], with bioenergy and biofuel being [64,65] the most commonly described. While thermo-chemical catalytic and biochemical conversions are possible, this review will focus only on biochemical processes because the product of interest (biopolymers) requires microorganisms for its synthesis [66]. Although the potential of cassava waste as a feedstock in biorefineries has yet to be fully exploited, the biotechnological approaches such as genetic engineering, that have been developed in recent decades facilitate significantly more efficient bio-based production from cassava waste [52,53]. Countries such as Thailand, Cambodia, Brazil, Vietnam, India, and China are among the major producers and processors of cassava into a wide range of products [67]. Organic acid production from different agro-industrial waste streams is well described e.g. microbial transformation of cassava into citric acid was optimized in Brazil [60], lactic acid and ethanol were achieved at high yields in Thailand [68] and enhanced production of succinic acid is reported in China [69]. The predominance of such countries may be not only due to the availability of feedstocks to be transformed into value-added products but also to the technological development that these countries have experienced in recent decades. Despite SSA being the most important cassava-producing region, there is a lack of industrial and technological development that hinders the bioconversion of biomass (e.g. cassava) into value-added products (i.e.

biopolymers) and therefore, SSA remains distant from the leading world processors. Most of the cassava production in SSA is located in deprived areas [70]. Hence technological development of cassava valorisation into added value chemicals such as biopolymers represents an economic opportunity as well as reducing dependence on fossil fuels. A few bioplastics have already been produced, showing promising results. Nevertheless, the biotransformation of cassava waste into biodegradable polymers is yet to be optimized [71].

4. Biopolymers

Biopolymers are a type of polymer produced from natural resources that represent an alternative to petroleum-based plastics. Biopolymers can be entirely synthesized by living organisms or chemically synthesized from a biological material [22]. A wide variety of characteristics such as the diverse structural composition and the alterable physical properties have turned biopolymers into interesting products for a wide spectrum of applications from commodity plastics for packaging to pharmaceutical and medical uses (e.g., heart valves) [54]. Classification by biodegradability properties and origin results in three groups: the first category, bio-based polymers, comprise biopolymers based on renewable resources, which are not necessarily biodegradable, albeit most of them are. The second group, biodegradable polymers, comprises biodegradable biopolymers, which do not need to be based on renewable resources. The third type, bio-based and biodegradable polymers, consists of both, biopolymers based on renewable resources and biodegradable polymers [72].

Many biopolymers with similar properties to traditional petroleum-based plastics such as polypropylene (PP) or polyethylene (PE) are commercially relevant but are not biodegradable. Consequently, most of the current interest is centred on three types of polymers which belong to the bio-based and biodegradable polymers group. These biopolymers are polylactic acid (PLA), PHA and starch-based polymers [72]. Another interesting characteristic of these biopolymers is their biocompatibility properties, which means they can be used in a variety of medical applications [66]. The following section focuses on the production and opportunities of PHA. Although the current worldwide production of biopolymers is dominated by PLA, recent publications show an increasing interest in PHA due to their faster and more reliable biodegradability times at lower temperatures [73]. PLA is a renewable polymer however, it does not offer the end-of-life advantages of PHA's [73,74].

The biopolymers market is currently dominated by Europe and North America with Metabolix (USA) dominating global production, while production in the Asia Pacific and Latin America begins to evolve [75]. In contrast, there is little reported activity for the African continent, with very few companies producing biodegradable plastics; an exception is Hya Bioplastics in Uganda [76].

Production of PHA presents two major challenges: (i) the cost of the substrate needed for the synthesis of the biopolymer and (ii) the cost of purification and its associated technologies. Some manufacturers report the use of feedstocks such as castor oil, but limited feedstock data is publicly available. Therefore, biopolymers' commercialization is hampered by economic factors [22].

4.1. *Polyhydroxyalkanoates (PHA)*

PHA (Fig. 4A) are a wide family of polyesters that are produced by various microorganisms; both native and genetically modified. They are lipid-like molecules and have similar properties to some petroleum-based plastics such as polypropylene (PP) and low-density polyethylene (LDPE). PHA have become a promising alternative to petroleum-based plastics [77] as they can be synthesized from renewable resources and biodegraded by microorganisms [78]. PHA are hydrolysed by specific depolymerases, which are secreted by PHA-degrading microorganisms, hence the polymer is degraded extracellularly to water-soluble products [78]. The bio-based and biodegradable characteristics strongly support PHA market growth among bioplastics [79].

More than 150 different PHA monomers have been described and different PHA polymers and copolymers can be obtained through combinations of single monomers depending on the carbon source used by the microorganism. Moreover, PHA show a wide diversity of characteristics and properties, therefore, allowing a broad range of applications. Widely studied PHA include polyhydroxybutyrate (PHB) which is one of the most abundant PHA homopolymers and; poly(3-hydroxybutyrate-co-3-hydroxyvalerate), a copolymer obtained after the combination of 3-hydroxybutyrate (3-HB) and 3-hydoxyvalerate (3-HV) [80,81]. PHA are divided into three categories depending on the number of carbon units: (i) short-chain length (SCL-PHA), (ii)

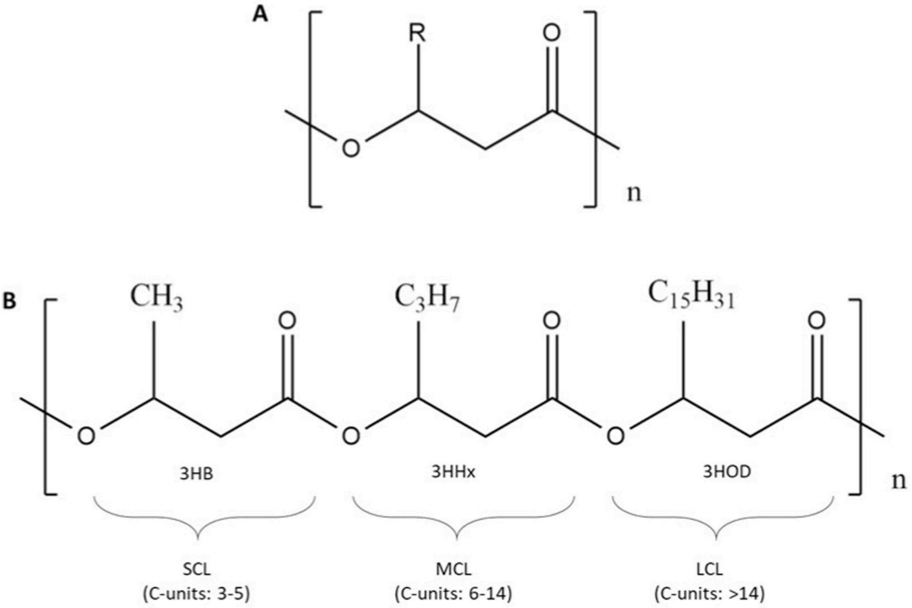

Fig. 4. General molecular structure of (A) Polyhydroxyalkanoates (PHAs). (B) Examples of short-chain length (SCL), medium-chain length (MCL) and long-chain length (LCL) -PHAs.

medium-chain length (MCL-PHA) and (iii) long-chain length (LCL-PHA) (Fig. 4B). The above-described monomers can be combined to form both, homopolymers and copolymers [66]. Table 1 shows the main characteristics for each category such as the number of carbon monomer units, the main properties and potential applications.

PHA are only produced by microbes and are stored as cytoplasmic granules which are insoluble in water [66], with a diameter ranging from 0.2 to 0.5 μm [66]. They can provide carbon and energy to the cell, enhancing cell lifetime under starvation conditions [86,87]. On the surface of those granules, a considerable number of proteins are found. Although the function of some of these proteins has not been defined yet, the supramolecular complex of protein-PHA interactions has exploitation potential. Jendrossek proposed the designation "carbonosomes" to the complex organized structures containing proteins on the surface of PHA [88].

PHB is one of the most abundant and common PHA, which belongs to the SCL-PHA group. It consists of linear chains of (R)-3-hydroxybutyrate units. PHB has been divided into three groups based on the number of monomer units: (i) high molecular weight storage PHB, (ii) low molecular weight PHB and (iii) conjugated PHB (cPHB). Firstly, high molecular weight storage PHB includes PHB polymers containing more than 10^3 units, and they are also known as "storage PHB". They are usually found in prokaryotes as inclusion bodies. Secondly, the low molecular weight PHB group comprises PHB polymers containing between 100 and 200 units of (R)-3-hydroxybutyrate. These types of polymers may be found in all organisms [66]. Lastly, conjugated PHB (cPHB) includes PHB polymers containing less than 30 units of (R)-3-hydroxybutyrate covalently linked to proteins [89].

The biochemical pathway for PHB synthesis comprises three main steps: (i) the condensation of two molecules of acetyl-CoA to acetoacetyl-CoA by a β-ketothiolase (PhaA); (ii) the acetoacetyl-CoA reduction into 3-hydroxybutyryl-CoA (monomeric precursor of the biopolymer) by an acetoacetyl-CoA reductase (PhaB) and; (iii) 3-hydroxybutyryl-CoA polymerization to obtain PHB, conducted by a PHB synthase (PhaC) (Fig. 5) [85].

4.2. PHA production

PHA are bio-based and biodegradable biopolymers that are entirely produced by various types of microorganisms. It has been reported that PHA are produced in response to carbon oversupply, resulting in carbon and energy reserves inside the cells. Nevertheless, carbon oversupply is not the only stimulus for the microbes to produce PHA: the limited supply of other nutrients such as nitrogen or oxygen restricts bacterial growth and leads to PHA synthesis [90,91]. PHA synthesis requires a carbon source that the microorganism uptakes and subsequently transforms into PHA. All PHA are synthesized from CoA-activated precursors by the action of PHA synthases that catalyse the polymerization [89]. Depending on the microorganism, different carbon sources can be used such as glucose, fructose, maltose or xylose. Nevertheless, not only sugars can be used as feedstock in PHA production. Vegetable-oil derivatives have also shown promising results in lab-scale studies [53].

Table 1
Main characteristics of the three categories of polyhydroxyalkanoates (PHA).

Category	Carbon monomer units	Main properties	Presence in nature	Relevant applications
SCL-PHA	3–5	Thermoplastic	Common	Packaging and textile [66,82]
MCL-PHA	6–14	Elastomeric	Common	Biomedical [82,83]
LCL-PHA	>14	Non-specific	Rare[a]	Bioplastics [84,85]

[a] Lcl-PHA have been blended with scl-PHA and mcl-PHA for application studies.

Despite the industrial production of PHA started in the 1980s, the interest in biopolymers production has increased in the last decades. One of the main problems detected in PHA production is the high process cost compared to petrochemical-derived plastics. In 2017, PHA cost was estimated to be $5–6.11/kg which is 3–4 -fold higher than their petrochemical competitors, being the cost of polymers such as polypropylene (PP) or polyethylene (PE) approximately US$0.60–0.87/lb [22,23]. One of the most limiting steps in the production is the feedstock price. Commercial synthetic carbon sources are expensive hence, using cheaper carbon sources from biomass resources has been proposed to improve the economic viability of the process [92]. Other factors directly influencing the high cost of the process are the production yield and PHA recovery efficiency in the downstream process [53]. PHA yield depends on different variables such as the bacterial species, components of the culture media, and culture conditions [93]. The following sections analyse two key variables of the PHA production process: the microbial cell factory, and the raw material used as feedstock.

4.2.1. Microbial cell factories commonly used for the production of PHA

PHA can be produced by many microorganisms natively whereas others can be genetically modified in order to synthesise biopolymers. Most of the native producers accumulate PHA as intracellular carbon and energy reserves [81]. A wide variety of organisms have been used to date to efficiently produce PHA for industrial applications. Gram-positive and negative bacteria and some eukaryotes have been reported to produce PHA [66]. Table 2 presents relevant studies showing different carbon sources (feedstock) and cultivation strategies for PHA production. As it can be observed, PHA production can be as high as 90% of the bacterial dry cell weight under optimized conditions [94]. *Cuapriavidus necator* (*C.necator* – formerly known as *Wautersia eutropha, Ralstonia eutropha* and *Alcaligenes eutrophus*) is a gram-negative facultative chemolithoautotrophic bacterium widely studied for its ability to efficiently produce PHA. *C. necato*r produces PHA natively, mainly PHB, in the presence of an excess of carbon and under nutrient stress [86]. This particular PHA-producing microorganism has three genes that are required for PHA synthesis which are clustered in a transcriptional unit called phaCAB operon. PHA can be produced under autotrophic conditions using H_2 as electron donor and O_2 as electron receptor thus, reducing CO_2 [89]. Although PHB is the most abundant biopolymer synthesized by *C. necator*, this bacterium can also produce copolymers such as poly (3-hydroxybutyrate-co-3-hydroxyvalerate). The resulting biopolymer composition depends on different variables such as the carbon source or the biochemical pathway utilized [87]. Advances in genetic engineering have enabled the development of novel PHA-producing strains [95]. An interesting example is *E. coli*, whereby genes from *C. necator* were inserted to produce PHB [96]. Other microorganisms have also shown promising PHB production rates after genetic manipulation. Remarkably, all the studies depicted in Table 2 were carried out in technological and industrially developed countries. In contrast, most countries in SSA have not developed the technology to achieve similar production titres. Knowledge transfer from developed to developing countries, as well as the need for advanced technology provision can help to develop the SSA economy and development.

4.2.2. Use of cassava waste as feedstock for PHA production

Feedstock price is one of the major burdens in the process of PHA production [104]. With the objective to reduce the total production cost of PHA, a wide range of feedstocks have been tested as an alternative to synthetic commercial sugars (Table 3). The highest production values (in terms of intracellular PHA accumulation) are generally achieved using pure sugars (i.e. glucose) followed by alternative feedstocks with high content of carbohydrates such as cassava and sugarcane. The use of synthetic sugars as carbon source results in high process cost and therefore, researchers are working to find more efficient routes by using waste streams as carbon source [84]. Waste biomass has a high potential to be used as feedstock for the production of PHA. For example,

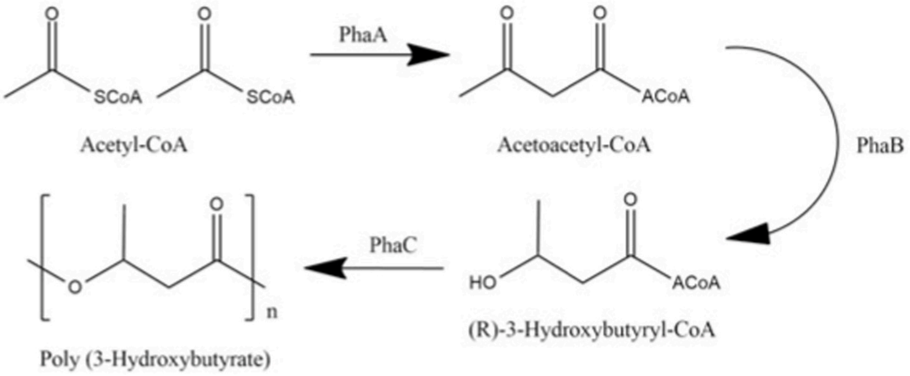

Fig. 5. Schematic illustration of the enzyme-catalyzed polyhydroxybutyrate (PHB) synthesis system.

Table 2
Relevant microbial systems used for the production of polyhydroxyalkanoates (PHA).

Cell factory	Carbon source	Cultivation Strategy	PHA content (% (g_{PHA}/g_{DCW}))	Reference
NATIVE				
C. necator	Waste rapeseed oil + whole cheese whey Hydrolyzate	Batch	95.40 ± 1.70	[97]
B. sacchari	Saccharose	Fed-Batch	72.60	[98]
P. putida	Decanoic acid + glucose	Fed-Batch	74.00	[83]
Ideonella sp. *O-1*	Syngas	Batch	77.90	[99]
B. megaterium	Sugarcane molasses	Fed-Batch	45.84	[100]
V. proteolyticus	Fructose	Batch	54.67	[101]
RECOMBINANT				
E. coli	Glycerol	Fed-batch	67.90	[96]
H. bluephagenesis	Crude corn extract liquid + Glucose	Fed-batch	*79.50*	[102]
M. extorquens	Methanol	Fed-batch	24.70 ± 1.60	[103]

lignocellulosic biomass can be pre-treated to release fermentable sugars that bacteria can use as carbon source to grow and produce PHA [105]. On the other hand, starchy materials from crops or wastewater are interesting resources because they are cheap, renewable and locally available [53]. Cassava waste has been seldom used as feedstock for PHA production with limited published work (Table 3).

5. Potential development of cassava waste biorefineries in Sub-Saharan Africa

5.1. *Market analysis*

The current global market of plastics relies mostly (99%) on petroleum-based plastics [19]. Nevertheless, thanks to the properties and advantages of bioplastics, the biopolymers market is expected to grow and diversify considerably in the following years. The global PHA market is expected to grow at a compound annual growth rate (CAGR) of c.a 6.3% over the next decade to reach approximately $119.15 million by 2025 [19,113]. The latest market data compiled by *European Bioplastics* and the research institute Nova-Institute reports that bioplastics production capacity will increase from 2.11 Mt in 2020 to 2.87 Mt in 2025 [114]. Some of the prominent areas that are driving the increase in biopolymers demand are the healthcare industry, the renewable materials market and the recent advances in PHA manufacturing technologies [75]. Although the above reports show promising market data for the near future, they are mostly focused on North America, Europe and the Asia Pacific. Currently, Europe and North America are the two largest biopolymers producing areas and these regions are expected to continue leading the ranking thanks to public and private investment in R&D. Nevertheless, the Asia Pacific market is also likely to witness significant gains [113]. Although more than 160 hydroxyalkanoates (HA) have been identified to date, the high production cost hinders their commercialization, hence commercial production of bioplastics is currently limited to a few types of PHA. During the 1970s, the oil crisis raised the interest in bioplastics and Imperial Chemical Industries (ICI, UK) became the first company to commercialise PHA. Currently, the most produced PHA are poly-3-hydroxybutyrate (P(3HB)) and poly-3-hydroxybutyrate-co-3-hydroxyvalerate (P(3HB-co-3HV)) and

Table 3
Production of polyhydroxyalkanoates (PHA) using relevant substrates and microbial systems.

Substrate	Cell factory	Process limitation	Polymer	Cultivation Strategy	PHA content (% (g_{PHA}/g_{DCW}))	Reference
Glucose	*C. eutrophus B10646*	Nitrogen limitation	P(3HB/3HV/4HB) and P (3HB/3HV/3HHx)	Batch	80.00	[106]
Cassava starch hydrolysate	*Cupriavidus* sp. *KKU38*	Nitrogen limitation	PHB	Batch	61.60 ± 0.07	[53]
Cassava waste	*Halogeometricum borinquense*	n.a	P(3HB-*co*-3HV)	Batch	44.70	[107]
Cassava extract + andiroba oil	*P. oleovorans*	Oxygen limitation	P(3HB-co-3HV)	Batch	74.00	[108]
Cassava starch	*Pseudomonas aeruginosa*	n.a	PHB	Batch	57.70	[71]
Paperboard mill wastewater	*Actinobacteria*	Phosphorous and Nitrogen limitation	n.a	Batch	15.44	[109]
Acetate	*n.a*	n.a	n.a	Batch	34.20	[110]
Sugarcane molasses and corn steep liquor	*Bacillus megaterium*	Nitrogen limitation	PHB	Batch	46.20	[111]
Acetate and soft drinks wastewater	*n.a*	n.a	n.a	Fed-batch	79.00	[112]

Metabolix (USA) is the largest market player, with an annual production capacity of 50,000 tonnes and with facilities in the USA and Europe. Another large company that focuses on P(3HB) and P(3HB-co-3HV) production is Monsanto (USA), which in 2004 rejected the idea of microbial production and moved into PHA production using plants. Nevertheless, they have not reported yet any plant-based PHA. Furthermore, PHA production using plants is controversially linked to the use of genetically modified crops. Other companies are increasing their production capacity of biopolymers, such as CJ CheilJedang (Korea), which acquired the intellectual property on bioplastics production from Metabolix. However, P(3HB) and P(3HB-co-3HV) are not the only biopolymers with commercial interest. Kaneka (Japan), P&G (USA) and Danimer Scientific (USA) are interested in Poly-3-hydroxybutyrate-co-3-hydroxyhexanoate (3HB-co-3HHx) production. Other companies such as Tianjin Green Bio (China), Bluepha (China), TianAn Biopolymer (China), BioCycle (Brazil), Biomer (Germany), Mango Materials (USA) and Newlight Technologies (USA) are currently developing commercial-scale PHA production facilities [95]. The above analysis shows that the biopolymers market is growing, and it is likely to further grow at higher rates but with the same geographical distribution. Furthermore, some countries such as China and India are expected to have a positive impact on the biopolymers (mainly PHA) market in the near future. However, Africa does not have an existing bioplastics market and limited growth projections in the near future [113]. Higher investment in research and innovation would be needed to develop the global bioplastics market opportunity for the SSA economy albeit, there is a clear market niche with huge potential in the region.

5.2. Techno-economic analysis: A case study of a cassava waste biorefinery for the production of energy and bioproducts

Cassava waste has been demonstrated to be a potential feedstock for PHA production. In the biorefinery context, feedstock production and biopolymer manufacture should be co-located to minimize costs associated to transport as exposed in Section 4.2.2 and therefore, realize the potential and associated economic benefits [115]. SSA is the major cassava producer in the world, but most countries have very limited technological and industrial resources, constraining the biopolymers market development. Techno-economic analysis may be useful to evaluate the feasibility of cassava biorefinery platforms; the few reports that have been carried out to date focused on the feasibility of integrated biorefineries to co-produce bioproducts such as succinic acid, glucose syrup and bioethanol in combination with heat and power production [116]. Other relevant works report the potential use of cassava-based industrial waste in biorefineries to produce several products such as biofuels, biogas or biosurfactants [117], and future perspectives on the integration and use of cassava in the bioproducts industry [15].

In this section, the work published in 2020 by Padi and Chimphango [116] is showcased as a case study. This work focuses on two major questions: "*What are the opportunities of cassava waste biorefineries to provide significant energy supply in SSA?*" and "*Is there potential for product diversification in a cassava waste biorefinery?*". Different by-products can be obtained from cassava waste [15]. Biogas, bioethanol, succinic acid, and glucose syrup are some of the products with high commercial and industrial interest [116]. Consequently, succinic acid was chosen as the main by-product of interest to study the techno-economic feasibility of a cassava waste biorefinery [116]. This organic acid and its derivatives are used extensively in the plastic, polymer, and pharmaceutical industries [118]. Padi and Chimphango studied the feasibility of commercial waste biorefineries for cassava starch industries using South African fiscal conditions as a model of cassava-producing regions in SSA. Five scenarios were considered for their integration into a cassava starch plant. For each scenario, different cassava waste types were used, and diverse by-products were obtained. All scenarios assumed cassava bagasse and cassava wastewater are to be supplied by the plant, and cassava stalks are recovered from the fields. Fig. 6 shows the process diagram of a cassava waste biorefinery which targets zero wastewater and solids disposal. In this biorefinery platform, cassava bagasse, cassava wastewater and 10% of cassava stalks were used for the co-production of succinic acid and bioethanol combined with the production of heat and power from the 90% of cassava stalks remaining [116]. The main parameters and assumptions employed in this TEA study were (i) the percentage of cassava stalks available for the biorefinery, (ii) models for obtaining mass and energy balances as well as (iii) equipment costing and sizing, and plant life. The analysis revealed that the biorefinery plant has the potential to meet the energy demand for both, the biorefinery and cassava starch process, showing a surplus of 121–200 MW of electricity, which is the net power produced in the biorefinery plant minus the power needed by the starch process. The potential surplus power for all scenarios suggests opportunities for energy self-sufficiency in integrated waste biorefineries [116]. On the other hand, the annual production of succinic acid projected in this integrated biorefinery is within the industrial scale capacities range (10–30 Gg SA/a). The outcome of this work shows that the exposed approach has realistic commercial potential. The use of wastewater not only represents an advantage as carbon source but also aids in reducing the consumption of fresh water and thus, mitigating environmental problems [116].

Among the five scenarios, the model simulating the co-production of succinic acid, bioethanol, heat, and power using 10% cassava stalks, cassava bagasse and cassava wastewater as feedstock; required higher total capital investment values than all the other four scenarios studied. The biorefinery throughput was projected at 7.29 Mg/h, 377.83 Mg/h and 450.89 Mg/h when using cassava bagasse, cassava wastewater and cassava stalks, respectively. The other four scenarios were: scenario (I): combination of cassava bagasse and cassava starch wastewater for biogas production and cassava stalks for producing combined heat and power; scenario (II): combination of cassava bagasse and cassava wastewater for the production of bioethanol with all cassava stalks used for production of combined heat and power; scenario (III): combination of 10% of cassava stalks, cassava bagasse and cassava wastewater for bioethanol production with 90% of the cassava stalks used for combined heat and power production and scenario (IV): combination of 10% of the cassava stalks, cassava bagasse and cassava wastewater for co-production of glucose syrup, bioethanol with 90% of the cassava stalks used for combined heat and power production). The study demonstrated promising profitability, thanks to the integration of the succinic acid production in the process. This work confirmed that feedstock price is a major determinant factor for a biorefinery process as has been discussed in section 4.2.2. This study shows encouraging results for cassava waste biorefineries in SSA. Although techno-economic studies will be key for a PHA production plant using cassava waste, and such studies are still scarce for this particular bioproduct; the above-exposed case study paves the way to develop further feasibility studies for the development of cassava waste biorefineries. Due to the lack of techno-economic studies in this field, estimations of the capacity of the process were performed by our research group (non-published results). Considering the total amount of cassava waste generated in Africa in a year, 40 Mt [13], and based on previous data for the production and extraction of PHA from biomass sources with similar starch composition, a resulting quantity of 4 Mt of PHA could potentially be obtained annually in a biorefinery platform. Such estimations were made based on 62%, 65% and 25% recovery yields for the pre-treatment, fermentation and downstream processes, respectively [21]. On the other hand, around 19.5 Mt of petroleum-based plastics are currently being used every year in the African continent [18]. The estimated production of PHA from cassava waste would represent 20% of the usage of total plastic in Africa. This can potentially facilitate the replacement of a significant portion of petroleum-based plastics for biodegradable and bio-based ones. In addition, this will contribute to reducing plastic waste management needs, which is a current challenge in the continent.

Integration of the cassava processing plant with the biorefinery

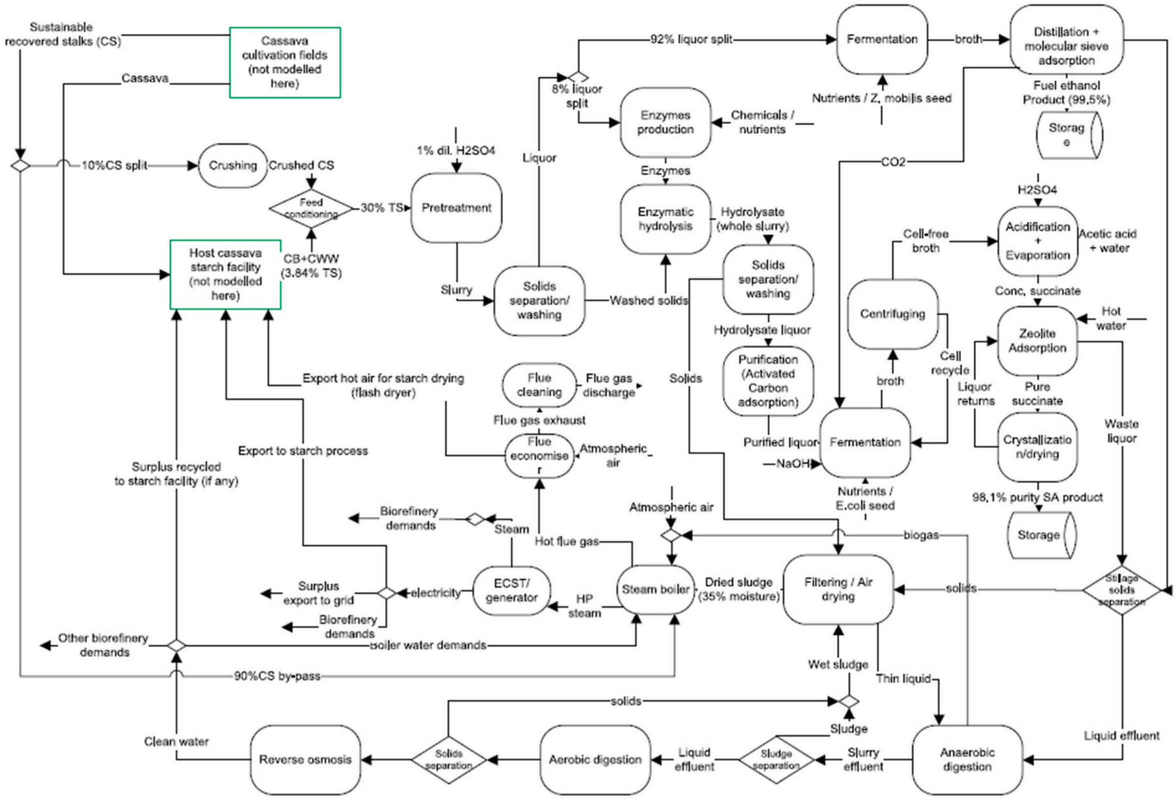

Fig. 6. Cassava waste biorefineries for heat, power, and succinic acid, integrated in cassava starch processing. Reproduced with permission from Padi & Chimphango [119].

reduces costs, leading to a more profitable process, and self-supply of energy contributes to substantial avoided costs, contributing to financial viability where it displaces conventional fuel or electricity in an energy-intensive process. This could e.g., be in traditionally high energy consumption systems such as wood processing, sugar, or tea production, or growth sectors such as cement. While there are not currently significant cassava-biopolymer industries in SSA, the rapid urbanisation of the continent and economic development provide an opportunity for expansion, since obtaining products of industrial interest enables a potential increase in profitability where market opportunities exist. Thus, the development of cassava waste biorefineries producing not only PHA but also relevant by-products such as succinic acid (which has an estimated market value of USD 6–9/kg [120] and a market size of USD 181.6 million [121]) or bioethanol (which has an estimated value of USD 0.9–1.1/L and a market size of USD 64.8 billion [122]) could support profitability [116].

5.3. Life cycle analysis (LCA)

The interest in biopolymers has significantly increased in recent decades due mainly to the environmental benefits they offer compared to their petrochemical-derived counterparts. In particular, biopolymers which are both bio-based and biodegradable, such as PHA, are the most interesting [123]. The production from renewable resources and biodegradability properties make them an environmentally-friendly alternative to petrochemical polymers [21]. However, farming practices to produce those feedstocks often incur significant embodied energy and therefore, there is a need to consider the environmental impacts based on the LCA of PHA in comparison to petrochemical polymers. Most LCA studies of PHA are based on simulations and laboratory or small-scale production plants. Albeit there are several significant studies, the pioneering work on PHA LCA was published only in the early 2000 and concluded that PHA production required more energy than the polymers obtained from petroleum [124]. However, the knowledge and the technology available two decades ago have evolved [72]. Interestingly, an LCA of PHA produced from corn grain revealed that PHA production offers environmental advantages both in terms of greenhouse gas emissions and non-renewable energy consumption over petroleum-based plastics. The residues generated in the study after the fermentation step to produce PHA and the recovery process were used as fuel in a cogeneration power plant [125]. Another study compared PHA and petrochemical polymers concluding that GHG emission from the production of 1 kg of PHA was 0.25–0.5 kg of CO_2 whereas petroleum-based plastics production resulted in 2 – 3 kg of CO_2 emissions. The low CO_2 emissions from PHA production were attributed to the fixation of CO_2 by the feedstock biomass and bacterial respiration during the fermentation process [24]. Furthermore, another recent study analysed the LCA of PHA obtained from two different feedstocks – glucose and cheese whey – and PHA obtained using genetically engineered plants. The study concluded that genetically modified plants do not show any advantages over the microbial process using renewable resources. Although the PHA recovery process involves much fewer energy requirements in genetically modified plants compared to microbial fermentation, the global process using genetically modified organisms requires 4.5-fold more energy [119]. Although biopolymers have been considered to have a lower environmental impact than petroleum-based plastics, a more recent study analysed different biopolymers, including PHA, and concluded that none of the commercial biopolymers, including those currently under development, were environmentally sustainable [126]. In contrast, the use of land for feedstock production can contribute to an increase in competition due to the crops being harvested for food use. Consequently, this can lead to an increase in poverty and issues related to food access. This may be the case in SSA despite the SSA region offers large crop cultivation fields and capacities. The use of waste crops can potentially contribute to promote the production of biopolymers without affecting the food supply [127].

Although the literature is scarce, some authors have already published studies analysing the LCA of PHA produced from waste. For example, Kedall and co-workers showed that PHA production from the cellulosic fraction of residual materials, that otherwise is disposed of in the environment, requires half of the energy needed for PHA obtained from a dedicated agricultural feedstock [127]. Here, the key factor is whether the feedstock is a dedicated crop or a waste by-product. Developing more sustainable processes for biopolymers production may be supported by the development of more efficient practices in crop cultivation, technological improvements during the production process and the use of fermentable residues, such as waste crops originated from different food industries [127,128]. This will not only contribute to bioplastics manufacturing sustainability but also, to a circular economy by decreasing the energy demand for materials production and the reduction of waste, thus, contributing to solving important environmental issues [28]. A key issue with most LCAs of agricultural residues is devising a methodology that appropriately treats the residue and allocates proportionate emissions from the main feedstock production. It is possible to obtain very favourable results if it is assumed that emissions associated with the disposal of the waste residue are avoided and thereby credited to the biopolymer; whereas higher emission intensities will result if it is assumed that the agrochemical and other inputs associated with crop production should be allocated to the cassava residues on a mass or energetic basis. These assumptions should be guided by consideration of the overall production, markets and trends and the methodology adapted accordingly.

However, regardless of the methodology chosen further development of PHA obtained from agricultural residues and cassava-based biorefineries must consider the life cycle and environmental impacts to identify process hotspots, isolate preferred process schemes and, optimize these environmentally and economically.

6. Conclusions and future perspectives

A range of solutions can be implemented to reduce the cost of PHA production such as the use of genetically modified strains (i.e. PHA-overproducing strains or strains capable to utilize substrates more efficiently) by developing the use of waste biomass resources as low-cost feedstock as an alternative to the use of synthetic sugars [95,129]. The use of alternative substrates to synthetic sugars has attracted much attention because it contributes to the circular economy principles [130]. Waste crops and in particular, cassava waste, can be considered an adequate resource for the development of integrated biorefineries for bioenergy and bioproducts in SSA, which is the major cassava producer worldwide. The development of bioenergy strategies and policies in SSA countries (particularly South Africa and Nigeria) will be key in the implementation of biorefinery approaches alongside the utilization of key enabling technologies. Studies regarding the techno-economic feasibility of a cassava waste biorefinery in South Africa indicate that the development of integrated biorefineries for the production of value-added products has great potential to provide positive economic and social impact provided that self-supply of energy is achieved. Although a promising and feasible scenario can be envisaged, technologies for biopolymers production from waste crops must be further optimized to return both, environmental and economic benefits. Nevertheless, the present study confirms the practical conversion potential, enabling mass-energy balance and techno-economic assessments.

An important step toward this objective is the implementation of processing plants near the production areas to avoid transportation and consequently, decrease associated costs [131]. To achieve this, a social analysis of cassava biorefinery mobilisation should be carried out to ensure appropriate acceptance in SSA. Importantly, government-driven policies to promote cleaner production systems and reduce plastic waste and pollution will be necessary to promote the transition to a more sustainable bioeconomy. Knowledge transfer and capacity building between countries with developed technologies and the SSA region will also be essential to realize the potential of cassava waste biorefineries for PHA production. Ethical aspects and regulations are to be considered: cassava is an edible crop representing one of the major sources of calories in SSA but, the dietary driver remains constant in the face of climate change and urbanisation. Finally, there is a need to consider a holistic perspective on sustainability: going beyond environmental LCA to also consider the impact of cassava processing and biorefinery establishment on livelihoods, farming practices, projects, and community scale economics to establish the most appropriate development trajectories for appropriate demonstration and innovation programmes to stimulate the sector and its potential benefits.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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