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Review

Lignocellulosic feedstock: A review of a sustainable platform for cleaner production of nature's plastics

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ABSTRACT

The utilization of lignocellulosic feedstocks is the most promising, sustainable, and eco-friendly approach towards the production of polyhydroxyalkanoate since it entirely avoids the consumption of food crops. The use of these renewable and inexpensive feedstocks can make the production of polyhydroxyalkanoates affordable and facilitate the competitive commercialization of these carbon-neutral bio-based polyesters and their copolymers. Nevertheless, lignocellulosic biomass currently needs pretreatment to realize high sugar yields for the microbes to synthesize the polyhydroxyalkanoates. Steam pretreatment with dilute acids, followed by cellulase enzyme pretreatment, is a relatively practical approach to decompose these rigid biomasses into sugar monomers. However, the cost of commercial cellulase preparations continues to obstruct the large-scale economic conversion of lignocellulosic materials. Development of an eco-friendly consolidated bioprocessing system employing thermophiles for the single-step conversion of lignocellulose to polyhydroxyalkanoate, which excludes pretreatment and enzyme addition steps, and could be operative at low capital investment, would be an important breakthrough for the bioplastic industry. The scope of the present review is to highlight the significant and valuable research and development activities made in recent years to biosynthesize polyhydroxyalkanoates utilizing low-cost lignocellulosic biomass as the potential raw material. The future opportunity for the economical production of polyhydroxyalkanoate through unprocessed lignocellulosic biomass using thermophiles is also discussed.

Contents

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1. Introduction

Synthetic thermoplastic polymers, or plastics, have come to be a "ubiquitous workhorse" in the contemporary economy due to their unique versatility, durability, and low cost (World Economic Forum, 2016). While they have fueled a revolution in commercial and consumer convenience, current synthetic polymers and conventional recycling practices are neither sustainable nor environmentally friendly. The common petrochemical-based plastics, such as polyethylene, polyvinylchloride, polypropylene, polystyrene, polyester, nylon, acrylic, polyamide 6, and poly (ethylene terephthalate) are highly durable, yet imperishable. Their ever-increasing buildup on land and in the ocean has been a menace to the planet (Gallo et al., 2018; Varsha and Savitha, 2011). Without the rapid implementation of active preventive measures, the environmental impacts and economic cost of plastic waste will continue to multiply. Under the USDA's led "Bio-Preferred program," a presidential memorandum mandating federal governments and agencies to track and expand purchase with subsequent use of biobased products made from plants and other renewable agricultural materials (Rosato, 2014). Since then, under many new federal procurement programs, "bioplastics" have been designated as the preferred choice in areas such as adhesives and tapes, insulating foam, composite panels, biodegradable films, carpets, and others.

Polyhydroxyalkanoates (PHAs) and their copolymers such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (Keenan et al.), which are green bio-polyesters made naturally by certain microorganisms (Fig. 1), showcase a broad range of thermal and crystallization behavior, and an extensive array of mechanical properties (Kourmentza et al., 2017; Kumar et al., 2014; Raza et al., 2018). This versatility positions them as attractive biomaterials suitable for applications and, products which span consumer goods, automotive, healthcare, biomedical, packaging, electronics, textiles and 3D printing materials (Table 1).

During the 14th European Bioplastics Conference in 2019, an annual market data update predicted the global PHA production capacity is set to increase from about 2.1 million tons in 2019 to roughly 2.4 million tons in 2022, (Bioplastics market data, 2019). Although this current market potential appears limited relative to the total polymer market, the possibility to customize monomeric units/blocks in PHAs provides the longer-term potential to cover an even more comprehensive performance range than petroleum-based polymers. Nevertheless, no matter how versatile this polymer can be in terms of its applications, there are several reasons why PHA has not become a mainstream commercial product, including: (i) higher costs compared to petroleum-based commodity plastics where, for example, the price of poly(propylene) and poly(ethylene) is roughly USD0.6–0.9/pound and the price of poly(ethylene terephthalate) is about USD 0.5–1.0/pound, compared to a cost of PHA ranging between USD 2.25–2.75/pound (Kourmentza et al., 2017); ii) expensive PHA extraction methodology required to ensure high quality; iii) a limited and unreliable

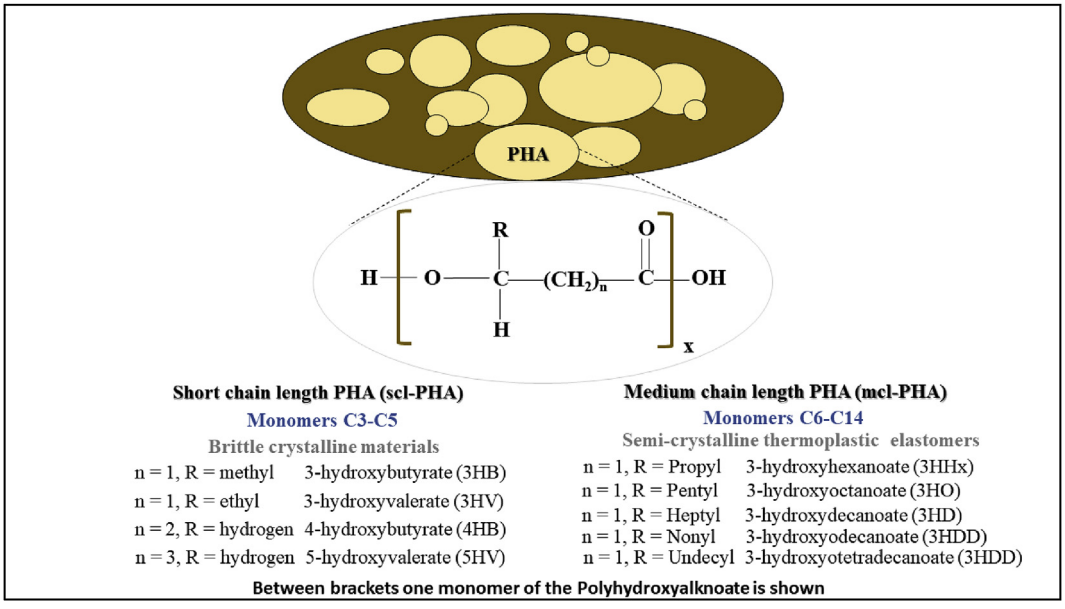

Fig. 1. General structure of polyhydroxyalkanoates (PHAs) and its co-polyesters.

Table 1
Industrial applications, market share and other characteristics of biodegradable polymers.

Industry	[a]Global production capacities in 2019 (% share)	Applications	Major Supplier	References
Automotive and transport	7	Interior components: fuel lines and foam seating	Biomer (Germany)	(bio!CAR, 2017; Sharif Hossain et al., 2016; Tseng, 2013)
Electrics and electronics	2	Phone covers, screens & camera components	Data not available	(Plastics supplier Supla Tainan, 2013; Ravenstijn, 2010)
Agriculture & Horticulture	5	Mulching films, plant pots, & plant clips film	Kaneka (Kaneka, Germany); BOR-M-501F (Bioplast, Russia)	(Organic Agriculture, 2015; Accinelli et al., 2016; Guilbert et al., 2005; Kasirajan and Ngouajio, 2012; Scott, 2005)
Packaging	58	Carrier Bags, Food packaging, foam, paper coating	MATER-BI and Origo-Bi (Novamont, Italy), Biopolynov (NaturePlast, France), Inego (Natureworks, USA); Nodax (Danimer Scientific, Georgia); Biocycle (PHB Industrial Brasil, SA); BOR-M-501F (Bioplast, Russia); Mitsubishi (Japan)	(Environmental Leader, March 2010; Beverage daily.com, September 2017; Biron, 2017) (Byun and Kim, 2014; Gonçalves de Moura et al., 2017; Jabeen et al., 2015; Peelman et al., 2013)
Textiles	11	Clothes, carpets, & furnishings, Non-woven fabric	Sorona (Dupont, Germany); Metabolix (Cambridge, MA)	(Bioplastics News, August 2017; Bio Plastics Info)
Consumer goods	7	Cosmetics (Disposable razors, Stabilizers, liner, & powders, injection molded caps for hair care products); Household items (disposable cups, knives and forks, Toys, writing instruments, nappy linings)	Biopol (by Imperial Chemical Industries/Zeneca-Monsanto (UK);	
Mirel (Metabolix/Yield10 Bioscience, USA)	(Bio-cosmetics, 2016), (Biron, 2017)			
Building and Construction	4	Composite materials	Not Available	Skerlos (2006)
Medical Industry	5	Medical (Surgical tools, bio-implants, blood vessel replacements & bone replacements); Drug delivery	Tephaflex (Tepha, USA); Chemie-Linz (Austria); Imperial Chemical Ind., UK)	(Nair and Laurencin, 2006; Ulery et al., 2011)
Bioremediation	1	Cleaning Oil Spills	Bio-on (Bologna, Italy).	Minerv Biorecovery, Bio-on (2017)

[a] Worldwide manufacturing Capacities of Biopolymers in 2017 (European Bioplastics, nova Institute, 2017) Total market capacity = 2.05 million tons dollars [33].

Table 2
SWOT analysis of PHA (bioplastics).

STRENGTHS	WEAKNESSES
Technical	***Technical***
• Indissoluble in water	• Affected by acids and bases including bleach, restricting its employment as 'plastic' packaging
• Impervious to hydrolytic degradation	• Materials can lose their durability and become more fragile with time, due to re-crystallization with exposure to ambient temperature
• Resilient to UV exposure	• Presently they show low elongation to break percentage, with high intrinsic levels of brittleness
• Good light barrier in visible region	• Opaqueness due to high crystallinity
• High modulus and strength	• Decompose thermally at temperatures right above their melting point (usually about 180°C), making them sensitive to the required processing temperatures
• Good barrier properties to water	• The synthesis is a time-consuming process compared to plastics obtained from conventional fuels such as oil
• Wide range of possible applications	• Geographic resource dependency - bioplastic production depends on availability of suitable raw material
Environmental	***Marketing***
• Biodegradable and readily compostable	• Costly, low-productivity process resulting in high price
• Wide end of life options	• Generally, exhibit poor impact resistance, compared to many fossil fuel-based plastics, limiting end-use applications
Marketing	
• Biocompatible	
OPPORTUNITIES	**THREATS**
Technical	• Small scale of production
• Ingenious formulations based on reactive plasticizers, latest biosynthesis strategies, and innovative blends can enhance PHA properties	• Indifference exhibited by public to counter higher product costs
• Potential for cost reduction through innovative production strategies and economies of scale	• Unique growth conditions (such as unbalanced nutrient conditions) make the current PHA biosynthesis setups expensive, relatively slow, and inefficient. This limits their scalability and productivity
• Academic/industrial partnerships for the development of engineered polymer properties	• Difficulties encountered in synthesizing from inexpensive agro-based feedstocks
• Technology advancement, and the potential range of polymer properties, provides opportunity for applications in multiple industrial sectors	• Bottlenecks in downstream purification and recovery process may not be resolved
Environmental	• Increasing competition in the bioplastics sector
• Substituting PHA products to replace the hard-to-recycle, non-biodegradable/non-bio-based commodity plastics	• Drop in oil price, making conventional plastics increasingly competitive
• Growing focus on the environment, including increasing public awareness	
Political	
• Positive attitude of government towards green procurement policies	
• More regulation favorable to bioplastics nationally and internationally	

supply chain, with PHAs only available in relatively small quantities from suppliers. On an industrial scale, all these factors have raised a significant concern with regard to the economic viability and marketability of PHAs. The cost of production is presently exorbitant for large-volume applications, mostly finding acceptance in higher-value medical uses. Therefore, to compete with fossil-derived plastics, we need to develop a high yield, cost-effective process to manufacture PHAs. Table 2 reflects the overall SWOT (Strengths, Weaknesses, Opportunities, Threats) analysis for PHA bioplastics.

Recent research focus has revealed that the exploitation of suitable waste biomass from agricultural and forest sources in the form of lignocellulose biomass (LCB) can account for around a 40–50% dip in the substrate cost, thus enabling production of high-performance PHA's at a competitive cost, besides providing LCB valorization (Everest et al., 2010; Kourmentza et al., 2017). However, LCBs are innately resistant to direct bioconversions on a commercially viable time scale, and therefore require expensive physical, chemical physiochemical, and/or enzymatic pretreatment regimes to reduce the recalcitrance of lignocellulose matrix, and decrystallize cellulose (Balan et al., 2009). At present, these pretreatments are technologically demanding and not commercially viable (Brodin et al., 2017). Preprocessing of lignocellulosic biomass, the first step, can in itself claim nearly 33% of the aggregate cost of value-added product production (Kang et al., 2014). Moreover, these pretreatment processes generate numerous LCB derived side-products such as acetic acid, furfural, hydroxymethylfurfural (HMF), and lignin derivatives which every so often constrain cellular growth, disturb the fermentation efficiency, and lower the net sugar yield resulting from hydrolysis (Kucharska et al., 2018).

Distinct strategies to solve or decrease the effect of these inhibitory compounds and increase the net yield of PHA have been investigated including (i) detoxification of the hydrolysates using physical, chemical, physicochemical and/or biological methods; (ii) screening and selection of microorganisms with high resistance to inhibitors; (iii) genetic and metabolic engineering and/or adaptive evolution of microorganisms to increase their resistance to inhibitors; (iv) using diluted hydrolysate solution (as in fed-batch fermentation). Nevertheless, these technologies represent a substantial additional cost, are laborious and time-consuming, and can require significant operating expertise. Integrated or consolidated bioprocessing offers an attractive alternative to reduce the cost of producing bioplastics. In principle, the process can consolidate all current processing steps (pretreatment, hydrolysis, enzymatic saccharification, and PHA production) into a single step, by using microorganisms that have the dual ability to both degrade LCB and accumulate PHA. Thus, consolidated bioprocessing (CBP) of LCBs to PHA in one step has the potential to greatly reduce the price of production of PHAs from the substrate side and improve conversion efficiencies. So far, there is no research evidence of the presence of a single microorganism that can perform synergistic bioconversion of unprocessed lignocellulosic biomass to PHAs. Nevertheless, finding a microbial strain that can act as a CBP host, and aid in one-step conversion of lignocellulose to PHA has the potential to bring down the costs more than 50% compared to other cellulases dedicated fermentation routes such as simultaneous saccharification and fermentation (SSF) or separate hydrolysis and fermentation (SHF) (Cao et al., 2014).

High-temperature bioprocessing employing thermophiles (which typically function at $\geq$60 °C) and their thermostable

enzymes are attractive candidates to breakdown lignocellulosic biomass (Bhalla et al., 2013; Blumer-Schuette et al., 2014; Mehta et al., 2016). The thermostable enzymes, in fact, offer distinct advantages as robust catalysts in these processes, that can survive the harsh bioprocessing conditions with high temperatures synergistically promoting better enzyme penetration and cell-wall disruption of the raw materials (Turner et al., 2007). Moreover, thermophiles are known to possess a rigid cellular membrane, which makes them resistant to toxic compounds that can be released during pretreatment (e.g., phenolics, aldehydes, and organic acids). These characteristics of thermophiles improve the overall performance of enzymatic hydrolysis and fermentation, besides offering less time needed to achieve maximum PHA accumulation owing to their faster growth rate compared to their mesophilic counterparts (Bhalla et al., 2013) (Kourmentza et al., 2017).

With this background in mind, we hypothesize that development of a thermophilic consolidated bioprocess for sustainable conversion of unprocessed lignocellulosic wastes (without any physico-chemical pretreatment) to bioplastics (polyhydroxyalkanoates, PHAs) at lower cost and with greater yield, can prove to be a breakthrough for the PHA industry. To verify this hypothesis, this review article is guided by the following research questions.

1. What are the ongoing activities in the field of producing PHAs with useful physicochemical properties from lignocellulosic biomass?
2. What are the current bottlenecks associated with the use of lignocellulosic materials that are impeding production of high quality PHAs from these materials at a competitive cost?
3. Can integrated or consolidated bioprocessing of lignocellulosic materials to PHA offer an attractive alternative to greatly reduce the cost of production of PHAs from the substrate side and improve conversion efficiencies?
4. How well does the use of thermophilic microorganisms that possess thermostable machinery for direct conversion of unprocessed (no-pretreatment) lignocellulosic materials to PHAs supplement the development of consolidated bioprocessing for conversion of lignocellulosic biomass to PHAs in one step?

2. Methodology for data collection, selection and review

This study tries to answer the stated research questions by using an integrative literature methodology where an eclectic range of relevant, high-quality papers were collected, filtered, and analyzed. We started our search for literature in the recognized publisher databases and websites such as Google Scholar, Scopus, Elsevier, Science Direct, Wiley Interscience, and Springer link, in November 2017. Firstly, specific keywords: polyhydroxyalkanoates, lignocellulosic biomasses, thermophiles, pretreatment, and copolymers were used in order to collect the publications appropriate to the objective of this paper; and subsequently the references and bibliographies in these papers were used to garner additional pertinent articles. The abstract, introduction, and conclusion of each article were examined, and a manageable set of relevant studies were selected, based on the following considerations.

(a) Primarily include peer-reviewed published studies and refer to non-peer-reviewed publications (e.g., commercial websites) with suitable caution.
(b) Include articles from active/well-known researchers in the field, while considering publications from a wide range of authors and not limiting sources to well-cited or popular papers.
(c) Strike a balance between older, established research and new material that has accumulated in recent years.
(d) Check the commercial websites to find out more about claimed cutting-edge technology in the related field, and then follow these leads to determine the validity of the information in peer reviewed and/or patent literature.
(e) Consult previous review articles on PHAs to help ensure identification of all relevant literature.
(f) Check original sources by retrieving significant papers cited in more recent research studies.

Reviewing the existing research led to further questioning, which sometimes persuaded us to revise our initial research questions and renew the literature search accordingly. To facilitate this process, we kept careful notes to track of our thought processes while reviewing the literature. In particular, we have kept the review centered on PHA production from cellulose, hemicellulose, and lignin fractions obtained from lignocellulosic biomasses, excluding studies that dealt with the biosynthesis of bioplastics other than PHA from the lignocellulosic feedstocks. Our purpose is to outline routes for PHA production that may have the capacity to use carbon sources from agricultural waste, which does not compete with food resources, and to consider the challenges faced in current bioconversion, with an emphasis on strategies that seem promising for thermophilic bioprocessing. In all, 250 articles were studied, and work from 170 papers have been included in this review article.

3. Feedstocks for PHAs

So far, PHA production has depended on the use of first-generation sugar-based cultivated feedstocks, like food crops, whey, molasses, sugar cane, corn sugar, palm, and vegetable oils (Jiang et al., 2016). These feedstocks can readily be hydrolyzed into their monomeric sugars, such as glucose, for PHA production (Choi and Lee, 1997). Nevertheless, the utilization of these feedstocks currently relies upon massive amounts of land, water, chemicals, and energy for growth, harvesting, transport, and processing. Also, the usage of these edible feedstocks in polymer industries reduces their availability in the food supply chain and raises food prices. Bulk scale production of PHAs using edible items can thus create food scarcity (Jiang et al., 2016), besides augmenting the total price of PHAs. In 2017, PHAs had an average industry price of 2.50 USD per lb. (around 5 USD per kg) (Green Chemicals Blog, 2012; Kourmentza et al., 2017), three times higher than the current price for polypropylene (PP) and polyethylene (PE) (around 0.60–0.87 USD per lb.). Additionally, the production of PHA by conventional means using these expensive refined substrates in bio-refineries requires sterilization, which further impedes their widespread commercialization (Song et al., 2009).

To decrease costs and reduce organic waste entering landfills, PHA can be made from organic waste streams. These low-value waste materials include (i) sugar-rich derivatives (sugar-producing plants saps/juices and sugar-rich byproducts from sugar manufacturing industries); (ii) triacylglycerols and fatty acids abundant feedstocks (edible, non-edible waste oils, crude glycerol, and industrial wastewaters); (iii) C1 carbon sources (e.g., methane and carbon dioxide), and (iv) cellulosic raw materials (lignocellulosic biomass hydrolysates, corn steep liquor, brans, and straws) (Fig. 2).

Out of these waste feedstocks, second-generation lignocellulosic plant biomass (LCB) such as corn stover, dedicated energy crops, rice straws, wood chips, etc. are the widely available renewable

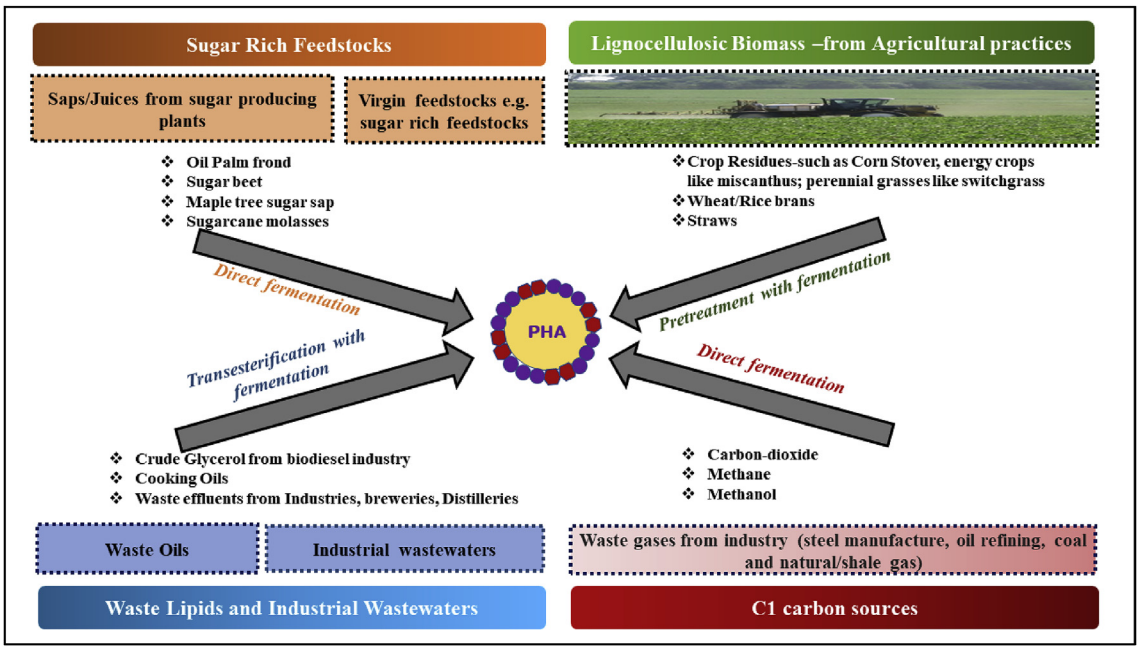

Fig. 2. Waste feedstocks for PHA production.

bioresources that have a steady and abundant supply amounting to a global yield of about 150 billion tons per year (David et al., 2018). In the US alone, about one billion dry tons of second-generation lignocellulosic biomasses are available per year (Agbor et al., 2014), predicted to increase to 1.6 billion tons by 2030 (Poli et al., 2016).

Generated from accessible atmospheric carbon dioxide (CO_2), water, and sunlight through biological photosynthesis (Isikgor and Becer, 2015), lignocellulosic biomass has gained a reputation of being a non-competitive and a sustainable resource of organic carbon on Earth, which can be produced swiftly and at a minimal cost. Also, they are the non-edible portion of the plant, and therefore they do not adversely affect food supplies. Hence, with enormous availability, lignocellulosic feedstocks provide critical advantages over many biomass materials to sustain current and future production of biofuels, biomolecules, and biomaterials, while boosting rural economies and assisting in the transition to a bio-based economy.

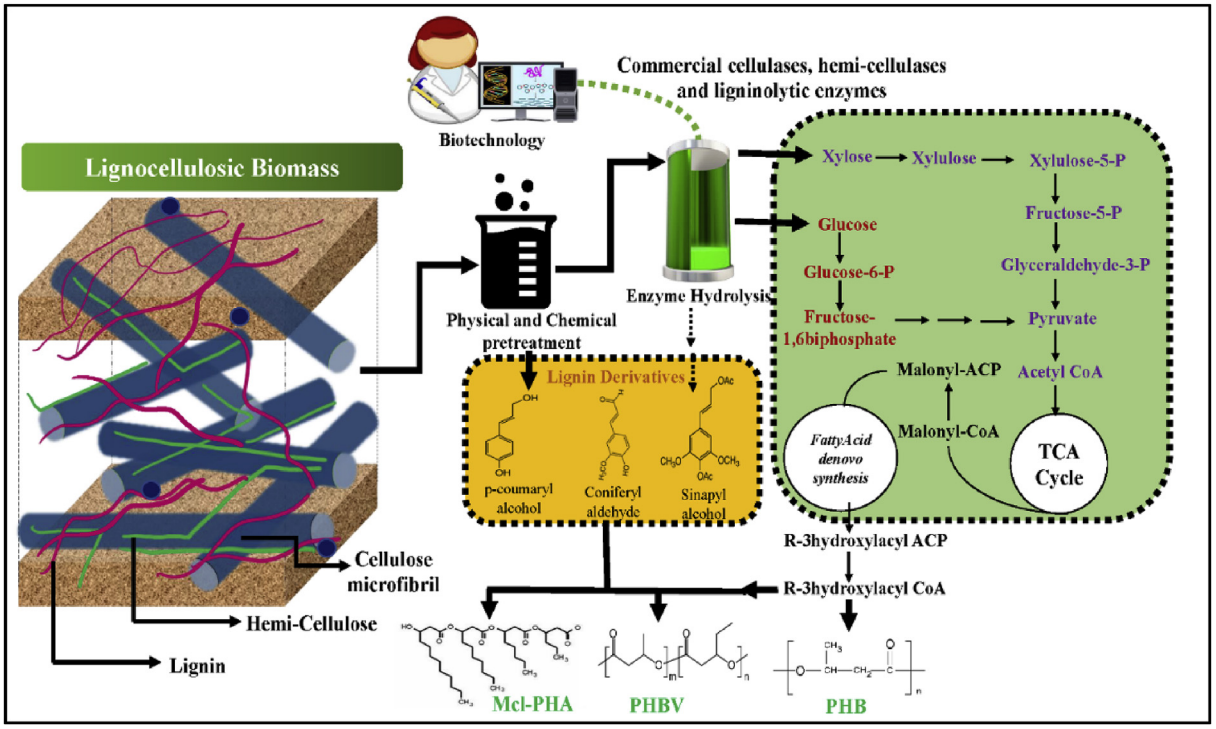

Fig. 3. LCBs as potential sources to produce PHA monomers and copolymers.

Lately, synthesizing PHAs by fermenting hydrolysates of the mixtures of cellulose and hemicellulose, rich in glucose, xylose, arabinose, mannose, galactose, and rhamnose has caught much research interest. As far back as 1995, it was estimated that it would cost about USD630 for LCB hydrolysates to produce a ton of poly-hydroxybutyrate (PHB), which was comparable to the cost of PHB obtained using molasses (USD 576), but 3–4 times less than the use of pure refined sugars: glucose (USD1705), fructose (USD2605) and sucrose (USD2405) (Ramsay et al., 1995). Based on the reliability of these relative conversion estimates, and the consequent notion that LCBs would be an economical feedstock from which to generate PHAs, the following sections review case studies related to microbial conversion of lignocellulosic biomass hydrolysates to poly(3-hydroxybutyrate) homopolymer and/or copolymers.

4. Bioconversion of lignocellulosic biomass fractions to PHA: Case studies

Lignocellulose is composed of cellulose (40–50%), hemicellulose (20–50%), lignin (20–30%), extractives, and several other phenolic compounds (Anwar et al., 2014). Of the three chief components, lignin is most intractable to degradation, making LCB remarkably impervious against hydrolysis and enzymatic attack. Cellulose retains a considerable degree of crystallinity, and it forms a rigid framework that acts as a load-bearing structure of the cell wall. (Ramsay et al., 1995). Hemicellulose, a heteropolymer of xylose, arabinose, galactose, and other sugars, is not crystalline and thus is more prone to hydrolysis than cellulose (Yu, 2007). A pretreatment process is required to remove lignin (at least partially), decrystallize cellulose, partially depolymerize hemicellulose and increase the porosity and accessibility for hydrolysis of the lignocellulosic materials (Balan et al., 2009). Subsequently, both components (cellulose and hemicellulose) can be hydrolyzed to monomeric sugars, making LCBs a potential source for the biosynthesis of PHAs. Meanwhile, using the concept of integrated biorefinery, biomass fractionation can generate lignin-rich streams, which can also be converted by parallel processes into other PHA copolymers (see section 4.4) or for some cases can also be utilized as fillers into the PHA matrix leading to enhanced functionality and processability of the resultant bio-polyester (see section 4.5). The general scheme presenting the PHA production process from lignocellulose components is shown in Fig. 3.

4.1. Poly-hydroxybutyrate (PHB) homopolymers from cellulose-rich lignocellulose

Ideally, for any microbial strain to grow on lignocellulose, the particular strain must possess the enzymatic machinery to hydrolyze lignocellulosic polysaccharide components, i.e., cellulose, hemicellulose and, lignin into their simple monomeric forms. Until today, not many microorganisms have been confirmed to produce PHB in a single step from lignocellulose directly. For example, *Saccharophagus degradans* ATCC 43961, has been reported to directly utilize tequila bagasse as a carbon source (with no pretreatment) for PHB production (Alva Munoz and Riley, 2008). Gao et al. showed PHB production in a single step by a cellulolytic recombinant *Escherichia coli*, but the obtained concentration of PHB (0.05 g/L) was low (Gao et al., 2015).

Subsequently, it is the hydrolysates from numerous agro-industrial lignocellulosic wastes rich in pentoses and hexoses - e.g., sugarcane molasses (Lopes et al., 2014), wheat hydrolysate (Van-Thuoc et al., 2008), rice bran (Huang et al., 2006), tequila bagasse (Alva Munoz and Riley, 2008), liquified wood (Koller et al., 2015), maple wood (Pan et al., 2012b), wheat straw (Cesario et al., 2014a, 2014b), etc.- that have been used for PHB production. Table 3 compares the productivities and accumulation of PHB homopolymers obtained under various studies using different kinds of lignocellulosic hydrolysates as the feedstock.

Generally, the conversion of LCBs into any final product can have varying efficiencies based on the grade and type of the lignocellulosic biomass, bacteria, fermentative conditions, and preprocessing skill used. However, it is the preprocessing/fractionation treatment methodology applied towards the hydrolysis of LCB which significantly affects the conversion efficiency. As evident from Table 3, different fractionation techniques for hydrolyzing lignocellulose have been used, including chemical (alkaline, acid), physicochemical (steam explosion, autoclaving, steam-exploded trembling aspen, Ammonium Fiber Expansion), enzymatic (commercial or in-house enzymes), or their combinations. The success of the fractionation methodology used usually depends on the characteristics of the plant biomass used, which can have a distinct chemical composition and structural characteristics (Brodin et al., 2017). However, it is with dilute acid pretreatment combined with enzymatic hydrolysis that higher productivity of PHB has been obtained compared to prior LCB hydrolysis processes using concentrated sulfuric acid and/or harsher physicochemical methods (Table 3). The justification behind this observation lies in the concentration of inhibitory compounds that are released during the degradation of the agricultural biomass. In addition to mono- and oligosaccharides, three crucial groups of compounds are also released during the pretreatment. These are emitted volatiles such as organic acids (acetic acid, formic acid, levulinic acid), furaldehyde (5-hydroxymethylfurfural and furfural), and aromatic or phenolic compounds (4-hydroxybenzoic acid and 1,2-dihydroxybenzene (catechol)) (Kucharska et al., 2018). At low to moderate concentrations, almost all of these compounds can reduce microbial fermentations. However, it is the aromatic hydrolysates, in particular, that can even inhibit microbial activities at concentrations as low as 1 mg/ml (Jönsson et al., 1998; Yu and Stahl, 2008). Furthermore, phenolics retrieved from the pretreated biomass are also known to influence enzyme performance adversely. Kim et al. (2011) had registered a 50% decline in the percentage and magnitude of cellulose hydrolysis due to both inhibition and precipitation of the enzymes by the phenolics (Kim et al., 2011). Similar results were observed in 2016 by Michelin et al. who observed reduced cellulases and hemicellulases activity due to β-glucosidase or β-xylosidase enzymes degradation, by the phenolics extracted during pretreatment of sugarcane bagasse (Kim, 2018; Michelin et al., 2016). The harsher is the pretreatment condition, the more is the inhibitory compounds during LCB hydrolysis released in the medium, which significantly reduces microbial growth and hence PHB production. Evidently, low PHB production levels (0.39 g/L) were reported by Bowers et al. (2014), who used radiata wood chips hydrolysates derived using steam explosion in the presence of sulfur dioxide, which generated (Bowers et al., 2014) high amount of fermentation inhibitors (furfural, hydroxymethylfurfural, and other free phenolics). Similarly, with alkaline (1% NaOH) pretreatment on wheat bran, Annamalai & Sivakumar, (2016) obtained low PHB accumulation and yield of 62.5%, and 0.319 g/g, respectively (Annamalai & Sivakumar, 2016).

On the other hand, in a very similar study, but with enzymatically hydrolyzed wheat bran and cassava bagasse hydrolysates, Ramadas et al. (2009) stated production of 1.06 g/L of PHB (Ramadas et al., 2009). Similarly, with acid saccharified water hyacinth hydrolysates and supplementary enzymatic treatment using cellulase enzyme (extracted from *Aspergillus niger*), a PHB concentration reaching 4.3 ± 0.4 g/L has been reported (Radhika and Murugesan, 2012). This PHB concentration derived from the water hyacinth hydrolysates agrees with the work of Gowda & Shivakumar (2014), who studied a combination of acid and

Table 3
Summary of PHB production from hydrolysates or sugars obtained from various lignocellulosic biomass.

Feedstock	Pre-treatment	Enzymatic Hydrolysis	Micro-organism	Reactor type	Production rates (g/L/h)	PHB concentration (g/L)	% PHB accumulation (w/w)	Reference
Wheat bran hydrolysate	Alkaline (1%NaOH)	Commercial cellulase of Trichoderma reesei and β - glucosidase of *Aspergillus niger*	*Ralstonia eutropha* NCIMB 11599	Batch	0. 0.255	0.319	62.5	Annamalai & Sivakumar (2016)
Wheat bran hydrolysate	NA	Crude enzyme preparation from *Aspergillus oryzae NM1*	*Halomonas boliviensis* LC1	Batch	NA	1.08	33.8	Van-Thuoc et al. (2008)
Water hyacinth hydrolysates	Acid	Cellulase from *Aspergillus niger*	*C. necator, Ralstonia eutropha*	Batch	0.130	4.3	58.3	Radhika & Murugesan (2012)
Bagasse hydrolysate	Acid	*Innate enzymes*	*Bacillus thuringiensis*	Batch	NA	4.2	39.6	Gowda & Shivakumar (2014)
Sugarcane Bagasse hydrolysates	Dilute Acid	Commercial enzymes	*Ralstonia eutropha*	Batch	NA	6.3	57	Yu & Stahl (2008)
Oil palm empty fruit hydrolysates	NA	In-house prepared cellulase cocktail.	*Bacillus megaterium* R11	Batch	0.260	12.48	51.6	Zhang et al. (2013)
Rice straw hydrolysate	2% H_2SO_4	NA	*Bacillus firmus*	Batch	NA	1.7	89	Raveendran et al. (2013)
Wheat bran, potato starch hydrolysates	NA	Commercial enzymes	*Bacillus sphaericus* NCIM 5149	Batch	NA	1.06	6.8	Ramadas et al. (2009)
Detoxified Maple wood hydrolysate	Acid	NA	*Burkholderia cepacia. B. cepacia* ATCC 17759	Batch	0.04	NA	51.40	(Pan et al. (2012a,b))
Detoxified Wheat straw hydrolysate	AFEX (Ammonium Fiber Expansion)	NA	*B. sacchari* DSM17165	Batch	NA	0.19	60	Cesario et al. (2014b)
Detoxified Wheat straw hydrolysate	AFEX (Ammonium Fiber Expansion)	NA	*B. sacchari* DSM17165	Semi-Batch	1.6	105	72	Cesario et al. (2014a)
Sugar cane bagasse hydrolysates	0.5–4% of H_2SO_4	NA	*Burkholderia* sp. F24	Batch	0.12	NA	48.56	Lopes et al. (2014)
Sugar cane bagasse hydrolysates	1% of H_2SO_4	NA	*Burkholderia* sp. F24	Fed Batch, 5L	0.28	NA	49.31	Lopes et al. (2014)
Detoxified Sugarcane bagasse hydrolysates	Acid	NA	*Burkholderia cepacia* IPT 048	a 10-l bench scale bioreactor	0.29	2.3	53	Silva et al. (2004)
Detoxified Sugarcane bagasse hydrolysates	Acid	NA	*B. sacchari* IPT 101	a 10-l bench scale bioreactor	0.39	2.7	62	Silva et al. (2004)
Pinus radiata wood	Steam explosion	Celluclast and Novozyme	*Novosphingobium nitrogenifigens and Sphingobium scionense*	Batch	0.08	0.39	32	Bowers et al. (2014)
Hemicellulosic fraction of poplar wood	NA	NA	*Pseudomonas pseudoflava*	Batch	0.02	0.17–0.19	17–22	Bertrand et al. (1990)
Xylose; xylose with propionic acid	Steam-exploded trembling aspen	NA	*Pseudomonas cepacia*	Batch	0.072	0.11	45	(Ramsay et al., 1995; Young et al., 1994)
Coir pitch hydrolysates	Delignified by autoclaving	Commercial enzymes used	*Azotobacter beijerinickii*	Batch	0.05	2.4	48	Sathesh Prabu & Murugesan (2010)
Sunflower hydrolysate	Hydrothermal treatment	Cellic CTec3	Recombinant *Ralstonia eutropha* NCIMB11599	Batch	NA	7.86	72.53	Kim et al. (2016)

PHB = Polyhydroxybutyrate; NA = Not Available.

enzymatic hydrolysis on bagasse as a carbon feedstock for the production of PHB (4.2 g/L) using *Bacillus thuringiensis* IAM 12077 (Gowda & Shivakumar, 2014). Also, the synthesis of PHB accumulating up to 57 wt.% of the cell mass (6.3 g/L PHB) has been reported using dilute acid-treated sugar cane molasses hydrolysate (Yu and Stahl, 2008).

Prevalently, acid pretreatment, which can strongly breach lignin, solubilize hemicellulose, hence making crystalline cellulose more accessible to breakdown, and consequently yielding higher concentrations of monomeric sugars, has received much attention from researchers (Verardi et al., 2012). Nonetheless, enzymatic hydrolysis is preferred to acid hydrolysis as it is environmentally innocuous, prolongs mild operational conditions (hence lower release of inhibitors), with no need for corrosion resilient processing equipment, and most of all, offering a prospective for almost complete hydrolysis of cellulose content in the biomass with evidently higher PHA yields (Hui et al., 2013). Unfortunately, however, the inflated cost associated with the use of the enzymes, combined with their slow rate of reactions, presently obstructs their use in the large volume industrial applications (Nduko et al., 2012). In support, while some studies have established that the cellulase enzyme cost was only varied from $0.1 to $0.4/gal of total metabolite production cost, supporting that the current bioconversions technology relying on cellulolytic enzymes are economically sound (Aden and Foust, 2009). Others point out that the cellulase enzyme still costs between $0.69 to $1.47/gal of the final product, revealing that the high enzyme costs negatively drive the feasibility of commercial cellulose conversion to value-added products, when the enzyme is procured from the existing industrial vendors (Liu et al., 2016). Facilitated by the US Department of Energy (DOE), the cost-shared subcontracts to industrial enzyme producers have resulted in substantial progress towards lowering the cost of enzymes for saccharification of lignocellulosic biomass, by a factor of up to 20 since 1999 (Stickel et al., 2014). Still, the present enzyme loadings per gram of cellulose remain high compared to that required for per gram of starch hydrolysis, leading to net utility cost of enzymes to depolymerize lignocellulosic biomass unproductively elevated.

Henceforward, a study by Matsumoto et al. in 2011, explored the use of ruthenium (Ru) solid metal catalyst under aqueous solution as an alternative catalyst for cellulose hydrolysis. They reported an accumulation of 42% PHA in a recombinant *E. coli* grown on Ru-catalyzed cellulosic hydrolysates, which was the same as that obtained using a comparable concentration of analytical grade glucose (Matsumoto et al., 2011). However, even here, the hydrolysates were found to contain 5- hydroxymethylfurfural, which was the principal contributor to the toxicity of the hydrolysate and inhibited cell growth. Later, in 2014, a study performed with orange peels as the substrate used hot water pretreatment of 70 °C for 2 h, and with no detoxification, a recombinant strain of *Bacillus subtilis* yielded 1.24 g/L PHB with 41% accumulation/g of dry cell weight in a batch reactor. Although the obtained PHB production is still low, the mild hydrolysis would make this a promising process if the PHB concentration can be increased (Sukan et al., 2014). A review by Brodin et al. (2017) lists recent advances that have been made with regard to fractionation of lignocelluloses, including supercritical fluids and ionic liquids that have been projected as attractive substitutes, due to the rapid reaction rate and the usage of green solvents (Brodin et al., 2017).

Selecting less recalcitrant feedstocks with concurrent mild pretreatment conditions, unquestionably represent a promising approach to reduce the release of toxic inhibitors during LCB utilization. However, because it is lucrative to utilize several varieties of lignocellulose for the biosynthesis of PHAs if they are to make a significant, cost-competitive impact on the market (Jönsson et al., 2013), quite a few unconventional strategies can be additionally be considered to skirt the problems caused by inhibitors in the microbial production of PHA's. Hence, in the next part of the review, a general overview and discussion are provided on strategies and directions for overcoming the effects of toxic inhibitors and their effects on PHA production, including (a) detoxification of hydrolysates, (b) use of a tolerant bacterium (c) use of a diluted hydrolysate solution (as in fed-batch fermentation), (d) use of a large inoculum, and (e) a combination of these approaches.

4.1.1. Use of detoxified LCB hydrolysates

To mitigate the problems of low PHB accumulations in the above studies, detoxification methods like activated charcoal, membrane filtration, ion-exchange chromatography, over-liming, and/or enzymatic detoxification using laccase, which remove or eliminate microbial inhibitors from the hydrolysate (Nieves et al., 2015), have been tested prior to microbial fermentation by various researchers. Pan et al. (2012a,b) combined over-liming with low-temperature sterilization to remove 65% of total inhibitory phenolics present in the maple wood hydrolysate obtained by dilute acid treatment. Using the obtained detoxified maple wood hydrolysate as substrates, a higher PHB production of 8.72 g/L broth and 51.4% of dry cell weight was achieved after 96 h of fermentation in batch culture (Pan et al., 2012a). More compelling has been the use of activated carbon as an adsorbent, which is claimed to be efficient enough to remove more than 90% of polyphenols from the hydrolysates, allowing PHB content to reach nearly 90% of cell dry weight (Kucera et al., 2017). Ammonium Fiber Expansion technology (AFEX), which can selectively limit the formation of degradation products, is another strategy that had been exploited to prepare wheat straw hydrolysates. Using *Burkholderia sacchari* for the fermentation of AFEX treated hydrolysates in shake flasks containing mainly glucose, xylose and arabinose, an accumulation of 60% PHB was reported under batch conditions (Cesario et al., 2014a, 2014b), which increased to 72% PHB accumulation under semi-batch conditions, corresponding to a concentration of 105 g/L PHB.

Evidently, detoxification procedures can reduce the level of furfural toxicity, but parallelly, they intensify the complexity of the method and add detoxification time and operational cost, diminishing the economic viability of LCB for PHA production (Nieves et al., 2015). In cases where activated carbon has been employed as a sorbent for detoxification of the hydrolysates, the recovery of activated charcoal post-application poses an additional challenge, with its recovery being practically impossible. As an alternative sorbent, the innovative application of lignite to detoxify wood hydrolysates is promising. Lignite's detoxification capacity is comparable to that of activated carbon, but at a lower cost, enabling a cost-efficient detoxification methodology. The experimental results have demonstrated that the usage of lignite as a sorbent noticeably enhanced the capability of utilizing wood hydrolysates and improved final yields of PHA (2.1 g/L compared to 0.9 g/L using activated charcoal) (Kucera et al., 2017). In the future, finding such cheaper absorbents, or methods that can replace the high-priced activated carbon is highly anticipated. In any case, due to the concerns of the viability, rationality, and affordability of physicochemical pretreatments, the utilization of microbial methods to detoxify lignocellulose hydrolysates is attractive, and a cleaner approach, with relatively few side-reactions and low energy requirements. To economize ethanol production attempts with the application of wild and/or recombinant microorganisms expressing ligninolytic enzymes for detoxifying the lignocellulose hydrolysates, have already been made with much success (Chandel et al., 2011). Hence, future experiments focused on eliminating inhibitors using microorganisms and/or their enzymes requires due exploration in the production of PHAs.

4.1.2. Use of tolerant microbial strains

Genetically recombinant 5-hydroxymethylfurfural resistant strains have been employed as another approach for overcoming hydrolysate toxicity for improved PHA production. In an engineered hydroxymethylfurfural resistant *E. coli* LS5218 (reported to be capable of degrading furans including furfural alcohols), grown on cellulose hydrolysate catalyzed by ruthenium, dry biomass weight touched 5.6 g/L with a PHB content of 59%, with the results comparable to yields achieved during the use of analytical grade glucose (Nduko et al., 2012). Moreover, the productivity was higher than that reported in their previous work, where a PHB accumulation of 42% was achieved in a non-resistant recombinant *E. coli* grown on glucose-rich Ru-catalyzed cellulosic hydrolysates (Matsumoto et al., 2011). In another study, an adapted tolerant strain of *Ralstonia eutropha* was engineered, which enabled it to grow on diluted bagasse hydrolysates and efficaciously decrease acetic acid, formic acid, furfural, and acid-soluble lignin while producing PHBs (57% of dry cell weight) (Yu and Stahl, 2008).

Supposedly, a highly tolerant inoculum of the microbes, developed through adaptive laboratory evolution (ALE) on hydrolysates, may formerly have a superior expression of the responsible enzymes, which can make them biodegrade the inhibitors (Yu and Stahl, 2008). Hence, information and understanding of how a strain metabolically responds to inhibitors present in lignocellulosic biomass hydrolysates, as done recently for the study of tolerance and metabolic response of Pseudomonas taiwanensis VLB120 (Wordofa and Kristensen, 2018), can be valuable to designing intelligent metabolic strategies for the development of robust hyper-tolerant fermentative PHA strains.

4.1.3. Use of fed-batch fermentation

Limiting conditions of essential nutrients, with the abundance of carbon in the growth environment, kindles the intracellular accumulation of PHB as energy reserves (Kourmentza et al., 2017). Fed-batch feeding processes allows maintenance of such specific nutritional conditions between a maximum and a minimum of preestablished concentration thresholds, alongside high cell densities. And specifically, in experiments where the processing of lignocellulosic is involved, the use of fed-batch mode can aid in diluting the levels of inhibitory substances, compared to when the organism is grown in batch cultures. Hence, inhibition in microbial growth and polymer production observed in batch modes of fermentation in the presence of dehydrated products of the sugars and acid components in lignocellulose hydrolysates can be avoided in fed-batch cultivations (Jiang et al., 2016). To date, fed-batch fermentation with particular feeding schemes has been endeavored in many studies, yielding high intracellular PHB productivities (Kim et al., 1994; Kulpreecha et al., 2009; Schmidt et al., 2016). As an example, a PHB concentration of 12.3 g/L (with 0.49 g of PHB g/g of cell biomass) mass fraction, have been reported by Lopes et al. with a fed-batch bioreactor run with sugarcane bagasse hydrolysate (Lopes et al., 2014). Huang et al. (2006) obtained superfluous cell concentration of 140 g/L, compared to other studies, with 77.8 g/L PHB in a repeated fed-batch fermentation, when extruded rice bran and extruded cornstarch were used as carbon sources. Thus, semi-batch or fed-batch production modes are one of the most cost-effective means to achieve enriched PHA productivity, provided contamination can be sidestepped, and the genetic stability of the strain is secured (Huang et al., 2006).

4.1.4. Use of large inocula

The use of the large size of initial inoculum can decrease the time needed for adaption and growth of each bacterial cell and consequently can minimize the inhibition problems. In a classic work by Yu and Stahl in 2008, they had reported that the cell growth of *R. eutropha* was prohibited in the solution of dilute acid pretreated bagasse when an inoculum of less than 1.2 g/L was put to use. Apparently, the highest PHB mass fraction in biomass of 40.2% by weight was obtained in batch mode operated shake flasks with *Ralstonia eutropha* by commencing with a higher level of starting inocula concentration of 6 g/L (Yu and Stahl, 2008). Hence, the use of concentrated or a high percentage of initial inoculum can somehow be considered as yet another strategy enabling achievement of reasonably increased PHB accumulations if perhaps recycling and reusing the cells can be done at a justifiable cost. In modern industrial or lab settings, however, this is a tedious task, particularly if used in a fermentation broth that contains many solids (Jönsson et al., 2013), unless the microorganism can be recirculated.

4.2. PHA from hemicellulose rich lignocellulosic biomass

Forty to forty five percent of lignocellulosic biomass consists of hemicellulose. Consequently, in the pursuit of supreme yield and productivity of PHB during the consumption of lignocellulosics as carbon source, comprehensive consumption of diverse sugars derived from hemicellulose is indispensable (Kim et al., 2010). Additionally, the gentler conditions demanded for the hydrolysis of hemicelluloses to monomeric pentose sugars, make them an alluring candidate as a PHA feedstock (Dietrich et al., 2019). Nevertheless, only a few microbial strains with the capability to assimilate pentose sugars like xylose released from hemicelluloses and accumulate PHAs have been documented in the literature. The potential of a microbial strain (*Pseudomonas pseudoflava,* here*)* to assimilate pentoses as PHAs was first reported by Bertrand et al. (1990). *Pseudomonas pseudoflava* also successfully grew on and utilized hemicellulose rich poplar wood hydrolysate (at concentrations lower than 30% (v/v)) as a carbon and energy reserve for its growth (Bertrand et al., 1990). Since then, the capabilities of many other microbial strains to metabolize pentoses and produce PHAs have been reported, including the capabilities of *Novosphingobium nitrogenifigens* and *Sphingobium scionense* who accumulated PHB content in biomass of 32% corresponding to 0.39 g/L with pentose rich radiata wood chips hydrolysates (Bowers et al., 2014). Recently, researchers have been chalking out the xylose utilization pathways in microorganisms for the better utilization of xylose as a carbon source. Based on this concept, in 2016, *Ralstonia eutropha* NCIMB11599, was engineered to uptake and assimilate xylose, by the insertion of *xylAB* genes of the xylose utilization pathway of *E. coli* for the production of P(3HB) from sunflower hydrolysate solution in NCIMB11599. Interestingly, 7.86 g/L of P(3HB) with 72.53 wt.% content were obtained by this recombinant strain (Kim et al., 2016). This is, by far, the highest accumulation percentage registered in the literature with xylose as the carbon source. The findings are optimistic in terms of better economics for the production of PHAs using various agricultural and forestry wastes. Nevertheless, the utilization by a bacterium of mixed sugars (hexoses and pentoses) in lignocellulose hydrolysates can be convoluted by a universal regulatory mechanism called carbon catabolite repression (CCR) (Obruca et al., 2015). Because of this phenomenon, in the presence of mixed sugars derived from the lignocellulose, consumption of one of the sugars (usually glucose or other hexoses) is preferred sequentially over other sugars (usually pentoses), reducing the efficacy of the conversion. To economize the bioconversion of lignocellulosic, adapting, or engineering of CCR negative microorganisms for simultaneous consumption of mixed sugars represents a viable and cost-effective approach.

In Gram-negative bacteria, the concomitant transportation of sugars is facilitated by the phosphotransferase system (PTS). In 2014, a team of researchers, reversed the CCR phenomenon in

Burkholderia sacchari, by mutating it to internalize hexoses and pentoses by a non-PTS uptake system. This UV mutant consumed sugars, primarily glucose and xylose, simultaneously, although with not much difference in PHB accumulation compared to its wild type (Lopes et al., 2014). In yet another recombinant *E. coli,* harboring the PHB synthesis genes of *Ralstonia eutropha,* the CCR phenomenon was negated by knocking down a *ptsG* gene, leading it to accumulate PHB at 11.5% of dry cell weight (total of 2.3 g/L) in xylose and glucose experiments. For the wild type *E. coli*, the PHB production was 7.1% of the cell dry weight (2.1 g/L) (Sumner et al., 2007). Thus, a simple modification in the bacterial metabolism, allowing them to simultaneous consume hexose and pentose sugars, can contribute to the designing of clean processes with an effective avenue for PHA productivity derived out of lignocellulosic. However, in all, the PHA concentrations and productivities obtained via xylose fermentations are low (1.65 g/L) compared to when hexoses are the predominant fermenting sugars (105 g/L) (Cesario et al., 2014a, 2014b). If the efficacy factors linked to the conversion of hemicellulose hydrolysates to PHA can arrive at the same production effectiveness as glucose-rich hydrolysates, the versatility factor for designing integrated processes (that can incorporate several product streams from fractionated biomass), can be vastly expanded. This improvement in niche microbial fermentation can help to make the production cost of PHA bioplastics compete with commodity, petroleum-based plastics. Moreover, this economic advantage is heightened by the fact that the utilization of mixed sugars present in LCB hydrolysates enables microbes to directly produce PHA block copolymers, which have a broader range of useful physical and mechanical properties.

4.3. PHA copolymers from lignocellulosic hydrolysates

PHA comprise a large class of polyester that has been classified according to the total number of carbon atoms they have: short-chain-length (SCL) PHA contain 3-5 carbon atoms, and medium-chain-length (MCL) PHA has six or more carbon atoms. MCL-PHA normally exist as copolymers which comprise 3HB linked with 4-hydroxybutyrate (4HB), 3-hydroxyvalerate (3HV), 4-hydroxyvalerate (4HV), hydroxypropionate (HP), hydroxyhexanoate (HHx), hydroxyoctanoate (HO) units, and/or their combinations, as major and minor constituents (Fig. 1). While PHB, a homopolymer comprising 3-hydroxybutyrate (3HB) subunits, is the most prevalent and commercially produced polyhydroxylanoate, PHA copolymers are in demand in the polymers market as they can be engineered to accommodate assorted functional groups in the side chains, resulting in their versatile thermal and mechanical properties that can be tuned to meet the performance requirements of a comprehensive array of applications.

Notably, SCL-PHB is stiff and brittle, while PHA copolymers can exhibit elastomeric properties (Rigouin et al., 2019). Tagging of longer than four hydroxyalkanoate monomers with 3HB within the copolymer's framework can reduce the fragility of the resultant copolymer with enhanced elastomeric properties. Hence they are in demand in packaging or biomedical applications where flexible, bio-competent, and decomposable materials are required (Ten et al., 2015).

Conventionally, co-addition in the medium of expensive carbon substrates, to name, odd-fatty acids (propionic acid, valeric acid, and/or enanthic acid), has been a widely exploited practice, for synthesizing PHA copolymers (Bertrand et al., 1990; Choi and Lee, 1999; Koller et al., 2015; Le Meur et al., 2012). Nevertheless, this supplementation of excess acids in the medium (usually provided in the pure form) to control the copolymer composition, adds substantially to the absolute cost of PHA copolymer product (Sun et al., 2007). Moreover, with the productivity of these copolymers relatively low compared to the homopolymers (Le Meur et al.,

Table 4
Summary of PHA Copolymers production using lignocellulosic biomass.

Feedstock	Microbe	Reactor	Product	Production rates (g/L/h)	PHA concentration (g/L)	% PHA accumulation (w/w)	Reference
Xylose and Octanoic acid hydrolysates	*Pseudomonas putida* KT2440	Batch	MCL-PHA****	NA	0.37	20	Le Meur et al. (2012)
Wheat bran hydrolsates (WBH) and rice bran hydrolysates (RBH), with unhydrolysed corn starch	*Bacillus* sp. CFR-67	Batch	PHBV**	NA	5.9	NA	Shamala et al. (2012)
Sawdust hydrolysates	*Brevundimonas vesicularis* and *Sphingopyxis macrogoltabida*	Batch	MCL-PHA****	NA	0.3	78	Silva et al. (2007)
Beechwood Xylan hydrolysates	Recombinant *E. coli* expressing cellulose and PHA genes.	Batch	P(LA-co-3HB)***	NA	0.22	40.4	((Salamanca-Cardona et al., 2016; Salamanca-Cardona et al., 2014)
Cellulose hydrolysates	Recombinant *E. coli*	Batch	PHBV**	NA	NA	42	Matsumoto et al. (2011)
Extruded rice bran and corn starch (1:8 g/g) hydrolysates	*Haloferax mediterranei*	Fed Batch	PHBV**	NA	77.8	55.6	Huang et al. (2006)
Liquefied wood hydrolysates	*Cupriavidus necator*	Fed-Batch	PHBV**	2.84	60.5	NA	Koller et al. (2015)
Rice-based ethanol stillage hydrolysates	*Haloferax mediterranei*	Batch	PHBV**	0.17	16.42 ± 0.02	71 ± 2	((Bhattacharyya et al., 2014)
Cellulose hydrolysates	Recombinant *E. coli* LS5218	Batch	PHBV**	NA	3.3 ± 0.2	59	Nduko et al. (2012)
Grass biomass hydrolysates	*Pseudomonas* strains	Batch	MCL-PHA****	NA	0.3	33	Davis et al. (2013)
a. Barley biomass hydrolysate (BBH), b. Miscanthus biomass hydrolysate (MBH), and c. Pine biomass hydrolysate (PBH)	*Ralstonia eutropha* 5119	Batch	PHBV**	NA	1.8, 2.0, and 1.7 PHA, respectively	54, 44, 63, respectively	Bhatia et al. (2018)

PHBV** = Poly (3-hydroxybutyric acid-co-3-hydroxyvaleric acid).
P(LA-co-3HB) *** = Polylactic acid-co-3-hydroxybutyrate).
MCL-PHA**** = medium chain length PHA.
NA = Not available.

2012), PHA copolymers are yet to be produced on a large scale. Hence, the use of unrefined, low-cost renewable resources like natural residues, waste effluents, etc., which are rich in different carbon compounds, offers the potential for the direct, cost-effective synthesis of PHA copolymers without the use of expensive carbon substrate supplements. After adequate upstream processing, LCBs are potent to act as feedstocks for the biosynthesis of hydroxyvalerates (HVs) and other copolymeric precursors (Table 4), which would be a highly desirable outcome for the PHA industry.

Shamala et al. (2012) have shown the productive utilization of the cellulose and nutrient-rich wheat and rice bran hydrolysates to produce polyhydroxybutyrate-co-hydroxyvalerate (HB-co-HV) copolymer with a fermentative concentration of 5.9 g/L of PHA from 10 g/L of biomass (Shamala et al., 2012). Hydrolysates obtained from barley (Bhatia et al., 2018), rice-based ethanol industry stillage (Bhattacharyya et al., 2014), and sawdust (Silva et al., 2007) have also been explored for PHBV production. Furthermore, some studies have evaluated grass biomass as a carbon source for the production of MCL-PHA. Wildtype *P. putida* W619 has been reported to assimilate MCL-PHA when grown on perennial ryegrass biomass hydrolysates as sole carbon source. Compared to the *P. putida* KT2440 strain, this strain accumulated 75 times more MCL-PHA per g of dry cell mass (25–34% of the CDM) (Davis et al., 2013).

Lignocellulosic feedstock, coupled with efficient pretreatment, is a clear choice for exploration of direct MCL-PHA production and, along similar lines, liquefied wood prepared with microwave-as a pretreatment was investigated as an economical carbon source for the biosynthesis polyhydroxybutyrate-co-hydroxyvalerate (HB-co-HV) polyester using a microbial strain *Cupriavidus* necator (Koller et al., 2015). The microwave aided liquefaction resulted in a mix of degradation products comprised of odd number compounds such as 4-oxopentanoic acid (levulinic acid). Levulinic acid (LevA) monomer is a renewable chemical derived cost-effectively from forest and agricultural waste residues, paper mills sludge, and cellulose wastes from paper production processes. This cellulosic derived platform chemical is a potential 3HV precursor and has been used to enhance the accumulation of P(3HB-co-3HV) inside the bacteria (Alsafadi and Al-Mashaqbeh, 2017; Alva Munoz and Riley, 2008; Ashby et al., 2012; Bhattacharyya et al., 2014; Huang et al., 2006; Keenan et al., 2006; Koller, 2018; Shaghaleh et al., 2018). A recent study established that the use of a feed containing 1 g/L LevA increases PHBV co-polyester production by 100% (Berezina and Yada, 2016).

Hence, within the concept of a forest biorefinery, the main advantage that has been observed from using detoxified hemicellulosic and cellulosic hydrolysates rich in levulinic acid and pentose sugars, is the production of P(3HB-co-3HV), other short-chain lengths, as well as medium-chain length PHA copolymers. Since, these substrates also contain components such as tannic acid, terpenes, as well as lignin-derived complex aromatics compounds, that are known to constrain fermenting microorganisms (Coz et al., 2016), choice of substrates which are low in lignin and hemicellulose (with higher cellulose content) and hence release minimal variety and concentration of inhibitory compounds is imperative. Apparently, in a model study where softwood hemicellulose hydrolysates (which have a favorable sugar profile for fermentation) were used as a feed, a lofty first-rate PHA concentration of 60.5 g/L was reached (Dietrich et al., 2019; Koller et al., 2015).

Henceforth, the cautious choice of the lignocellulose raw material with the pretreatment steps, in concurrence with efficient, affordable, and green downstream PHA extraction and purification schemes, is vital to realize the industrial scale PHA production from lignocellulose biomass. With the process gaining popularity and the extensive research being carried out related to such substrate orientated strategies for PHA cost reduction, the vision of synthesizing low-cost PHA biopolymers with commercially competitive mechanical and thermal polymer properties, is not far off. Likewise, the prospects of generating PHA copolymers from lignin fractions of LCB have received favorable consideration.

4.4. PHA copolymer from lignin fractions of LCB

Among the inexpensive substrates, while cellulose has remained the preferred choice from the industrial viewpoint, lignin's exploitation for PHA production is still quite nascent. Lignin is a heterogeneous aromatic polymer that plants use to strengthen cell walls and protect their cellulosic/polysaccharides components. Nevertheless, depolymerization of this aromatic biopolymer is a challenging task, owing to their structural complexity and high stability of lignin held by strong C–C and C–O bonds (Sun et al., 2018). In most cases, lignin is burnt for energy recovery (NREL, 2014). Hence, transforming leftover lignin to biopolymers is a valuable "waste to wealth" strategy.

To date, only a handful of microbes have been reported to metabolize lignin-derived monomers as carbon sources employing the β-ketoadipate pathway (Kumar et al., 2017). *Pseudomonas putida* KT2440, is one such aromatic catabolizing bacterium, which has largely been exploited to produce MCL-PHAs. When fed with alkaline pretreated corn-stover that was rich in lignin, its extractives (*p*-coumaric acid and ferulic acid), inorganic components, and acetate at 32, 23, 11, and 8% wt./wt., respectively, the strain KT2440 accumulated MCL-PHA at 34–39% dry cell weight with corresponding volumetric concentration ranging from 0.15 to 0.17 g/L (Linger et al., 2014). Likewise, bacterial strains of *Pseudomonas putida* mt-2, *Cupriavidus necator, Ralstonia jostii, and Amycolatopsis* sp. has been stated to assimilate MCL-PHAs from alkaline pretreated lignin, at 60, 168, 288, and 13 mg/L, respectively (Salvachúa et al., 2015). Next, a well-studied lignin valorizing bacterium *Pandoraea* sp. ISTKB (Kumar et al., 2015, 2016) was studied for PHA production. This strain was cultured aerobically on 4-hydroxybenzoic acid, p-coumaric acid, vanillic acid, 2,6-dimethoxyphenol, and kraft lignin or syringol as carbon sources, and PHA accumulation of 247, 170, 72, 69, and 18 mg/L respectively have been reported (Kumar et al., 2017).

Biodegradation of kraft lignin with subsequent production of PHA has also been recently reported from a β-proteobacterium *Cupriavidus basilensis* B-8, with corresponding volumetric productivity of polyhydroxyalkanoate (PHA) being 128 mg/L and 319.4 mg/L in batch and a fed batch fermentation, respectively (Shi et al., 2017). Later, a marine bacterium, *Oceanimonas doudoroffii,* isolated from an area of the sea polluted with allantoin (Numata and Morisaki, 2015) and *Ralstonia eutropha* H16 (Tomizawa et al., 2014) have also been shown to possess PHA synthesizing capability using lignin or several lignin derivatives as sole carbon sources. In the future, newly isolated microorganisms must be assayed in order to identify efficient PHA production from lignin. Also, finding an efficient conversion route along with associated molecular mechanisms for the valorization of lignin to PHA offers a meaningful prospect for the comprehensive exploitation of LCBs and improves the affordability, feasibility, and sustainability of modern lignocellulose biorefineries. Towards this end, Wang et al. (2018) made an exhaustive study with *Psuedomonas putida* A514 as a model organism and constructed a genome-scale metabolic flux model for A514 under conditions where the strain was cultivated on vanillin acid, a lignin substitute. This ingenious research has not only generated insights into the potential genes involved in PHA synthesis but has also laid the foundation for research into the molecular mechanisms and pathways of lignin consolidated

bioprocessing into PHA (Wang et al., 2018). Additionally, integrated lignocellulose biorefinery concepts can be a channel to funnel the research towards lignocellulosic fiber-reinforced bioplastics.

4.5. Composite lignocellulosic fiber reinforced PHAs

Although biosynthetic is an important route to obtaining PHAs with variable functionalities, blending is another strategy that can provide a relatively simple and effective means to combine different polymer properties; for example, low crystallinity, full biodegradability combined with biocompatibility (Li et al., 2016). Cellulose is a crucial biopolymer resource, and recently the blending of cellulosic fillers in its different forms (cellulose fibers, cellulose derivatives, and nanocellulose) with PHAs have intrigued researchers globally. Modification of PHB/PHA properties by copolymerization and reinforcement of cellulose as a filler into a PHA matrix is not only allowing researchers to design biocomposite formulations with enhanced physical, mechanical and barrier properties (Tănase et al., 2015) but have also allowed them to adjust the PHA biodegradation properties to customer expectations (Li et al., 2016; Shaghaleh et al., 2018). The research to improve the compatibility of natural cellulosic fibers and PHA composite films by, for example, dip-coating using maleic anhydride, also needs a mention here (Zhao et al., 2017). Similarly, blending lignin with PHAs allows prospects for producing fully green composites at a reduced price, while providing a channel to valorize lignin.

Lignin has been recognized as a capable candidate for blending with PHA due to its amorphous nature and free functional groups bearing alcohol, aldehyde, or carboxylic acid moieties (Mousavioun et al., 2013). Lignin acts as a plasticizer forming a single phase with PHAs and propels the blend towards not only a favorable isothermal crystallization (Weihua et al., 2004) but also towards a reduced melt elasticity and viscosity relative to pure PHB (Mousavioun et al., 2013). The environmental studies examining degradation studies of PHB/lignin blends in garden soil have indicated reduced biodegradation with the concomitant resistant capacity of the blends to microbial attack (Mousavioun et al., 2012). In another study, enhanced imperviousness of a PHA/lignin blend for oxygen by 77% and carbon dioxide by 91% was observed compared to neat (HB-co-HV) polyester when 1 wt. % lignin was incorporated (Wang et al., 2016). Given the excellent thermal properties, antimicrobial, and barrier properties supplemented with rigidity and strength, of the PHA/lignin blends, they can be utilized for the packaging of various perishable goods. Thus, lignocellulose symbolizes a highly promising substrate for not only PHAs production but also material for post-synthesis property enhancements (Dietrich et al., 2019).

5. A case for consolidated bioprocessing of LCBs to PHAs using thermophiles

As reviewed above, research efforts made towards improvements in PHA production from lignocellulose are very encouraging. Yet, the required pretreatment and detoxification steps, in addition to upstream cost due to the extraneous addition of costly ligninolytic enzymes before fermentation, is currently a hindrance for an economically viable biorefinery. However, the potential benefits of producing PHAs with useful physicochemical properties from bacteria grown on LCBs as carbon sources provide compelling motivation to resolve these issues. Consolidated bioprocessing (CBP) integrates and accomplishes three steps in lignocellulosic biomass conversion: enzymes production, saccharification of lignocellulose, and fermentation of resulting sugars (C_5 and C_6) to valuable products, in a single vessel or reactor (in contrast to conventional approaches with each step performed independently), with low process complexity and elimination of the need to add externally produced enzymes and pretreatment. Development of eco-friendly CBP systems for single-step conversion of lignocellulosic biomass to PHA, which excludes pretreatment and enzyme addition steps, and which can be operated at relatively low capital investment, would be a major breakthrough for the PHA industry.

This CBP technology is reliant on a microbe or group of microbes having combined hydrolysis and fermentation ability (Singh et al., 2017), which permits them to grow directly on unprocessed/untreated LCB. Thermophilic bacteria possess highly active thermostable cellulolytic, hemicellulolytic, and ligninolytic enzymes for competent biomass hydrolysis (Bhalla et al., 2013; David et al., 2018). Indeed, the literature reveals that some thermophilic bacteria that can degrade lignocellulosic biomass without a physicochemical pretreatment. *Anaerocellum thermophilum* DSM 6725, a thermophilic anaerobic bacterium that grows optimally at 75 °C, can efficiently utilize various types of unprocessed plant biomass, including hardwoods such as poplar, low-lignin grasses such as Napier and Bermuda grasses, and high-lignin grasses such as switchgrass (Yang et al., 2009). The thermophilic bacterium *Caldicellulosiruptor bescii* grows at 78 °C on high concentrations (200 g/L) of both crystalline cellulose and unprocessed switchgrass (Basen et al., 2014; Brunecky et al., 2018). The thermophilic isolates belonging to the genus *Myceliophthora* are known to degrade many unprocessed plant biomasses and produce efficient enzyme mixtures for biomass degradation (Van den Brink et al., 2013). A hyperthermophilic anaerobe, *Caldicellulosiruptor saccharolyticus* DSM 8903, has been shown to have very high cellulolytic activity with the capability of deconstructing switchgrass (SWG) and microcrystalline cellulose (MCC) without enzymatic or chemical pretreatment (Talluri et al., 2013). *Clostridium thermocellum* has a reputation for its excellent cellulolytic capabilities attributed to the presence of an enzyme associated "cellulosome" complex on its outer cell wall, that allows it to processively depolymerize crystalline cellulose with an efficiency which is comparable to commercially available cellulolytic enzymes (Akinosho et al., 2014; Singh et al., 2017). Species of genus *Geobacillus* (Antoine et al., 1997; Bhalla et al., 2013; Brumm et al., 2015; Zambare et al., 2011), *Thermoanaerobacter* (Cao et al., 2014; Chang and Yao, 2011; Currie et al., 2014), *Deinoccocus-Thermus* spp. (Wu et al., 2015) are known for decomposing biomass at elevated temperatures. Furthermore, the potential for members of the genera *Thermotoga*, *Rhodothermus*, *Anoxybacillus*, and *Rhodothermaceae* strain RA to produce thermostable enzymes for biomass saccharification has also been documented recently (Lee et al., 2018).

An ideal CBP thermophilic microorganism should be able to delignify lignin, hydrolyze cellulose, hemicellulose to fermentable oligomers, ferment glucose or xylose or their oligomers, be moderately resistant to common pretreatment inhibitors (furans, polyphenolics), be resistant to LCB inhibitors, and produce PHA in high titer. To date, however, no ideal thermophilic organism has been identified for the conversion of LCB to PHAs. Nevertheless, over the last few years, the use of extremophiles, and especially thermophiles, as whole-cell biocatalysts for industrial production of PHAs in a biorefinery approach, has gained interest. Interestingly, a few thermophilic strains such as *Thermus thermophilus* HB8 (Pantazaki et al., 2003, 2005); *Chelatococcus* sp. (Ibrahim et al., 2010, 2016; Ibrahim and Steinbüchel, 2010); *Caldimonas manganoxidans* (Hsiao et al., 2016; Lin et al., 2017); *Bacillus shackletonii* K5 (Liu et al., 2014); and *Geobacillus* sp. AY 946934 (Giedraitytė. G. & Kalėdienė, 2015) have been shown to produce PHB. To the best of our knowledge, Table 5 displays thermophilic PHA producing bacteria recorded to date. Even a thermophilic cyanobacterium strain *Synechococcus* MA19 photoautotrophically accumulates PHB up to

Table 5
Overview of literature describing thermophilic PHA production.

Feedstock	Microbe	Operating Conditions	Reactor	Product	Cell dry weight(g/L)	Production rates (g/L/h)	PHA concentration (g/L)	% PHB (w/w)	Reference
Sodium gluconate or Sodium octanoate	*Thermus thermophilus* HB8	70 °C	Batch	MCL-PHA with side chains of 3HD, 3HO, 3HV, 3HB	NA	NA	NA	40 −45	(Pantazaki et al., 2003, 2005)
Glucose	*Chelatococcus thermostellatus* sp. MW9	50 °C, 7.3 pH	Batch, 250 ml	PHB	3.94	0.155	2.88	73	(Ibrahim et al., 2010, 2016)
Glucose	*Chelatococcus* sp. strain MW10	50 °C, 7.3 pH	fed-batch fermentation (CFBF), 2L	PHB	12.7	NA	7	55	Ibrahim et al. (2010)
Glucose	*Chelatococcus* sp. strain MW10	50 °C, 7.3 pH	Cyclic fed-batch fermentation (CFBF), 42L	PHB	115.0	0.063	16.8	40.4	Ibrahim et al. (2010)
Glucose	*Chelatococcu ssambhunathii* LMG 26063 TC	50 °C, 7.5 pH	Batch	PHB	4.83	0.024	1.46	54.4	Ibrahim et al. (2016)
Glucose	*Chelatococcu daeguensis* LMG 25471	50 °C, 7.5 pH	Batch	PHB	3.29	0.044	2.63	44.5	Ibrahim et al. (2016)
Starch/Glucose	*Chelatococcus daeguensis* TAD1	50 °C, 5.37 pH	Batch	PHB	4.50	0.122	3.44 ± 0.3	76.5	Xu et al. (2014)
Glycerol	*Chelatococcus daeguensis* TAD1	50 °C, 5.37 pH	2-stage Fed Batch	PHB	2.8	0.434	17.4	76.2	Cui et al. (2015)
Glucose	*Caldimonas manganoxidans*	55 °C	Batch	PHB	10	0.225	5.4 ± 1.1	59	Hsiao et al. (2016)
Glucose	*Geobacillus* sp. AY 946034 strain	55 °C	Batch	PHB	1.9	NA	1.3 ± 0.5	68.9	Giedraitytė. G. & Kalėdienė (2015)
Carbon dioxide	*Synechococcus* sp. MA19	50 °C, 8 pH	Batch	PHB	4.5	0.0092	4.4	62	Nishioka et al. (2001)
Carbon dioxide	*Synechococcus* sp.	50 °C, 8 pH	Batch	PHB	NA	0.00091	0.8	30	Miyake et al. (1996)
Glucose	*Aneurinibacillus* sp.	55 °C, 7 pH	Batch	PHV along with two minor analogues, 3HO, and 3HPB	NA	.33 (mg/L/h)	267.8 mg/L	10 −15	Xiao et al. (2015)
Sodium gluconate	*Thermus thermophilus* HB8	70 °C	Batch	PHB	1.14	0.0085	0.47	42	Papaneophytou & Kyriakidis (2012)

Here: PHB = Poly-hydroxybutyrate; PHV = polyhydroxyvalerate; MCL-PHA = Medium chain length polyhydroxyalkanoate; 3-HD = 3-hydroxydecanoate; 3HO = 3-hydroxyoctanoate; 3HV = 3-hydroxyvalerate; 3HB = 3-hydroxybutyrate; 3HPB = 3-hydroxy-4 phenyl-butanoate; NA = Not Available.

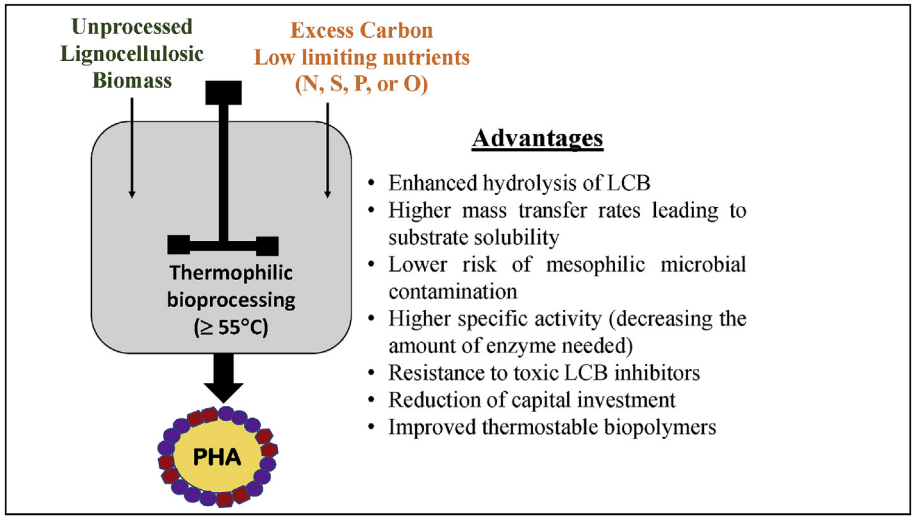

Fig. 4. Thermophilic conversion of lignocellulosic biomass to PHA.

62% (w/w) of dry cells utilizing carbon-dioxide (CO_2) as sole carbon, under nitrogen-limited conditions (Nishioka et al., 2001). More recently, a thermophilic PHA producer, *Aneurinibacillus* species from the phylum Firmicutes has been shown to produce poly(3HB-co-3HV) at 55 °C using glucose as a substrate (Xiao et al., 2015). Moreover, an SG4502 bacterium has been isolated from a sewage site, having the closest match with *Pseudomonas* sp., which is capable of producing medium chain length PHA (MCL-PHA) using biodiesel fuel (Satoh et al., 2011). This strain could also produce MCL-PHA from acetate, octanoate, and dodecanoate as sole carbon sources at cultivation temperatures up to 55 °C.

Although the optimal cultivation temperature range, 50–75 °C,

is higher than industrial fermentation temperatures, the higher energy expense for this aspect of the process can be more than compensated by the potential advantages, discussed above, for production of PHA from thermophiles in a consolidated setup. Moreover, the use of thermophilic microorganisms has many additional potential rewards over fermentation at lower temperatures. High-temperature bioconversion of LCBs enables higher specific activity (decreasing the amount of enzyme needed), and higher stability (allowing extended hydrolysis times) along with higher rates of feedstock conversion due to better enzyme accessibility and cell-wall disorganization achieved at thermophilic reaction conditions (Bhalla et al., 2013). In particular, thermophiles are known to possess rigid cellular membranes, which makes them resistant to toxic compounds that can be released during LCB degradation (phenolics, aldehydes, organic acids, and phenolics) (Ou et al., 2009; Varga et al., 2004). Other benefits of using a whole thermophilic cell or their cell-free extracts in a biorefinery include higher mixing rates, a lower risk of mesophilic microbial contamination, increased diffusion rates, and improved mass transfer, which allows increased flexibility for the process configurations. The use of thermophiles can help eliminate the use of hazardous chemicals (used in pretreatment) and expensive enzymes for the hydrolysis step, allowing effective and low-cost saccharification and fermentation of unprocessed lignocellulosic feedstock and direct conversion to the PHA end product in a single step (Fig. 4).

6. Future directions

Ideally, the development of a novel form of consolidated bioprocessing which can convert lignocellulosic biomass into PHAs will consolidate all steps (i.e., pretreatment, enzyme hydrolysis and saccharification, and PHA production utilizing hexose and pentose sugars) in one step. If a pretreatment step is still required, the applied procedure should at least avert the destruction or loss of monomeric sugars, should minimize the production of inhibitors, and should reduce reactive chemical consumption while improving the formation of sugar monomers in the hydrolysis step. Hence, critical scientific improvements centered on supplementary economic and environmentally friendly practices need to be developed both in academic and in industrial laboratories. As an example, the prospect of fusing enzyme catalysis with sonication offers an opportunity worth investigating for the valorization of second-generation lignocellulosic wastes into value-added end products. Other strategies to solve or decrease the inhibition of microbes, enzymes and the fermentation mechanism by LCB derivative compounds, also require extensive research to resolve. These strategies include the selection of a feedstock with a higher cellulose or a lower lignin fraction, and/or genetic engineering of the agricultural plants at the sources themselves, in order to reduce the amount of lignin.

7. Concluding remarks

PHA production from lignocellulose is still at the inchoate stage, but the future looks promising. An improvement in fermentation processes with inexpensive forestry and agricultural waste can completely change the shape of the global biopolymer industrial sector, permitting production costs that can compete with petroleum-based polymers, while offering beneficial biodegradable and biocompatible properties, environmental sustainability, and new biopolymer markets with novel applications. The present article reviewed the advances that have been made with respect to the use of lignocellulosic biomass (LCB) hydrolysates to synthesize biopolymers. From the discussions presented, it is evident that polyhydroxyalkanoates (PHAs), a class of natural polyesters, are viable substitutions for synthetic polymers in terms of functionality and processability. However, it is also apparent that the high price of sugar-based cultivated feedstock, low polymer yield, and inefficient recovery techniques are significant obstacles to PHA's bulk, cost-competitive production. As an alternative to conventional feedstocks, LCB appears to have promising potential for sustainable PHA production. LCBs are low cost, do not interfere with food supply chains, are renewable, and are carbon neutral. However, the necessity to pretreat LCBs to fractionate them into cellulose, hemicelluloses, and lignin, currently makes their overall bioconversion to PHA technologically demanding and less economical. On the other hand, an eco-friendly consolidated bioprocessing (CBP) system, an essential component of which includes the elimination of pretreatment and a multitude of external enzymes addition steps, can alleviate the production expenditures and reduce the chemical usage. Additionally, the CBP approach simplifies the operating procedure, with enzymatic and fermentation systems being completely compatible. Therefore, one or more microorganism (wild and/or engineered) which not only demonstrates superior capability to utilize unprocessed/untreated lignocellulosic biomass but also shows the capability to produce PHA, could change the competitive landscape of the polymer industry in favor of biodegradable PHAs rather than petroleum-based polymers. In this context, the use of thermophilic microorganisms (growing at $\geq$50 °C) that possess thermostable machinery for biomass hydrolysis, makes them especially appropriate for industrial scale conversion of untreated LCB to PHAs. Hence, we confirm our posed hypothesis that a consolidated form of lignocellulosic bioprocessing has the potential to reduce production costs of PHAs from the substrate side with minimal to no requirement for pretreatment. The ultimate goal for a successful CBP process is to attain superior PHA yields from the native unprocessed lignocellulose biomass; and the use of thermophiles provides an important strategic direction for meeting economic competitiveness and sustainability targets. Moreover, since the hydrolysis of lignocellulosic feedstock leads to the production of a variety of added value platform chemicals (such as aliphatic acids, aldehydes, and aromatic compounds), sustainable production of PHA in integrated lignocellulose biorefineries employing thermophiles can provide an extensive and robust infrastructure for the economic valorization of globally abundant LCB waste.

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