

Review article

Production of bioplastic through food waste valorization

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ABSTRACT

The tremendous amount of food waste from diverse sources is an environmental burden if disposed of inappropriately. Thus, implementation of a biorefinery platform for food waste is an ideal option to pursue (e.g., production of value-added products while reducing the volume of waste). The adoption of such a process is expected to reduce the production cost of biodegradable plastics (e.g., compared to conventional routes of production using overpriced pure substrates (e.g., glucose)). This review focuses on current technologies for the production of polyhydroxyalkanoates (PHA) from food waste. Technical details were also described to offer clear insights into diverse pretreatments for preparation of raw materials for the actual production of bioplastic (from food wastes). In this respect, particular attention was paid to fermentation technologies based on pure and mixed cultures. A clear description on the chemical modification of starch, cellulose, chitin, and caprolactone is also provided with a number of case studies (covering PHA-based products) along with a discussion on the prospects of food waste valorization approaches and their economic/technical viability.

1. Introduction

The Food and Agriculture Organization (FAO) of the United Nations reported that around 1.3 billion tons of food is lost or wasted every year globally. It is found that this amount corresponds to one-third of all food resources produced for human consumption. Note that sources of food waste include household, commercial, industrial, and agricultural residues, while the compositional matrix of food wastes varies broadly based on source and type (Xue et al., 2017). Food waste means a substantial loss of other resources such as land, water, energy, and labor. FAO defines food waste as “food losses of quality and quantity through the process of the supply chain taking place at production, post-harvest, and processing stages.” In more specific terms, food losses occurring at the end of the food chain correspond to “food waste (FW),” which is contingent on consumer behavior, purchase intention, and retailer mar-

keting strategy. In general, the most FW is being disposed of via landfilling, composting, and fermentation. Although European Union guidelines stated that food waste should preferentially be used as animal feed, it became illegal because of disease control concerns (Saleemdeen et al., 2017; Cerda et al., 2018). Thus, the valorization of food waste through production of value-added products can be an ideal and practical end use.

Depending on geographically-specific circumstances, the generation patterns of FW may differ greatly across the world. In broad terms, waste generation is affected by a list of variables, including crop production options/models, internal infrastructure/capabilities, distribution chains/channels, and purchase/usage habits of consumers. Table 1 summarizes the types of FW and their origins in the food industry. In the UK, 15 million tons of food were wasted annually (Saleemdeen et al., 2017). In Malaysia, it is estimated that 6.7 million tons of FW are

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Table 1
Types of wastes and their origins in the food industry.

Order	Types of FW	Origins	Reference
1	Waste from preparation, processing, and rendering of meat, fish, and other food stuffs originating from animals	Slaughter house, butcher shops, fish processing plants, egg processing plants, tallow processing plants	(Jayakumar et al., 2008)
2	Waste from preparation and processing of fruit, vegetables, grain, edible oil, cocoa, coffee, and production of canned foods.	Fruit and vegetable processing plant; starch manufacturer; malt house; grist and husting mill; oil mill; manufacturer of coffee, tea, cocoa, and canned foods; tobacco processing plants.	(Preethi et al., 2012)
3	Waste from sugar factory	Sugar manufacturers	(Albuquerque et al., 2010)
4	Waste from dairy factory	Dairies	(Bosco and Chlampe, 2010)
5	Waste from production of baked foods and sweets	Bakeries, confectioners, candy producers	(Leung et al., 2012)
6	Waste from production of both non-alcoholic and alcoholic beverages	Breweries, wineries, liqueur producers, distilleries, and non-alcoholic beverage and fruit juice producers	(Preethi et al., 2012)

generated annually in 2020 (Bong et al., 2017). Approximately 567 to 726 million tons of FW (equivalent to up to 40 wt% of the total food production) are generated annually in the USA (US EPA, n.d.). This quantity of FW is equivalent to USD 218 billion (Gunders and Bloom, 2012). Likewise, it is also comparable to the annual energy loss of over 456,250 cal per capita, which is enough to support a male adult (daily calorie intake = 2500) for 180 days (Buzby et al., 2014). In Spain (an agriculturally-focused country), about 8 million tons of FW were produced in 2014 (González-Torre and Coque, 2016). If such waste was properly converted into value-added products, huge economic and energy losses can be saved. In France, the government has already implemented a policy for stimulating valorization of FW through recovery of energy (e.g., biogas) and value-added materials (e.g., bioplastic) with a punitive law amid a FW epidemic (De Clercq et al., 2017); implementation of this policy was estimated to save 88 million tons of FW per year with a corresponding cost of USD 167 billion (Gore-Langton, 2017).

Although several papers reported the simultaneous conversion of FW into energy and bioplastics, most of them emphasized bioplastic production processes, operating conditions, and new bacterial/archaeal species used in the fermentation process (Khanna and Srivastava, 2005; Chee et al., 2010; Chen and Patel, 2011; Bugnicourt et al., 2014; Kiran et al., 2014; Koutinas et al., 2014; Salgaonkar and Bragança, 2017). Among them, only a limited number of studies reported the potential production of polyhydroxyalkanoates (PHA) from a single species of FW, such as waste cooking oil (Destroches et al., 2012) and cheese whey (Valentino et al., 2015).

The production of synthetic plastic from the irreversible process (e.g., petroleum extraction) is an environmental burden (e.g., compared to bioplastic). Also, microorganisms in nature have not evolved to efficiently degrade petroleum-derived polymers (Harding et al., 2007). The average energy requirement of bioplastics production is obviously less than traditional petro polymer (57 MJ kg^{-1} compared to 77 MJ kg^{-1}) to be beneficial toward global warming problem (Gironi and Piemonte, 2011). Therefore, due to similar functions of bioplastic and conventional polymer, bioplastic is an ideal alternative in the context of environmental sustainability. Over the past decade, enormous efforts have been put into converting FW into PHA as a practical option for FW valorization (Fig. 1). Indeed, with increased attention on sustainable development and renewable materials worldwide, issues of efficient conversion of FW into PHA have been gaining more attention. Yet, the technical completeness to convert FW into PHA is an initial stage of development. However, it shows great potential for commercialization with economic viability. Therefore, this review highlights the potential of FW processing techniques for production of bioplastics (e.g., PHA) and their economic viabilities. Specifically, we reviewed 193 studies, including 145 articles published after 2010, to summarize the current knowledge about valorization techniques for FW with the main emphasis on PHA production. Special case studies are also provided at the end of this work.

2. Current status of bioplastic production and food waste feedstock collection and sorting

2.1. Desirable bioplastic production from food waste

FW is being generated from all stages of the food supply chain including post-production, handling/storage, manufacturing, wholesale/retail, and consumption stages (Ravindran and Jaiswal, 2016). In general, around 30 wt% food becomes FW. In 2015, 39.6 million tons of FW (15.1 wt% of MSW) were generated in the US, but only 5.3 wt% of them is used for anaerobic digestion and composting (Gunders and Bloom, 2012). The European Union generates 90 million tons of FW annually. Among them, 38 wt% is originated from the food manufacturing sectors (Pfaltzgraff et al., 2013). Thus, the conversion of FW into value-added chemicals can be the desired end use of food waste for increasing global sustainability. The water content of FW generally ranges from 75 to 85 wt%. The mass portion of organic matters is 60 to 70 wt% (dry basis) (Rhu et al., 2003). Table 2 summarizes the properties of FW that are suitable for production of bioplastics and bioenergy. Fig. 2 provides a full-screen of not only process of bioplastics production but also routes of waste biomass transfer and energy consumption. Starch, cellulosic, oily plant, human being, and livestock interacted with each other for energy transfer through physical/chemical/biological way during the conversion process. The figure provides an ideal and economic platform to optimize expense and energy (fuels) recovery.

Production of bioplastics such as PHA is an ideal strategy for FW disposal. One reason for this is that FW is landfilled and yields undesirable results, such as greenhouse gas (GHG) emissions and groundwater contamination. Production of bioplastics from FW is a renewable sustainable process, in which materials are synthesized from the carbon neutral resources. Some bioplastics are biodegradable and compostable under industrial conditions (Dietrich et al., 2017). Compostable bioplastics break down by 90% in several months but can also undergo industrial composting processes (Siracusa et al., 2008). Such bioplastics should meet the specifications and evaluation criteria of international standards (e.g., EN 13432, EN 14995, and ASTM D6400) for biodegradable plastics/products, such as composability.

The environmental benefits from utilization of bioplastics are one of the driving forces to expand their further use. Ceresana in Constance, Germany, predicted that the world market for bioplastics in 2021 will be three times larger than that in 2014, generating a total of USD 5.8 billion in revenue. For a specific case, NatureWorks in Minnetonka, MN, USA announced that polylactic acid (PLA) was produced at a capacity of 1.5×10^5 tons in 2009. This capacity is expected to increase to 8.0×10^5 tons in 2020. Note that Ceresana and NatureWorks are leading international market research and consultancy companies. Approximately 80% of the polymer market may be replaced by bioplastics in Western Europe (Shen et al., 2009). Groot and Borén (2010) performed an LCA of industrial production of PLA in Thailand, indicating that bioplastics can offset environmental problems compared

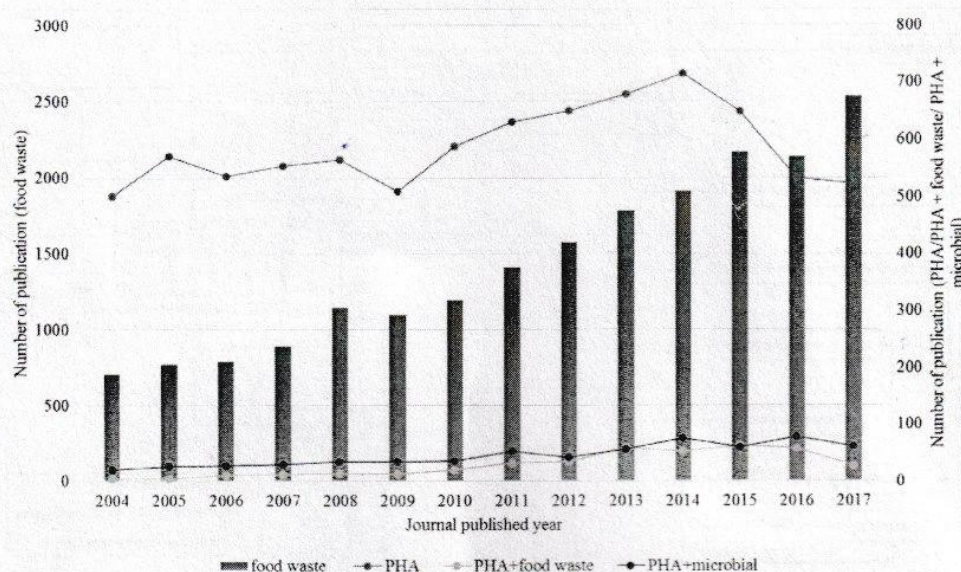


Fig. 1. Science citation index publications on PHA and food waste from web of science.

with using petro-derived polymers (e.g., GHG emissions and climate change).

2.2. Current status of bioplastic production

PHA is one of the key elements to drive the market for biodegradable polymers. PHA is an important polymer family that has been in development stage for a while but to finally enter the commercial market at of which production capacities are estimated to quadruple in the next five years (Chen et al., 2016; Briassoulis and Giannoulis, 2018). It has been proven to have the great potential as a substitute for traditional plastics due to its biodegradability and rubbery-like properties.

The unique properties of PHA are recognized as better oxygen barrier (than both non-biodegradable polypropylene (PP) and polyethylene terephthalate), better water vapor barrier (than PP), and the fat/odor barrier. Such superior physico-chemical properties of PHA (e.g., in reference to PP) have promoted its usage in various fields including food packaging (Reddy et al., 2003; Chen, 2009; Ahmed et al., 2018). The poly-4-hydroxybutyrate (P4HB), polyhydroxyvalerate (PHV), polyhydroxyhexanoate (PHH), polyhydroxyoctanoate (PHO), and their copolymers (e.g., poly-3-hydroxybutyrate (P3HB)) are the most commonly used bioplastics (Figure 3) (Ren et al., 2011). PHA can be stored as granules in the cell cytoplasm by microorganisms under stress conditions caused by the limitation of a nutrient, electron donor, or acceptor. Fig. 4 presents a scheme for the biosynthesis process of

PHA. The procedure mainly goes through as: substrate preparation, PHA-accumulating fermentation, and PHA extraction (Seratim et al., 2008). Their physico-chemical properties are determined by the operating parameters and the bacterial species chosen for the fermentation process (Weber et al., 2002).

PHA has been widely used for various purposes, including packaging, medical applications, energy, and fine chemicals (Chen and Wu, 2005; Chen, 2009; Chen and Patel, 2011; Liang and Qi, 2014; Koch and Mihályi, 2018). Commercialized PHA production has already been implemented by many manufacturers such as MetaboliX* (Woburn, MA, USA), Tianjin Green Bioscience Co., Ltd. (Tianjin, China), and Biocycle PHB Industrial SA (Serrano, SP, Brazil). Global generation of PHA from commercial manufacturers reached 2.05 million tons in 2017 (European Bioplastics). As summarized in Table 3, most raw materials used in the PHA industry are food crops, sugarcane, and vegetable oil. The current industrial expense for PHA production is 5–10 times higher than that of petroleum-derived polymers. Therefore, the major hurdles for commercial production of PHA and its practical use are high production costs, low-efficiency downstream processing, and high energy consumption for sterilization of the fermenters (e.g., pure glucose) (Koller et al., 2017). In particular, the feedstock cost for PHA production represents half of the overall production cost (Salgaonkar and Bragança, 2017). In an effort to seek low-cost feedstocks at large-scale (relative to traditional raw materials), enormous studies have been conducted. Among various alternative feedstocks for PHA production,

Table 2
Properties of potential food waste applied in PHA production.

Order	Type of food waste	Potential materials	Characteristics	Reference
1	Used cooking oil	Palm oil, rapeseed oil, soybean, sunflower seed	High content of lipid (fat) can be converted into biodiesel (fatty acid methyl esters: FAMES)	(Mozejko and Giesielski, 2013)
2	Animal by-products	Blood, fats, residues from intestines	High nitrogen content or high levels of BOD and COD	(Lin et al., 2013)
3	Organic crop residues	Straw, stover, peels, fruit pomace	These fractions consist of important sources of sugars, lipids, carbohydrates, and mineral acids Provided water, soluble sugar, and cellulose Succinic acid production	(Bussemaker and Zhang, 2013; Cesário et al., 2014b)
4	Mixed domestic waste	Cheese whey, waste bread, nuts and nut shell	High content of protein, starch, fat and fatty acids	(Pais et al., 2014)

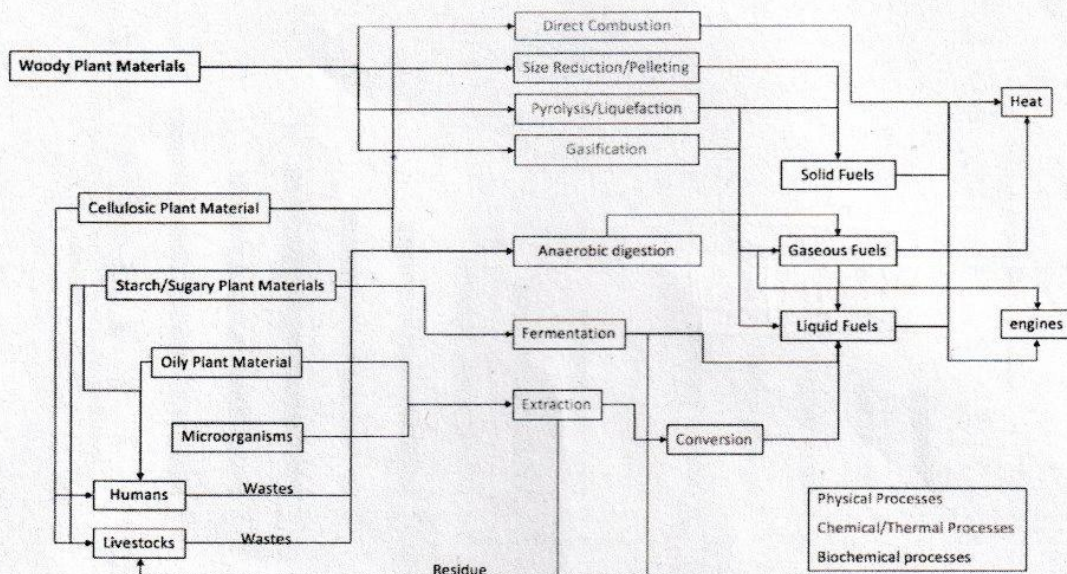


Fig. 2. Routes for transforming energy from biomass.

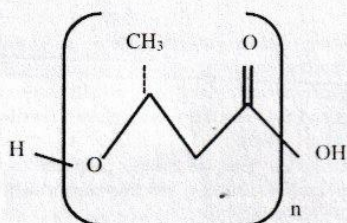


Fig. 3. Structure of poly-3-hydroxybutyrate (P3HB), the most common type of PHA.

agro-industrial waste streams (e.g., glycerol from biodiesel production, lignocellulosic waste from the food industry and forestry, and petrochemical plastic waste) have gained great attention since FW provides a

strategic means for lowering the overall production cost (Chee et al., 2010).

In Europe, lactic acid, PLA, PHA, and bioethanol are produced from a surplus whey containing lactose. Considering that the sugar and food oil industries generate a tremendous amount of lignocellulosic waste (e.g., empty fruit bunch (EFB), palm oil mill effluent (POME), and palm kernel shell (PKS)), FW containing sufficient amounts of carbon sources and nutrients can be a great potential for PHA production through bacterial fermentation. Thus, various types of FW also offers a strategic means for diversifying microbial strains in the fermentation process. Such technical advancements provide an innovative production pathway for bioplastics via mixed cultures or excess activated sludge from wastewater treatment plants (Lam et al., 2017). Comparing with pure culture technology, mixed culture cost less on sterilization. In reference to the pure culture technology, the cost for mixed culture in line with sterilization during the treatment process is lower which is an

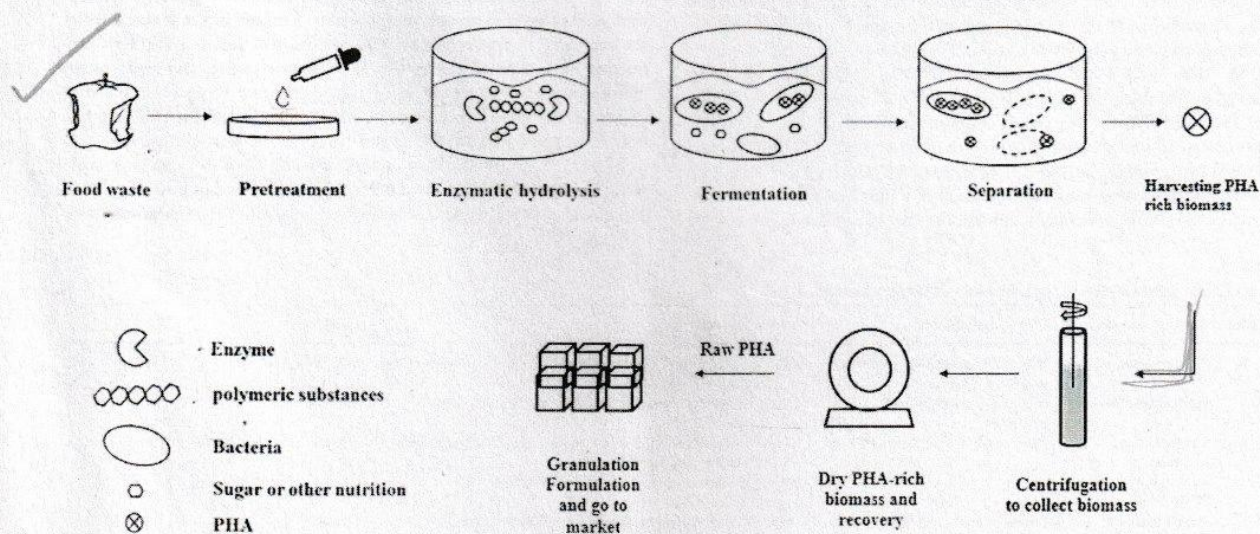


Fig. 4. PHA biosynthesis process scheme.

Table 3
Global PHA producers and their substrates.

Order	Company	PHA type	Substrates	Production capacity (tons per year)	Reference
1	Metabolix, (USA)	P3HB	Corn	50,000	www.metabolix.com
2	MHG Bio, (USA)	Mcl-PHA	Canola oil	20	www.mhgbio.com
3	Biocycles, (Brazil)	P3HB	Cane sugar	100	www.biocycle.com.br
4	Bio-On, (Italy)	PHA	Beet sugar	10,000	www.bio-on.it
5	TianAn Biopolymer, (China)	P3HB, P3HBV	Corn	10,000	www.tianan-enmat.com
6	Tianjin GreenBio (China)	Etyl 3-HB P(3,4HB)	Sucrose	10,000	www.tjgreenbio.com

important technical advantage (Nielsen et al., 2017).

2.3. Food waste feedstock collection and sorting technologies

Most parts of FW can be recycled (if separated), and recycling will help reduce the overall expenditures on waste management. Also, it is important to improve the recycling rate of food waste, especially for FW from complex MWF. Collecting and sorting from the source of waste generation can effectively reduce the cost of the subsequent steps to offer a strategic means for maximizing yield and profit, to reduce environmental burden, and to improve the reuse efficiency of material. Based on generation source, FW can be classified as industrial, agricultural, and household FW. The total amount of FW from industrial processes and agriculture is large, but the composition of FW is relatively simple. On the contrary, the composition of household FW is very heterogeneous.

In large-scale food production facilities, such as farms and food industrial plants, recycle systems are generally reserved for unpackaging and peeling functions. For example, a turbo separator can deal with 8–10 tons of FW per hour (Scott*, USA). In commercial applications, one system can serve two functions of collection and classification. STREAM* Corporation (Malaysia) effectively collects wet FW from kitchens and transfers waste in containers or delivers them directly to FW treatment plants. A specialized organic waste transport system integrated with a dehydrator, full vacuum, and gravity vacuum can be applied in kitchens of airport catering centers, restaurants, food courts, and food processing plants to facilitate more efficient collection and sorting of FW.

Different colored waste bags are being used for different waste streams. In Hong Kong, green waste bags are used to separate FW from municipal solid waste (MSW), while residual MSW can be packed in a common plastic bag (Lo and Woon, 2016). However, due to the complex composition and relatively high cost of MSW, large-scale processing for bioplastic production requires further research in many areas. The results of life cycle assessment (LCA) of two different waste collection systems indicated that automated separation of FW from MSW is more environmentally friendly than conventional methods, such as manual collection and truck transportation (Aranda Usón et al., 2013). In an actual case study, the performance of a pilot-scale FW collection system in Suzhou, China, was analyzed and evaluated based on local economic conditions, municipal facility conditions, and operation efficiency (Wen et al., 2015). The results indicated that integrated systems

featured strong economics and low environmental impacts, although the limited daily processing capacity and waste utilization rate were still problematic.

3. Technologies for converting food waste to fermentable substrates

Although FW is a good initial feedstock for production of bioplastics, it must be pretreated to improve or modify the physico-chemical and biological properties. This section discusses the commonly used pretreatment technologies (i.e., physical, chemical, and biological processes) and enzymatic hydrolysis and their effects on bioplastic production yield. Successful conversion processes refer to partial or total liberation of monomers from the FW (e.g., lignocellulosic components) with increasing accessibility of proteins, lipids, and polysaccharides (e.g., starch and cellulose) for subsequent enzymatic hydrolysis and fermentation (Barisik et al., 2016; Kim, 2018). Moreover, several methods can be integrated into a single treatment system to achieve better performance. For example, bioplastic production with physical/acid treatment (i.e., 60 min heating at 121 °C followed by 2% sulfuric acid digestion) of industrial FW mixture was able to achieve the highest 3-hydroxyvaleric acid (3HV) mole fraction of 22.9% in experiments (Elbeshbishy et al., 2011; Ahn et al., 2016b). Table 4 summarizes the sub-products generated/separated from FW transition processes and their applications.

3.1. Mechanical and thermal conversion of food waste to fermentable organic compounds

Physical pretreatment is conducted by the mechanical and thermal conversion processes. Ultrasound, microwaves, milling, and heating methods are also being used for pulverization to increase surface area, separation rate, biological conversion, or fermentable substrates (including glucose, proteins, fats, fatty acids, and starch) (Sasmal et al., 2012; Bussemaker and Zhang, 2013; Pagliaccia et al., 2016). In laboratory-scale PHA production, a study synthesized PHB using Jambul seeds dried in an oven at 60 °C to reduce the moisture content and then milled the seeds into fine particles. Lignocellulosic waste can be pretreated by a steam-explosion method (i.e., 160 to 260 °C and 0.7 to 4.8 MPa), which is a commonly used process to separate lignin and hemicellulose from cellulose (Agbor et al., 2011; Pielhop et al., 2016). Physical pretreatment is usually applied at the beginning to change the

Table 4
Organic residues and their applications.

Order	Organic residues	Applications in bioplastic synthesis	Reference
1	Fruits and vegetables	Antioxidants, flavonoids, phenols, carotenoids, lipids, phytochemicals, carbon source	(Mirabella et al., 2014)
2	Animal wastes, meat, and derivatives	Proteins, enzymes, collagen, gelatin, nitrogen source, trace materials	(Jayatilakan et al., 2012; Mirabella et al., 2014; Pleissner et al., 2016)
3	Dairy products	Carbon and nitrogen sources	(Mirabella et al., 2014)
4	Waste oil	Fatty acid and methyl esters, glycerol, erucic acid	(Bardhan et al., 2015)
5	Cellulosic biomass	Phytosterols, polypropylene, acrylic acid, isobutanol, thioester, esters	(Bardhan et al., 2015)
6	Lignin	PHA, adipic acid	(Langer et al., 2014; Vardon et al., 2015)

particle size or to separate the materials for the processing in the next steps. Thus, the physical pretreatment would not be applied alone but is always combined with other treatment methods.

3.2. Chemical conversion of food waste to fermentable sugars

Acid pretreatment is common for FW, especially for lignocellulosic materials (Mussoline et al., 2013). Acid treatment increases the accessibility of such low-cost and abundant feedstocks to hydrolytic enzymes while producing small amounts of cell growth inhibitors (Monavari et al., 2011). Acid-treated lignocellulose to lignocellulose-derived by-products can inhibit or deactivate enzymes as well as influence the performance of bacteria used in the fermentation step. The inhibitors include furan derivatives (e.g., furfural and 5-hydroxymethylfurfural (HMF)), lignin-derived phenolics (e.g., phenols are inhibitors to cellulolytic enzyme), and carboxylic acids (e.g., weak organic acids such as acetic, formic, and levulinic acids) (Monavari et al., 2011; Barisik et al., 2016; Kim, 2018). The performance of microbial bioplastic synthesis is contingent on the operating conditions of acid pretreatment (Ahn et al., 2016a, 2016b). Alkali pretreatment involves the use of alkaline solutions such as NaOH, Ca(OH)₂, and ammonia. Solvation is the first reaction that occurs during alkali pretreatment, leading to solid expansion (Carlsson et al., 2012). Alkaline pretreatment effectively hydrolyzes ester bonds between plant polysaccharides and lignin (Alvira et al., 2010) for lignin solubilization. Elbeshbishy et al. (2011) studied three combined physical/chemical pretreatments, including ultrasonication with heat, ultrasonication with acid (i.e., 1N HCl, pH = 3.0, and 24 h at 4 °C), and ultrasonication with base (i.e., 1N NaOH, pH = 11.0, and 24 h at 4 °C). The results showed that alkaline ultrasonication can achieve the highest increase rate of 30% of soluble chemical oxygen demand (COD) and 40% of soluble protein. The corresponding hydrolysis yield was 0.84 g g⁻¹ at a loading rate of 20 FPU g⁻¹ of pretreated paddy straws. Table 5 summarizes the raw materials from FW through various pretreatment methods. In PHA production, a combination of physical/chemical treatments is useful to achieve better performance or to enhance the final yield. In general, the combined pretreatment processes aim to increase in accessible surface area while lowering in degree of polymerization of raw materials (e.g., cellulose).

3.3. Biological conversion of food waste to fermentable substrates

White rot fungus aids in delignification, which in turn improves enzymatic saccharification rate and productivity (Kalyani et al., 2013). Several studies have adopted fungi as a FW pretreatment method (Isroi et al., 2011; Vasmaria et al., 2015). Cianchetta et al. (2014) evaluated selected white-rot fungi to improve carbohydrate yield from wheat straw and investigated the effects of five different fungi on enzymatic hydrolysis of wheat straw. The results of an optimized fungal strain-biomass combination showed that *Ceriporiopsis subvermispota* provided the highest yield of net carbohydrate and minimized weight and cellulose losses (Saha et al., 2016). Thus, appropriate fungal strain selection influences the specific biomass pretreatment. In reference to the chemical treatment, biological pretreatment of lignocellulosic biomass offers a way to save energy consumption while reducing intractability toward cellulolytic enzymes. Despite such benefits, the slow reaction kinetics and loss of polysaccharides during the biological process have been pointed out as the main technical demerits (Lemée et al., 2012). Bule et al. (2016) performed biodegradation of wheat straw using a white rot fungus that secretes three major classes of ligninolytic enzymes, namely lignin peroxidase, manganese peroxidase, and laccase. It was suggested that these unique lignin modification patterns are associated with the white rot (*P. radiata*) extracellular proteome which was expressed during the solid-state fermentation (pretreatment) of wheat straw as an efficient biodegradation method. Biological pretreatments are promising eco-friendly processes based on addition of specific

Table 5

Raw materials extracted from food waste using physical and chemical conversion methods.

(A) Results for physical methods			
Order	Technology	Provided characteristics and effects	Reference
1	Mechanical and thermal conversion	Mechanoacoustic and nonchemical effects; high recoveries of cellulose and hemicellulose and lignin removal product	Kourmentza et al. (2018a, 2018b)
2	Grinding	Improve surface area and better accessibility of the substrate to enzymatic hydrolysis	(Vega-Castro et al., 2016)
3	Milling	Reductions in particle size to extract sugars	(Yagi et al., 2018)
4	Thermal pretreatment	Enhances enzyme hydrolysis for fermentable substrates	(Valentini et al., 2018)
(B) Results of chemical methods			
Order	Technology	Provided characteristics and effects	Reference
1	Chemical conversion	Provide higher digestibility	(Sarabale and Ob, 2015)
2	Alkali pretreatment	Provide higher digestibility	Kourmentza et al. (2018a, 2018b)
3	Acid pretreatment	Make products more accessible to hydrolytic enzymes (produce smaller amounts of inhibitors and lower sugar losses)	(Sindhu et al., 2013)
4	Acid pretreatment	Make products more accessible to hydrolytic enzymes	(Ahn et al., 2016b)

Pretreatment of wheat straw

enzymes (e.g., peptidase, carbohydrases, and lipases) from microorganisms.

3.4. Enzymatic hydrolysis of food waste

Hydrolysis is the main mechanism to breakdown polymers into their corresponding monomers and/or intermediates. Enzymatic hydrolysis promotes the hydrolytic ability of FW and reduces volatile suspended solids. Converting polymeric structures into fermentable products (e.g., lignocellulose into carbohydrate and animal fat into fatty acids) is a critical step in this process. FWs containing lignocellulosic are a complex matrix of cellulose, hemicellulose, and lignin. Although cellulose and hemicellulose yield fermentable sugars via an enzyme hydrolysis step, lignin is one of the most recalcitrant structures as it consists of phenylpropanoid units (Saritha et al., 2012). Kiran et al. (2015) studied the effect of pretreatment with commercial enzymes on hydrolytic solubilization of raw FW collected from a cafeteria. The authors found that protease exhibited the highest reduction rate of volatile suspended solids among three types of enzymes, namely carbohydrases, proteases, and lipases, and the mixed enzyme treatment exhibited better reduction efficiency than that of single-enzyme treatment. Heng et al. (2017) optimized a three-step PHA production process of alkaline pretreatment, enzymatic hydrolysis, and biosynthesis conversion from rice husks with *Burkholderia cepacia* USM. Thus, multiple-step treatment methods can increase the biodegradability of most carbon sources, resulting in enhanced PHA production performance and efficiency.

Certain types of FW do not contain sufficient amounts of nutrients to maintain biological activity during fermentation, which can be resolved by utilizing a mixture of different FWs. Mixed enzymes produced through solid-state fermentation can hydrolyze proteins and sugary compounds (e.g. polysaccharides) in FW through the different pathways (Koller et al., 2005; Kwon et al., 2005; Matsakas et al., 2017; Paritosh et al., 2017). Hydrolysates and/or protein-rich FW can also substitute for commercial nutrient supplements for bioplastic production (Franek et al., 2000; Fitzpatrick and O'keefe, 2001; Vázquez and Murado, 2008). Platform chemicals for bioplastics, namely succinic acid, lactic acid, fumaric acid, and PHB, can be obtained from fermentation of sugars in household FW, such as dried foods and bakery products (Lin et al., 2013). Table 6 lists a production potential of platform chemicals for bioplastic production (Thompson and Thompson, 2004; FitzPatrick et al., 2010; Leung et al., 2012; Lin et al., 2013; Deng et al., 2016).

4. Bioconversion of fermentable substrates from food waste to bioplastics

4.1. Biological synthesis of bioplastics

Although 250 types of natural PHA producers have been identified, only a few bacteria have been adopted for commercial production of PHA. Such bacteria, including *Alcaligenes latus*, *Bacillus megaterium*, *Cupriavidus necator*, and *Pseudomonas oleovorans*, are found to convert different kinds of carbon sources into PHA. In particular, *C. necator* is one of the most widely utilized microbial strains to produce PHA (Reddy et al., 2003). Marine bacteria manifested a huge potential for bioplastic production, but their utilization for PHA production has been poorly reported (Takahashi et al., 2017). The latest research showed that the bacterium *Halomonas hydrothermalis*, *H. campaniensis* LS21 can grow in fabricated sea water as well as in FW-like mixed substrates consisting of cellulose, proteins, fats, fatty acids, and starch. The process produced approximately 70% PHB with a pH of 10 at 37 °C (Yue et al., 2014). In addition, Pandian et al. (2010) investigated *B. megaterium* SRKP-3-produced PHB from dairy waste and sea water, demonstrating a PHB yield of 0.1 g g⁻¹.

Natural bioplastic producers are classified according to an accumulation mechanism. One group of microorganisms requires limited

Table 6
Production potential of platform chemicals for bioplastic production.

Order	Platform chemical	Applications	Worldwide production (tons)	Production (kg kg ⁻¹ of glucose)	Amount of glucose required for production (tons)	Type of food waste	Amount of food waste required for production (tons)
1	Succinic acid	Polybutyrate, polyamides	1.5 × 10 ⁴	1.16	1.3 × 10 ³	Bakery product waste	2.7 × 10 ⁴
2	Lactic acid	PLA	1.5 × 10 ⁵	0.95	1.6 × 10 ⁵	Bakery product waste	3.2 × 10 ⁵
3	Fumaric acid	Polyester resin	1.2 × 10 ⁴	1.16	1.0 × 10 ⁴	Bakery product waste	2.1 × 10 ⁴
4	1,3-Propanediol	Poly(trimethylene terephthalate (PTT), polyurethane, copolyester, ethers	8.0 × 10 ⁴	0.54	1.5 × 10 ⁵	Waste cooking oil	1.5 × 10 ⁶
5	PHB	Food packaging materials, biocomposites	4.0 × 10 ⁵	0.43	9.3 × 10 ⁵	Bakery product waste	1.9 × 10 ⁶

nutrients (for instance, nitrogen, phosphorus, and oxygen) but excess the carbon sources for the biosynthesis process. The other group of microorganisms accumulates PHA through the exponential growth phase without the carbon source-starvation conditions (Khanna and Srivastava, 2005). These PHA-producing microorganisms integrated the carbon catabolic mechanisms with the PHA anabolic pathways of different kinds of carbon. Researchers found that the culture methodologies can be segregated into unadulterated cultures and mixed cultures on the basis of cultivation strategy.

4.1.1. Unadulterated culture

PHA production from unadulterated culture can be segregated into two key phases (Chen and Patel, 2011). The first is associated with cell growth due to available nutrients. Moreover, the biosynthesis of PHA is prevalent in the second phase under starvation conditions for nitrogen (N) and/or phosphorus (P). Nevertheless, growth-associated PHA-producing bacteria, for instance, *A. latus* and recombinant *Escherichia coli*, do not require limited nutrients. Nonetheless, the nutrient-feeding strategy can be applied for PHA production in a fed-batch mode. In regard to the fed-batch cultures of growth-associated PHA-producing bacteria, a nutrient-feeding strategy is essential for high-yield PHA production. This reflects that both cell growth and PHA synthesis can be enhanced as they occur simultaneously. Furthermore, the two actions require balance to avoid low PHA level.

4.1.2. Mixed culture

Mixed microbial cultures are cohorts of different microorganisms that can grow together on the same culture medium. When the nutrient growth is limited, three main steps are used to produce PHA from mixed cultures: anaerobic-aerobic process, aerobic dynamic feeding system (feast and famine), and fed-batch process (Samori et al., 2015; Hilliou et al., 2016a, 2016b). As revealed in key research works, activated sludge obtained from the wastewater treatment process has been assessed for potential mixture with FW for production of PHA. Different mixed culture modes have been investigated, including aerobic sequencing batch reactor (SBR) fed with brewery wastewater (Ben et al., 2016), dairy wastewater activated sludge fed with cheese whey (Bosco and Chiampo, 2010), and activated sludge from a waste stabilization pond fed with POME (Mohd et al., 2012). Venkateswar Reddy and Venkata Mohan (2012) carried out research on the consortia attained by operating an activated sludge system (applied for wastewater treatment) for PHA production through feeding with fermented FW. According to 16S rRNA gene analysis, the major groups of bacteria were *γ-proteobacteria* (39%) and *uncultured bacteria* (16%). In comparison with unadulterated culture, using activated sludge as a mixed culture eliminates the need for aseptic conditions, resulting in the lower operating cost.

The ideal industrial production of PHA is highly contingent on the development of strains that are capable of achieving high final cell concentrations within 60 h, including 48 h fermentation and 12-h turnaround processes. In addition, obtaining a higher PHA content from a direct and economical medium is also a key factor (Khanna and Srivastava, 2005). Genetic engineering is a critical means of developing strains that are capable of efficiently producing PHA from affordable renewable resources. Due to the development of genetically engineered bacteria, microorganisms like recombinant *E. coli* produce PHA that contains 3HB, in addition to 3HHx and 3HO monomers from soybean oil. Recombinant *C. necator* was found to contain the *Aeromonas caviae* PHA synthase gene, which successfully produced copolymer P(3HB-co-3HHx) from PKS (Loo et al., 2005; Fonseca and Antonio, 2006). Table 7 presents a comparison of unadulterated and mixed cultures.

4.1.3. Fermentation technology

With the progress in the cultivation techniques applied in large-scale production of PHA, it is identified that the type of fermentation used by PHA-producing bacteria plays a pivotal role in the production

of bioplastic. Batch and fed-batch reactors have been widely adopted in industrial fermentation processes. Fed-batch technology demonstrates higher PHA yield than batch cultivation methods. Since the concentration of N/P is limited in this process, the cell concentration can be easily controlled by adjusting the feeding rate of the carbon source. Therefore, a high initial concentration of carbon sources can be avoided to provide high osmotic pressure to the PHA producers.

A two-stage cultivation method has most commonly been adopted for industrial-scale production of copolymer (i.e., P(3HB-co-3HV)) (Hafuka et al., 2011). In the first step, bacterial cells are grown until a pre-determined cell mass concentration is achieved without being limited by the nutrient. Subsequently, cells are moved to the second-stage medium with restricted nutrients and consume only carbon source for production of PHA. Cells cannot multiply during the nutrient-deficient stage. Nevertheless, cells increase in size and weight due to intracellular accumulation of PHA as a storage product. PHB is produced by microorganisms like *Ralstonia eutrophus* and *B. megaterium* in response to conditions of physiological stress; they can be created in either pure or mixed cultures (Laycock et al., 2014). Solid-state fermentation is performed in the absence or near-absence of free water (Pandey, 2003). This process has the characteristics of low energy consumption, high volumetric productivity, and high titer of value-added products, low waste generation, and low catabolic repression (Hölker et al., 2004). As reported, various types of wastes were efficiently applied as substrates for microbial solid-state fermentation through which various products were economically produced. Easy pretreatment of solid waste can facilitate microbial colonization; this process requires grinding and material classification using various granulometries to obtain proper material homogenization and to ensure that this parameter has less of an effect on the succeeding steps. Some typical FW used for fermentation processes, namely sugarcane molasses, pressed juice, and wheat straw, are summarized in Table 8.

4.2. Physico/chemical modification of bioplastics

The conventional synthesis approach for bioplastics involves complete utilization of biomass or its single component (e.g., fiber, starch, cellulose, sugar, and lipid) by physical mixing and/or chemical cross-linking. Recent studies placed great emphasis on the conversion of biomass through separation of monomers or oligomers to create new polymers using industrial chemical biotechnology. Polysaccharides, such as starches, celluloses, and chitin, are sources of hemiacetal or hemi-ketal linkages (Abdul Khalil et al., 2012). These compounds lead to short oligosaccharide sequences or polymeric repeating units connected to other bioplastics. Altogether, polysaccharides comprise approximately 22 to 37% of FW resources (Tommonaro et al., 2016). Polysaccharides are recognized as unmodified polymers. Hence, for conversion of polysaccharides into bioplastics, bulk or surface chemical modification is required on the hydroxyl groups present in their backbone structures (Cunha and Gandini, 2010). Such modification necessitates the formation of derivatives such as chitosan. Surface modification then allows for compatibility and minimization of hydrophilicity of natural fibers via covalent bonds between the surface and matrix of the fibers. Modification of natural polysaccharides is generally based on decreasing hydrophilicity by reducing surface energy or by generating an adequate surface morphology (Cunha and Gandini, 2010; Sanchez-Vazquez et al., 2013). Fig. 5 demonstrates various bioplastics and their natural resources. However, compared with the biological synthesis of bioplastics, higher energy input is required for chemical synthesis, especially purification of polysaccharides from FW (Tommonaro et al., 2016).

4.2.1. Starch-based bioplastics via physico/chemical modification

Chemical modification of starch is well compiled in the literature. For example, starch nanocrystals can be prepared from partial acid hydrolysis on amorphous regions of starch granules (Angellier-Coussy

Table 7
Comparison of PHA production using unadulterated and mixed cultures.

Order	Biosynthesis process	Unadulterated culture	Mixed culture	Reference
1	Conditions	External nutrient limitation and excess carbon source	Internal nutrient limitation, anaerobic/aerobic or aerobic dynamic feeding	Albuquerque et al. (2010)
2	Substrate requirements	Single substrate	Waste materials	Colombo et al. (2016)
3	Growth type	Separately	Simultaneously	Kourmentza et al. (2009)
4	Media	Synthetic media	Complex media	Khanna and Srivastava (2005)
5	Fed-batch	Sequential batch reactor	Reactor configuration	Salehizadeh and Van Loosdrecht (2004)
6	Advantages	Higher volumetric productivity	Cheap substrate	Gurieff and Lant (2007)
7	Disadvantages	Expensive substrate, expensive equipment for maintaining aseptic operation	Low volumetric productivity	Kourmentza et al. (2009)

et al., 2009). Global generation of bread waste is as high as 27 million kg per year. Given that the main constituent of bread waste is a starch-based material, bioplastics derived from a succinic acid monomer are a viable option for producing bioplastics from bread waste (on the basis of the general alternation yield of 0.55 g succinic acid g⁻¹ bread). The properties and structure of starch can be altered through hydrothermal treatment without thermal degradation of the original morphology (Hoover, 2010). PLA can be produced by chemical conversion of corn or other carbohydrate sources into dextrose. Dextrose is fermented to lactic acid followed by polycondensation of lactic acid monomers or lactide. The starch can be customized under starch-filled polymer systems to improve the chemical compatibility between synthetic and starch polymers (Rahmat et al., 2009). Another type of starch polymer, known as thermoplastic starch, can be synthesized through the addition of plasticizers (e.g., polyols, glycerol, fructose, and urea). Both the mechanical and thermal energy transferred to starch dough during extrusion can help break hydrogen bonds in starch granule crystallites (Liu et al., 2009). However, the produced thermoplastics may lack mechanical strength and show high sensitivity to moisture. To improve the mechanical strength (or to chemically modify the surfaces) of these thermoplastics, they can be mixed with suitable nanofillers or blended with diverse forms of hydrophobic polymers (e.g., polyvinyl alcohol (PVA), polycaprolactone (PCL), polybutylenes succinate (PBS), PHB, and P(3HB-co-3HV) (Wang et al., 2008; Tang and Alavi, 2011).

4.2.2. Cellulose-based bioplastics via physico/chemical modification

Chemically modified cellulose is commonly employed. Cellulose serves as a linear polymer with repeating units of anhydro-D-glucopyranose, the monomer of which contains three hydroxyl groups. High-molecular-weight cellulose is highly crystalline. Conversely, cellulose exhibits poor solubility in aqueous media because of its strong inter- and intra-molecular hydrogen bonds among and within the individual chains (Sandhya et al., 2013). FW with high cellulose content includes peanut husks, citrus peels, straw, and corn. Many studies have focused on surface chemical modification of cellulose to enhance adhesion among polar OH cellulose fiber groups and also non-polar polymer backbones through creation of covalent active sites. Ethers, esters, and acetals are the most commonly used derivatives for modification of hydroxyl groups in cellulose structures.

Over the past years, various technical advancements in line the chemical modification of cellulosic bioplastic were achieved. In the papermaking industry, the following methods are commonly adopted: cellulose sialylation, esterification of the cellulose nanofibers, and cellulose ester elaboration (Cunha and Gandini, 2010). Pristine cellulose does not exhibit the physico-chemical properties of thermoplastics. However, plastic properties can be introduced into cellulose fibers by mechanical treatments. Furthermore, esterification of the hydroxyl group with the acid on the cellulose structure determines the properties of bioplastics (e.g., fluidity, resistance, and durability), which may be comparable to those of synthetic polymers. Formation of covalent

linkages of hydrophilic functional chains should effectively decrease both hydration and flow properties (HPS et al., 2016). Conversion of cellulose into polyols can also be achieved through liquefaction during manufacture of polyurethane polyesters and foams (Yu et al., 2006; Wang et al., 2008).

4.2.3. Chitin-based biopolymers via physico/chemical modification

Chitin is another type of biopolymer available in crustaceans and insect exoskeletons. Chitin is also found in other organisms, such as mushrooms and yeasts. Approximately 18 Tg of shell waste is produced annually and is a major source of chitin. Considering the low solubility of chitin, it cannot be used directly as an initial feedstock for bioplastics. However, chitin can be chemically modified to chitosan by alkaline N-deacetylation (Kumar, 2000; Rinaudo, 2006). Deacetylation results in generation of the corresponding primary amino functional group. The degree of deacetylation can be described as an actual percentage conversion of acetyl glucosamine to glucosamine. Deacetylation can significantly modify various properties (physical, chemical, and biological) of chitin (Hirano et al., 1989). Both α -/ β -forms of chitin are insoluble in a majority of solvents, whatever the natural variation in crystallinity. This insolubility serves as the main obstacle in the utilization of chitin. Chitin can be completely solubilized in acidic conditions when it is converted into its deacetylated product (chitosan) (Franca et al., 2011). Similarly, the literature provides a score of reviews on chemical modification of chitin and chitosan including dendrimer-linked hyperbranched polymers, poly (dimethylsiloxane)s, poly (2-hydroxyalkanoate)s, poly(ethylene-imine)s, block polyethers, poly (2-alkyl-oxazolines), and polyurethanes (Zohuriaan-mehr, 2005). Phosphorylation, acylation, alkylation, sulfonation, thiolation, and other chemical modifications of chitin have been explored for various purposes (Kurita, 2006; Jayakumar et al., 2008). For example, quaternized chitosan derivatives gained importance due to their high antimicrobial activity (Liu et al., 2012). Moreover, N-carboxy-methylated chitosan is being used in a variety of biomedical applications including wound dressings, antifungals, antioxidant agents, anionic polysaccharide across the intestinal epithelia, artificial bone and skin, apoptosis inhibitor, and blood anticoagulants (Chen and Tan, 2006). Fig. 6 presents a schematic diagram of chitin to chitosan conversion along with representative images of their natural resources.

Chitosan derivatives are different from pristine chitin. The rigid crystalline structure of chitosan shows high hydrogen bonding. The free protonate-able amino groups of the chitosan are soluble in mildly acidic aqueous solutions. However, they are insoluble in alkaline media and water (Pillai et al., 2009). Amino and hydroxyl moieties present in chitosan may be subject to chemical modification, allowing use in further diversified applications. In contrast, chitin only features two available hydroxyl groups for modification. Modifications of chitin and chitosan do not alter their original physicochemical and biochemical properties (Pillai et al., 2009).

Table 8
Examples of PHA production from food waste by fermentation.

Order	Strain	Bioplastic	Fermentation scale	Operation mode	Medium	Bioplastic content (%)	Reference
Unadulterated culture							
1	<i>Deffluicoccus varius</i>	PHA	600 mL reactor	SBR	Sugarcane molasses	37.3	Bengtsson et al. (2016)
2	<i>Cupriavidus necator</i> CCUG 52238	P(3HB)	100 mL flask	Fed batch	Pressed juice from oil palm frond	30.0	Zahari et al. (2012)
3	<i>Burkholderia sacchari</i> DSM 17165	P(3HB)	2 L stirred tank reactor	Fed batch	Wheat straw	70.0	Casario et al. (2014b)
4	<i>Cupriavidus necator</i>	P(3HB-co-3HV)	250 mL Erlenmeyer flask	Fed batch	Rapeseed meal, wheat bran	55.6	Cesário et al. (2014a)
5	<i>Cupriavidus necator</i> DSM 7237	P(3HB-co-3HV)	1 L bioreactor	-	Crude glycerol	78.9	Kachrimanidou et al. (2016)
Mixed culture							
6	Activated sludge consortia	PHA	1.6 L continuous stirred tank reactor	Fed batch	Brewery wastewater	39	Ben et al. (2016)
7	Activated sludge consortia	PHA	6 L reactor	SBR	Palm oil mill effluent	70	Mohd et al. (2012)
8	Activated sludge consortia	PHA	1 L reactor	SBR	Fermented cheese whey	58	Colombo et al. (2016)

4.2.4. Caprolactone-based bioplastics via physico/chemical modification

The ring-opening polymerization of ϵ -caprolactone using stannous octoate as a catalyst is an important method for preparing PCL. Due to its low glass transition temperature, the polymer chain was reported to exhibit segmental motion which should help transfer ions from one complex site to another (Ravi et al., 2016). The main procedure is chemical treatment of saccharides which requires a two-step conversion: (1) fermentation of saccharides to ethanol (and acetic acid) and (2) conversion of ethanol to cyclohexanone using chromic acid. Oxidation to cyclohexanone is achieved via a Bayer-Villiger reaction (Figure 7) of caprolactone. In general, these kinds of products are added with other natural materials to afford quality biodegradable polymers at low costs. Also, copolymerisation of lactic acid and ϵ -caprolactone has been investigated in an effort to increase degradation rates and to improve processability (Yu et al., 2014). Ishiaku et al. (2002) fabricated starch-PCL, which was later mixed with material exhibiting desired mechanical parameters. To this end, they employed sago starch which was extruded with a Rheomax at 80–95 °C under 350 bars. A desiccator having 95% H₂SO₄ was later placed with the extrudates for moisture absorption. PCL pellets (T_m = 60 °C) were placed in an internal mixer at 90 °C, followed by dried sago starch powder for 10 min. Hot starch-PCL blends were rolled with a two-roll mill to obtain thin sheets, which were stored in the desiccator immediately (Ishiaku et al., 2002).

4.3. PHA production using food waste as a substrate

The feasibility of PHA production using food waste as a substrate has been intensively evaluated, including information related to maximum PHA accumulation capacity, storage yield, and production rate. Saccharides (e.g., fructose, glucose, maltose, lactose, and xylose arabinose), together with n-alkanes (e.g., hexane, octane, and dodecane), n-alkanoic acids (e.g., acetic acid, propionic acid, butyric acids, valeric acid, lauric acid, and oleic acid), n-alcohols (e.g., methanol, ethanol, octanol, and glycerol), gases (e.g., methane and carbon dioxide), and acid (e.g., fatty acid and succinic acid) are considered key carbon sources for biosynthesis of PHA (Santhanam and Sasidharan, 2010; Poli et al., 2011). Most of the carbon applied in commercial PHA production is relatively expensive, such as unadulterated carbohydrates (e.g., glucose and sucrose), alkanes, and fatty acids. Unadulterated nutrients (e.g., amino acids and phosphate) are unaffordable, resulting in impracticality of the majority of developed biotechnological mechanisms. Cost-effective realization of the biotechnological processes is dependent on the existence of affordable nutrients that are put to use as sources of carbon, nitrogen, and/or phosphate for microbes (Liang and Qi, 2014).

4.3.1. Food waste as a carbon source

Fruits and vegetables can be used as the carbon substrates in the fermentation process to produce PHA. Some fruit products (e.g., citrus juice) are made through 50% extraction of fresh fruit, with the residues subsequently remaining as wastes. These wastes contain high amounts of sugars but low quantities of proteins. Citrus wastes are used to produce enzymes (in particular pectinase) of citric acid, succinic acid, dietary fiber, prebiotic oligosaccharides, and natural antioxidants, which can improve profitability (Matsumoto and Taguchi, 2013; Mamma and Christakopoulos, 2014). Similarly, direct fermentation of potato residues, in combination with potato starch, into lactic acid was carried out in septic systems (Smerilli et al., 2015). Preethi et al. (2012) employed hydrolyzed Jambul seeds as a sole carbon source in the production medium, and PHA accumulation in *R. eutropha* and SPY-1 reached 41.7 and 42.2%, respectively. Follonier et al. (2014) investigated nine kinds of pomace fruits, which included apricots, cherries, and grapes, as key carbon substrates. In addition, recovered pomace of apricots, cherries, and Solaris grapes were found to contain glucose concentrations of 47, 49, and 106 g L⁻¹, respectively. The eventual biomass concentration was 10.2 g L⁻¹, which included 12.4 wt % mcl-PHA, corresponding to volumetric productivity of mcl-PHA of

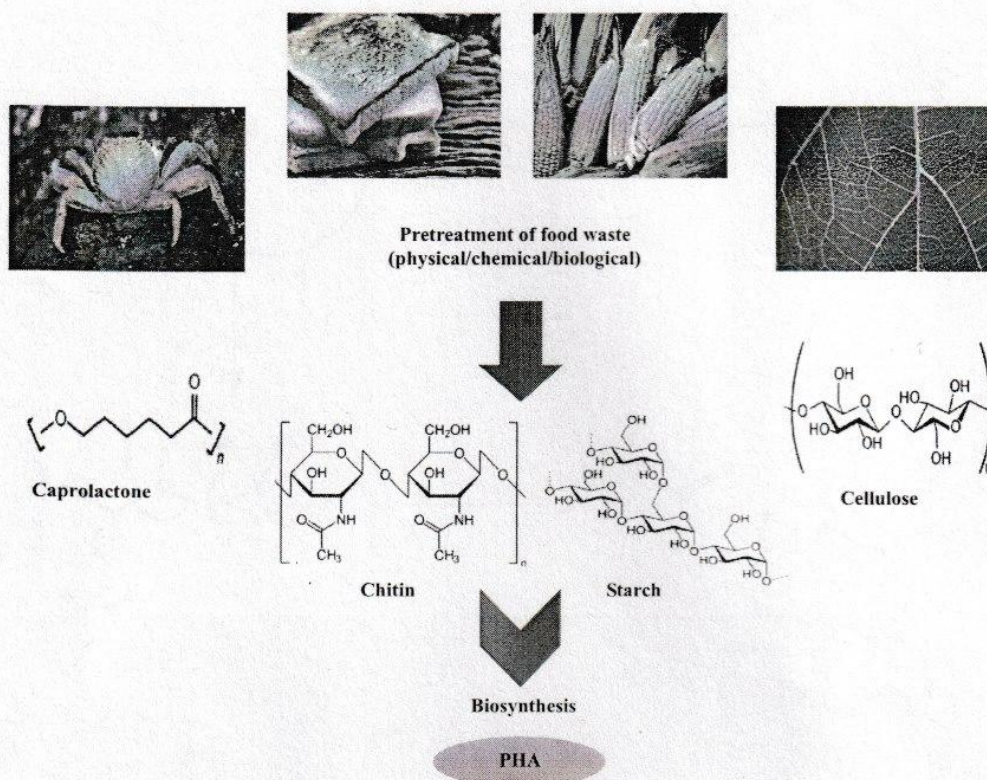


Fig. 5. List of bioplastics and their natural resources.

0.03 g L⁻¹ h⁻¹. Solaris grapes featured the highest amount of fructose; on the other hand, apricots had the lowest number of growth inhibitors. Assessment of both of these pomaces was carried out to determine their appropriateness for production of medium chain-length (mcl) PHA (i.e., 6–14 carbon atoms) in bioreactor fermentation with *Pseudomonas*

resinovorans.

Baei et al. (2010) reported production of poly-3(HB-co-27%-HV) from whey hydrolysate with the use of the *Azohydromonas lata* DSM 1123. Furthermore, *B. megaterium* CCM 2032 accumulated more than 50% of its biomass (w/w) in the supplemented whey media (Obrueca

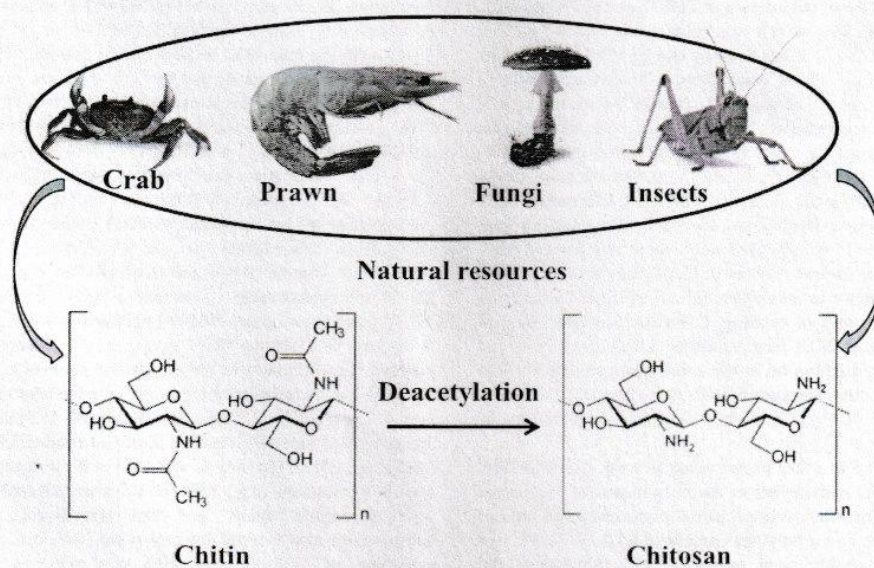


Fig. 6. Schematic of conversion from chitin to chitosan and their natural resources.

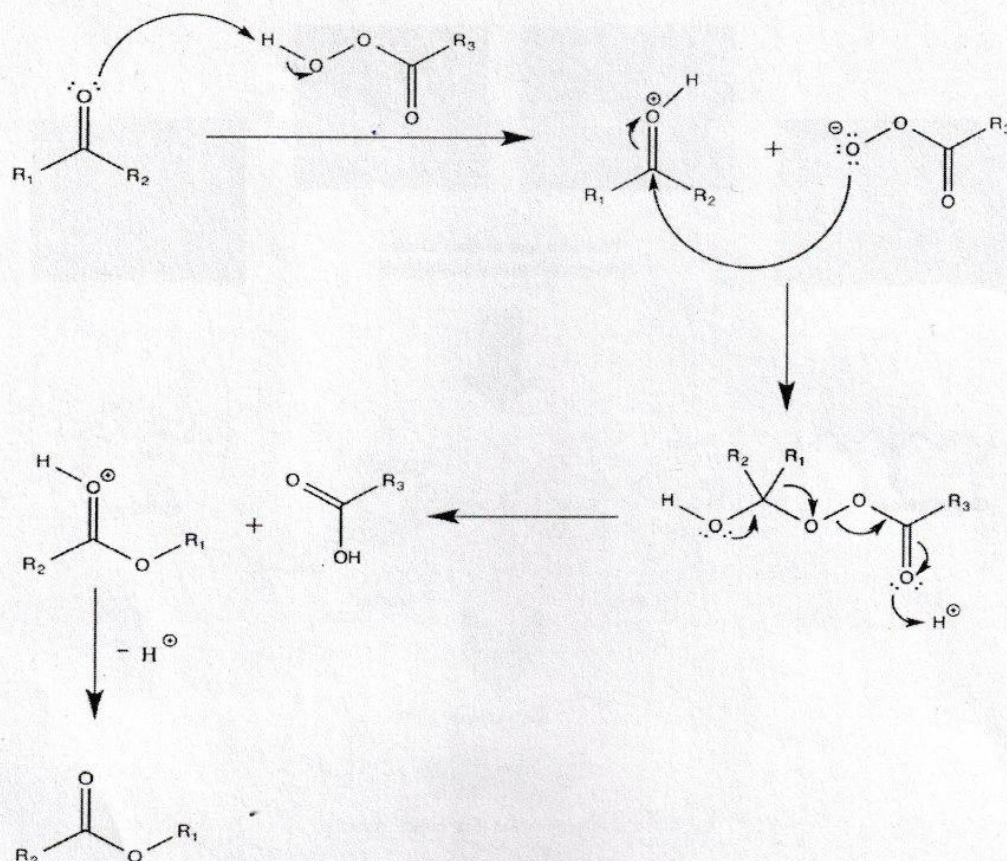


Fig. 7. Graph of Bayer–Villiger reaction.

et al., 2011). *Rhizobium etli* and *Pseudomonas stutzeri* were grown in a medium containing whey as the source of carbon, and their PHB contents were 25 and 28%, respectively (Baei et al., 2010). *B. thuringensis* IAM12077 was selected for accumulation of PHB from the FW mixture. The PHB content was 25.28% which was comparable to pure glucose (37.17%) (Shivakumar, 2012). Cheese whey can be used without any pretreatment. Obruca et al. (2011) carried out a direct transformation of the affordable residue of the cheese whey into PHB with the help of the bacterial strain *B. megaterium* CCM 2037. Using this mixture, the PHB content was enhanced by approximately 40% through introduction of 1% ethanol into the medium during the stationary stage of development (biomass of 2.87 g L⁻¹; PHB of 1.48 g L⁻¹). Laboratory-scale assays and semi-productive fermenters are needed for testing productivity when the medium is subjected to elevated cell density cultivation. There are diverse carbon sources of bioplastic production such as waste cooking oil, which contains plant, animal, or synthetic fat from frying, baking, or other types of cooking. *C. necator* has been used to produce the homopolymer PHB from rapeseed oil (Verlinden et al., 2011). Martino et al. used frying oil as the sole carbon source for PHB production in a batch cultivation system with *C. necator* DSM 428. The yield of PHB reached 0.29 g g⁻¹ with volumetric productivity of 0.14 g L⁻¹ h⁻¹ (Martino et al., 2014).

C. necator was utilized in other experiments as well; its cultivation was performed with used cooking oil as the only means of carbon for production of P(3HB). The biomass approached a concentration limit of 11.6 ± 1.7 g L⁻¹, which had a polymer content of 63.0 ± 10.7% (w/w) and volumetric productivity of 0.15 g L⁻¹ h⁻¹. Moreover, the

recovered PHB granules manifested a high level of purity above 90%; in contrast, the yield of product on the substrate was 0.77 ± 0.04 g g⁻¹ (Cruz et al., 2015). Also, palm oil-based waste cooking oil was utilized to enhance the manufacture of P(3HB) with *C. necator* H16 strain. It was generated 80% P(3HB) content (Kamilah et al., 2018). PHA was produced with the help of *C. necator* H16 in residual frying oil that had a 0.21 g L⁻¹ h⁻¹ volumetric productivity (Obruca et al., 2013). In fed-batch mode, wasted oil was used as the substrate of *C. necator* H16 for PHA production, wherein the corresponding biomass and PHA production were 138 g L⁻¹ and 105 g L⁻¹, respectively. The yield coefficient and volumetric productivity were 0.83 g PHA g⁻¹ oil and 1.46 g L⁻¹ h⁻¹, respectively (Obruca et al., 2010). PHB produced from used cooking oil was exploited as a key carbon source with help of *B. thailandensis* (Kourmentza et al., 2018a, 2018b).

Butyrate can be a precursor, which has a potential to increase (R)-3-hydroxyhexanoate content in poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) production via genetically modified *C. necator* H16 strains (Sato et al., 2015). Oleochemical industries generate large amounts of fatty acids and glycerol as by-products, both of which can be immediately put to use as feedstock for microbial PHA production (Fadzil and Tsuge, 2017). In total, 172 million kg of glycerol are generated annually through biodiesel production across the globe (Tan et al., 2013). Glycerol is well-known for its significant potential as a carbon substrate (e.g., relative to other affordable substrates like whey, sugarcane bagasse, and corn steep liquor). Validation of the optimization model with glycerol waste was carried out, wherein a maximum of 1.36 g L⁻¹ of PHA was achieved after 96 h. PHA

generation of 1.87 g L^{-1} was observed in 5 L lab-scale bioreactors with help of *Pannonibacter phragmitetus* ERC8 (Ray et al., 2016).

Spent coffee grounds (SCG) are substantial fraction of residues obtained from the coffee sector. Every year, substantial amounts of SCG are generated across the globe, followed by disposal as a solid residue. Cruz et al. (2014) cultivated *C. necator* DSM 428 in a 2 L-bioreactor with extracted SCG oil as an individual source of carbon in a bid to produce PHA. The culture reached a yield of 0.77 g g^{-1} , 78.4% polymer content, and productivity of $0.20 \text{ g L}^{-1} \text{ h}^{-1}$. Obruca et al. (2014b) examined several detoxification methods for conversion of hydrolysates of SCG into PHA by *Burkholderia cepacia*. Addition of ethanol prior to hydrolysis of SCG increased PHA yield by 25%. Extraction of oil from SCG also yielded high biomass and PHB yields (0.82 g g^{-1} of oil) compared with the other waste oils. The results may reflect the positive correlation between coffee oil and PHB yield in the presence of free fatty acids (Obruca et al., 2014a).

Lignocellulosic substances (e.g., wheat straw and rice straw) are renewable and are food process waste. They primarily consist of cellulose, in addition to hemicellulose and lignin. Both cellulose and hemicellulose are good sources of carbon in various biological mechanisms subsequent to hydrolysis of monomeric compounds (e.g., glucose, xylose, and arabinose) (Kamm and Kamm, 2007; Sandhya et al., 2013). The performance of lignocellulosic materials varies from case to case. Hydrolysate of alkali-acid pretreatment paddy straw as a source of carbon with *R. eutropha* MTCC 1472 achieved and 37.55% PHA accumulation at CDW of 19.2 g L^{-1} (Sandhya et al., 2013); wheat straw hydrolysates as the primary source of carbon for production of P (3HB-co-4HB) with *Burkholderia saccharin* in fed-batch cultures showed a productivity of $0.7 \text{ g L}^{-1} \text{ h}^{-1}$ (Cesário et al., 2014a). Sindhu et al. (2013) achieved the highest performance values ever reported for *Bacillus* species, PHB yield of 0.26 g g^{-1} and 89% polymer content. Also, pentose-sugar-rich hydrolysates can be produced from acid-pretreated rice straw as an individual source of carbon throughout production. Crude sugars were prepared from hydrolyzed corn stover with an on-site-prepared cellulose cocktail using a co-culture of *Trichoderma reesei* and *Aspergillus niger*. Moreover, PHA represented up yield of 0.243 g g^{-1} and 72.4% content from corn stover (Sawant et al., 2015). A comparison between wheat straw and the mix of commercial carbon sources (C6 as well as C5 sugars) was performed. Bioplastic content reached 60 and 70%, yield of 0.19 and 0.18 g g^{-1} , and volumetric productivity of 0.12 and $0.11 \text{ g L}^{-1} \text{ h}^{-1}$, respectively (Cesário et al., 2014b). This previous work provided a description of the fed-batch cultivations of PHA generation using actual lignocellulosic hydrolysates and demonstrated that wheat straw is valuable for biopolymer production.

Animal products and by-products (e.g., milk, cheese fats, and residues from intestines) can also be applied as substrates for PHA production. The experimental results showed a maximum specific growth rate of $0.10 \text{ g L}^{-1} \text{ h}^{-1}$ in two different fermentation temperature setups (Muhr et al., 2013). The volumetric productivity of bioplastic reached 0.036 and $0.050 \text{ g L}^{-1} \text{ h}^{-1}$, and the PHA contents were 20.1 and 26.6%, respectively. Table 9 presents the yield comparison of studies wherein FW was used as a carbon source.

4.3.2. Food waste as N and P sources

N, P, and minerals are the essential nutrients for PHA production. FW, particularly animal waste, meat derivatives, dairy products, and some vegetables, are capable of providing N and P sources for bioplastic synthesis (Jayatilakan et al., 2012; Mirabella et al., 2014). Accumulating lipids and unsaturated fatty acids are dependent on the carbon-to-nitrogen (C/N) ratio and in other cases, carbon-to-phosphorus (C/P) ratio. Constraints in N favor the collection of lipids and fatty acids in the oleaginous microbes. However, the adjustment of N content makes it difficult to use complex organic substrates. Ryu et al. (2013) enriched the consumed yeast lysate with glycerol to increase C/N ratio from 20 to 35. Smaller amounts of lipid content (by 50 and 61%) were achieved

at C/N ratios of 65 and 80, respectively.

As revealed in the former studies, the C/N/P ratio that governs the PHA synthesis is very case sensitive. Wang et al. (2007) reported that the highest PHA production yield was achieved at the C/N ratio of 100. Albuquerque et al. (2010) obtained C/N/P ratio data of 100:3:1, and PHA content reached 74.6%. Ahn et al. (2015) investigated the effects of C/N ratio in simulated rice straw hydrolysates using glucose and ammonium chloride on PHA collected by *C. necator*. Overall, the PHA collection rate was greater when subjected to more severe N-deficient conditions (for instance, C/N ratio of 360:1) in comparison with the weaker N-deficient conditions (for instance, C/N ratio of 3.6:1 or 36:1). Bioconversion yield relays controlled the conditions of microbial substrates. FW served as a promising source of P. For example, P recycling efficiency from waste is 51% in France (Senthikumar et al., 2014). Thus, options for P recycling and their application in PHA production require improvement for customization of P use.

5. Case studies of PHA products from food/agriculture waste

The bioplastic production efficiency from food/agricultural waste/biomass and its economic viability are contingent on several factors (e.g., type of waste generated in the selected area, processing cost, availability of the biomass, transport expenses, raw materials expenses, and other common industrial expenses). Apart from high productivity, industrial bioplastic production should comply with government standards for environmental pollution. As the type of waste produced in each season can vary, the productivity of bioplastics can be affected by changes in season, which hampers the supply of certain raw materials in a certain period. In general, only the feasibility of the synthesis cost has been tested at laboratory scale (Elissen and Kootstra, 2016). However, for industrial-scale production, one needs to consider or evaluate techno-economic/profitability, raw material supply, and production product markets.

Several research groups focused on using the developed methods for bioplastics through a cost analysis of the methods. However, limited case studies of biorefineries have been published. Here, considering the type of raw material and location for installing biorefineries, we reviewed some case studies that directly provide information on the production of biomass-based products, techno-economical possibilities, and cost analysis.

5.1. Case studies on palm tree biomass-based refineries

The efficient, cost-effective, and environmentally safe production of bioplastics depends upon several variables. The major factor considered for initialization of bioplastic production is availability of raw materials. The location of a biorefinery should allow a good supply of raw materials from neighboring areas. For instance, Malaysia has millions of hectares of palm trees. Thus, the availability of raw material in Malaysia made it a good destination to develop bioplastic industries or biorefineries (Shuit et al., 2009). In 2006, Malaysia was the largest exporter and largest producer (produced 15.88 million tons, equivalent to 43% of total world supply) of palm oil. The milling activity for palm oil generation and plantations left a huge amount of waste biomass, such as EFB. It was estimated that 50–70 tons of biomass waste can be generated from 1 ha of palm oil plantations. Thus, the waste biomass can be further utilized for generation of biofuels (e.g., bioethanol; 55.73 million tons of palm oil biomass is an oil equivalent of 15.81 million tons).

Moreover, some plants like palm costs can be further reduced by optimizing the location of the production plant and the type of biomass feedstock (Shuit et al., 2009). Several initiatives have been implemented in Malaysia including the Small Renewable Energy Power (SREP) program, Biogen program, EC-ASEAN COGEN program, Chubu Electric Power, and construction of a bioethanol plant to utilize biomass in energy production and to find cost-effective renewable energy

Table 9
Comparison of biosynthesis yield on different types of food waste as carbon sources.

Order	Substrate from food waste	Bioplastic	Microbial strain	Bioplastic and total plastic (kg kg ⁻¹ VSS)	Maximum concentration (g L ⁻¹)	Y (g organic acid substrate)	Y _{bioplastic} (g bioplastic g ⁻¹ organic acid)	Y _{total} (g bioplastic g ⁻¹ substrate)	Bioplastic content (%)	Bioplastic productivity (g L ⁻¹ h ⁻¹)	Characterization techniques	Cultivation time (h)	Scale	Reference	Remarks
1	Brewery waste-water	PHA	Activated sludge consortia			0.4	0.4	0.43	39		GC-MS		1 L SBR	Ben et al. (2016)	Mixed culture
2	Fermented cheese whey	PHA	Activated sludge consortia	81.4		0.24		0.70	58	0.45	GC-MS		1 L SBR	Colombo et al. (2016)	Mixed culture
3	Cheese whey	PHA	<i>Sporogonous acidogenic</i>	60–70		0.4–0.6	0.6–0.7	0.24–0.42		0.45–1.17	GC/MS		1 L SBR	Colombo et al. (2016)	Unadapted culture
4	Cheese whey	PHA	Recombinant <i>E. coli</i>	18.88		0.11	0.04	0.71	38.65	0.33	GC		fed-batch bioreactor	Pais et al. (2014)	Unadapted culture
5	Dairy waste	PHB	<i>Bacillus megaterium</i> SRKP-3		11.32						FTIR	36	3 L fermenter	Pandian et al. (2010)	Unadapted culture
6	Paddy straw	PHA	<i>R. etropia</i> MTCC 1472		7.21				37.55		FTIR, Thermogravimetric analysis, DSC	72–96	2 L stirred-tank reactor	Sandhya et al. (2013)	Unadapted culture
7	Pineapple waste	PHA	<i>Bacillus sp. SV13</i>		1.86			0.31	53.66	0.08	NMR, DSC	72	5 L fermenter	Suwastiningsih et al. (2015)	Unadapted culture
8	Spent palm oil	P (3HB-co-4HB)	<i>Cupriavidus necator</i>					0.75–0.80	81		¹³ C NMR, DSC		1 L Erlenmeyer flask	Rao et al. (2010)	Unadapted

(continued on next page)

Table 9 (continued)

Order	Substrate from food waste	Bioplastic	Microbial strain	Bioplastic yield (g bioplastic kg ⁻¹ VSS)	Maximum concentration (g L ⁻¹)	Y _{fermentation} (g organic acid g ⁻¹ substrate)	Y _{bioplastic} (g bioplastic g ⁻¹ organic acid)	Y _{total} (g bioplastic g ⁻¹ substrate)	Bioplastic content (%)	Bioplastic productivity (g L ⁻¹ h ⁻¹)	Characterization techniques	Cultivation time (h)	Scale	Reference	Remarks
9	Used cooking oil	PHB	<i>Cupriavidus necator</i> DSM 428					0.29	37	0.14	FTIR, GC, Wide-angle X-ray diffraction, measurements	27	10 L batch bioreactor	Martino et al. (2014)	Unadapted culture
10	Wheat straw, lignocellulosic	P (3HB-co-4HB)	<i>Burkholderia succchari</i> DSM 17165		105	0.22; 1.60	0.60; 0.19				NMR, SEC, DSC, TGA		fed-batch in 2 L stirred tank reactor	Cesari et al. (2014b)	Unadapted culture

Bioplastic_{end test} (bioplastic at the end of the test).Y_{fermentation} (conversion yield from soluble COD to organic acids).Y_{bioplastic} (conversion yield from organic acids to bioplastic).Y_{total} (conversion yield from soluble COD of the initial substrate to bioplastic).

sources (Ludin et al., 2004; Shuit et al., 2009; Ong et al., 2011).

In 2013, Indonesia produced 30 thousand tons of oil palm EFB, which consists of around 35 wt% of glucan, 20.3 wt% of xylan, and 3.1 wt% of arabinan (Kresnowati et al., 2015). In light of the availability of the biomass, Indonesia may also be a good choice for production of bioethanol and xylitol. On the basis of total cost for production of xylitol, a gross profit of 4.3 USD kg⁻¹ can be realized if biomass is used as a raw material. Likewise, non-food sugars produced from oil palm frond (i.e., around 42.8 wt% of glucan, 12.5 wt% of xylan, and 2.3 wt% of arabinan) can be used for economical production of P(3HB) (Zahari et al., 2015). It was estimated that the production cost of P(3HB) can be reduced to 3.44 USD kg⁻¹ by using renewable sugars generated from a palm frond, which was 41% lower than the cost of P(3HB) produced from commercial glucose. Apart from P(3HB) production, EFB was also explored for diverse applications such as biofuel for combined heat and power plants, ethanol production, methane recovery, composting (Chiew and Shimada, 2013). The use of EFB can lead to production of ethanol, methane gas, briquette, electricity, and paper (Sompong et al., 2012; Chiew and Shimada, 2013).

5.2. Case studies on banana biomass-based refineries

In 2012, the rejected and wasted proportions of total banana crops were 26.46 and 6.67%, respectively (Quinaya and Alzate, 2014). These rejected agro and food products are equally effective to produce bio-fuels, sugars, and PHB. It was theoretically demonstrated that the quantities of glucose, ethanol, and PHB produced per ton of banana were 316, 238, and 31.5 kg, respectively (Naranjo et al., 2014; Quinaya and Alzate, 2014). Moreover, banana peels are also important feed-stocks for production of diverse products. Generally, banana peels contain 40% starch that can be transformed into sugars after ripening. One ton of banana peels can be used to generate 57, 2, 25, and 5 kg of glucose, acetic acid, and methane, respectively (Quinaya and Alzate, 2014). The overall cost and margin analysis were estimated for production of PHB, glucose, and ethanol from bananas in three different scenarios (Naranjo et al., 2014). In the first scenario, PHB was a unique product, while banana peels were treated as residues scenario. The hydrolyzed starch prepared from banana pulp was used for PHB preparation. In a second scenario, glucose, ethanol, and PHB were produced in a biorefinery. In the last scenario, mass and energy integration of the processes was proposed. The cost estimated for PHB, glucose and ethanol in Scenarios 1/2/3 were 2.7/2.3/1.6, -/0.9/0.7, and -/1.3/0.6 USD kg⁻¹, respectively. In the cost analysis, Colombian labor costs of USD 2.14 h⁻¹ and USD 4.29 h⁻¹ were used, respectively, for operators and supervisors (Posada et al., 2012). In addition, the electricity, water, and vapor pressure prices used were USD 0.03044/kWh, USD 1.252/m³, and USD 8.18/ton, respectively. Moreover, corresponding economical margins of 22/43/106%, -/0/22.2%, and -/18.2/45.5% were demonstrated by comparing the market prices of the studied products. It can be concluded that scenario 3 showed mass and energy integration in the biorefinery. The production of PHB from residual banana can reduce the energy requirement by 30.6% and the water requirement by 35% (Naranjo et al., 2014).

5.3. Case studies on sugarcane biomass-based refineries

Techno-economic and environmental analysis were carried out for production of ethanol, PHB, and electricity from sugarcane bagasse in Colombia using Aspen Plus software (Moncada et al., 2013). A simulation for the techno-economical assessment was performed based on three scenarios according to the Cambodian conditions: (1) energy cogeneration, (2) arbitrary distribution, and (3) preselected pathways using optimization subroutines. The price of sugarcane that can be used for PHA production is 10 times lower than that of pure sugar (i.e., sugarcane 0.04 USD kg⁻¹ vs. glucose 0.44 USD kg⁻¹) (Suwannasing et al., 2013). In another case study, the P(3HB) production cost was estimated

to be USD 3.44 kg⁻¹ P(3HB) which is 41% lower than using commercial glucose (Zahari et al., 2015). The price fluctuation corresponding to the used methods can be stabilized by optimizing the methods relative to yield. In the study, Sugarcane bagasse was 0.0035 USD kg⁻¹, the total production cost of PHB was 3.32 USD kg⁻¹, and the total cost of refinery by-product ethanol was 0.57 USD L⁻¹. According to the market price, PHB was 3.12 USD kg⁻¹ while fuel ethanol was 1.24 USD L⁻¹. It was estimated that use of a biorefinery can reduce the selling price of PHB by 50% (i.e., from 3.12 USD kg⁻¹), making it competitive with conventional plastic (polypropylene: 1.58 USD kg⁻¹) (Moncada et al., 2013).

6. Conclusions

Bioplastic is a natural polymeric material that has been developed extensively over the last two decades due to its good biocompatibility, biodegradability, and material properties. As such, bioplastic production has become one of the most active research areas in recent years. Bioplastic can be applied in packaging industries, spray materials, appliance materials, electronic products, agricultural products, automation products, chemical media, and solvents. In the production of bioplastics, the interlinkage of biotechnology processes is a key strategy aimed at maximizing the use of food waste and increasing the potential revenue of the entire bioprocessing chain. Given that mass generation of FW is inevitable, the environmental burdens arising from waste disposal (e.g., water contamination and GHG emissions) should be mitigated. Therefore, this review demonstrated the potential of FW as a raw material for bioplastic production to address important environmental problems. Hence, physical, thermo-chemical, and biological methodologies required for preparation of bioplastic raw materials from FW are reported. Moreover, production of PHA based on un-adulterated/mixed culture and fermentation technologies was emphasized. Modifications of different FW compositions (e.g., cellulose, starch, chitin, and caprolactone) for PHA-derived products were also considered. Most importantly, governments, regulations, companies, public opinions, and consumers should work together to mitigate current environmental burdens arising from FW disposal.

Parameters

Bioplastic yield (g g⁻¹): the ratio of bioplastic concentration (g L⁻¹) and the substrate consumed (g L⁻¹) during the cultivation time.

Cell dry weight (CDW) (g L⁻¹).

Final polymer content (% w/w).

Volumetric productivity (g L⁻¹ h⁻¹): the value obtained by dividing the final bioplastic concentration over the total cultivation time (Δt , h).

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