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Agro-Industrial Waste as Potential Renewable Feedstock for Biopolymer Poly-Hydroxyalkanoates (PHA) Production

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ABSTRACT

Production of bio plastics using bacterially produced biopolymers is gaining momentum because of increasing concerns about environmental pollution caused by petroleum-based plastics, which are recalcitrant to microbial degradation and accumulate in the environment. Attempts to produce bio plastics are being made over the last few decades with little success. The mainstream substrates used for biopolymer production like laboratory-grade sugars, natural starch, and sugars from food crops like maize, vegetable oils, etc. are costly and also compete with food crops that result in a higher cost of production. In contrast, lignocellulosic waste from agriculture and related agro-industries can be used as potential feedstocks for the production of biopolymers and also, and they do not compete with food crops. Utilization of agro-industrial residues like paddy and wheat straw, corn cob, cane and beet molasses and bagasse, whey and wheat bran can replace commercial carbon sources, reducing production costs. Besides, other minor industrial wastes like extruded rice bran and corn starch, vinasse, coir pitch, empty oil palm fruit brunch, malt wastes, paper pulp hydrolysates, etc. may help further reduction in the economics of biopolymer production. This review summarizes different agro-industrial waste which can be utilized as potential renewable feedstocks for biopolymer production and their properties.

Keywords: Poly-B-hydroxybutyrate; Bioplastic; Agro-industrial waste; Lignocellulosic waste; Value-added products

INTRODUCTION

Plastics are cheap, versatile, and durable materials that have proven beneficial to society, enhancing life quality and economic activity. It plays an inevitable role in various operational sectors like food and industrial packaging, textiles, fibre, electronics, automotive, building materials, etc. These beneficial effects of plastics are attributed to their mechanical and thermal properties, such as durability and stability [1]. Following the post-industrialization era, plastic production has been increasing as never before and the trend continues still. In the year 2016-17, India's per capita polymer industries consumption was 11 kg which was very low as compared to consumption in the USA (109 kg), Europe (65 kg), and China (38 kg) Brazil (32 kg) [2]. Plastic industries are one of the fastest-growing industries in India expanding at 10-11% over the last few years [3]. Plastics are the polymers of compounds having a high molecular weight which include Polyvinyl Chloride (PVC), polypropylene (PP), polystyrene (PS), polyethene (PE), and polytetrafluoroethylene (PTFE). These plastics are not recyclable and have high persistence in the environment. The extensive use of plastics across the globe has contributed to enormous environmental pollution and heavy soil contamination. Since plastics are recalcitrant to degradation most of the time waste plastic is incinerated which produces dioxins, enhancing carcinogenic emission.

These environmental concerns have directed the research toward eco-friendly alternative sources of plastic which are biodegradable under appropriate natural conditions. Such biodegradable materials having plastic-like properties can be obtained from micro-organisms and transgenic plants using readily available cheap sources such as waste products from agriculture, forest, and related industries. Some of the important features of such bioplastics are:

i. Produced from sugars derived from renewable sources.

ii. Accumulate as intracellular storage material by many diverse groups of micro-organisms.

iii. Degrade completely to CO_2, water, and humic substances in a short period.

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Microbial biopolymers having plastic properties are mainly (Poly-Hydroxyalkanoates) PHA and are biodegradable into CO_2, water, and humic material [4]. The chemical properties such as inertness, optical purity, hydrophobicity, and the relatively high melting point as well as its bio-compactness and complete biodegradability make PHA an attractive and good alternative to synthetic plastics. Due to their complete biodegradability, more than 40 PHA's and their co-polymeric derivatives have emerged as good alternative materials. The best-characterized biopolymer among PHA's is Poly-3-Hydroxybutyrate (PHB) and many efforts have been made on its production optimization using pure culture and substrate. Among all the PHAs, PHB specifically has shown promise for the large-scale production of bioplastics as identified from its thermochemical properties like optical activity, very good barrier properties, piezoelectricity, partially crystallinity with high melting temperature and low permeability for water, oxygen, and carbon dioxide.

These bioplastics at present are not compatible with the present production equipment and existing management systems. However, the high cost of production will be the main reason for not consolidating these biodegradable polymers in many applications. The cost of bioplastics production is comparatively higher than conventional synthetic polymers and is the main constraint for its commercialization. Several efforts have been made by researchers using an approach like genetic engineering to synthesis PHB in some plants as reported in tobacco [5], sugar beet [6], flax [7], switchgrass [8], *Arabidopsis thaliana* [9], sugarcane [10], and rape and corn [11]. The most important bioplastic types in markets currently are starch derivatives, cellulosic esters, polylactic acids (PLA), PHB, and polycaprolactone (PCL).

"The proficiency and financial aspects of the assembling procedure of PHB are controlled by the carbon source, the bacterial strain, fermentation ingredients and purging of the polymer" [12]. Therefore, attempts need to be focused on the production process parameter and carbon sources that contribute to the major portion of costs. Process economics reveals that replacing traditional carbon sources (glucose) with renewable and inexpensive carbon substrates such as wastes and by-products from agriculture and related industries as feedstock may contribute to the reduction of overall production cost by 40%-50% [13]. There is a need for optimization of the process parameters for maximizing PHA accumulation and to explore the use of saccharified agri-residues for higher accumulation to decrease production costs.

MATERIALS AND METHODS

PHA production by bacteria: Historical developments

PHB was first described by a French scientist Lemoigne, in the year 1925. Following the first report, many micro-organisms like archaebacteria [14], Gram-negative bacteria [15], Gram-positive [16] and photosynthetic bacteria [17], and cyanobacteria [18] have been identified that accumulate PHB intracellularly. Macrae and Wilkinson noticed that *Bacillus megaterium* accumulated PHB homopolymer under wide glucose to nitrogen ratio in the culture medium and the absence of carbon and energy sources [19]. The notion that PHB is the only monomer of this polymer was challenged with the discovery of many different types of monomers. York et al., reported 3-hydroxyvalerate (3HV), 3-hydroxyhexanoate (3HHx), and 3-hydroxyheptanoate (3HHp) monomers from activated sewage sludge as the major and minor constituents, respectively [20]. In the year 1983, 3HHx was recognized in *B. megaterium* [16] and 3-hydroxyoctanoate (3HO) was identified from *Pseudomonas oleovorans* when grown with n-octane [21]. Till now nearly 150 different monomers of PHA have been reported and their production is dependent on specific substrates being fed in the medium [22]. There are two major groups of PHA; short-chain-length (SCL) PHA having up to five carbon atoms in a monomer and medium-chain-length (MCL) PHA which have six to fourteen carbon atoms. *Cupriavidus necator* a well-studied bacterium for PHB production was reported to produce SCL-PHA which was identified to produce 3HB, 3HV and 4HB monomers in the PHA chain [23,24]. *Pseudomonas oleovorans* and *Pseudomonas putida* are well-known accumulators of MCL-PHA which consist of (3HO) and 3-hydroxydecanoate (3HD) monomers as major components. SCL-PHAs have been produced on the commercial level by Monsanto [25]. MCL-PHAs are yet to be produced commercially because of their comparative low yield than SCL-PHA. *Alcaligenes latus*, *B. megaterium*, *C. necator*, and *P. oleovorans*, are among the widely employed micro-organisms for PHA production which have shown promise in utilizing various carbon sources like pure sugars, plant oils not excluding agro-industrial wastes. In the 1980s, a glucose-utilizing mutant of *C. necator* was employed by Imperial Chemical Industries (UK) for the industrial production of poly-(3hydroxybutyrate-co-3-hydroxyvalerate) [P (3HB-co-3HV)], which was sold under the trade name of Biopol™ [26]. The global and Indian companies engaged in biopolymer production using bacteria are given in Tables 1 and 2, respectively.

Applications of PHB

Biodegradable plastics are natural polymers having varied applications in a large number of fields due to the desired characteristics like biodegradability, biocompatibility, and negligible cytotoxicity. Therefore, bioplastics are gaining popularity as replacements for thermoplastics in different fields which include coating materials; medical and packaging (Table 1). PHBs have shown promising applications in packing in the food industry, medicine, pharmacology, and as general packaging materials. It is also used in automotive interior construction materials, agricultural materials, containers and bottles, electrical devices, manufacturing of latex paints, sanitary goods, etc. [27]. Bioplastics have also been used in tissue engineering, transplantology, pharmacology, pharmaceutical products, sutures, polymer films used in surgery and the manufacturing of non-woven materials [28]. PHAs as a source of organic acids in animal feed are also an emerging application of bioplastics. It is used for packaging materials, bags, containers, disposable cups, diapers, and also in surgical materials [29]. The inferior resistance and durability of bioplastics do not allow them to replace all petroleum-based plastics [27]. However, the main reason for not producing bioplastics on large scale is their comparative higher production cost. The carbon source is the single major important factor that controls the economics of PHA production; it is required in large amounts in the PHA production medium, accounting for just less than half of the production cost. Therefore, the selection of easily available and cheaper carbon sources is critically important.

Table 1: Global companies producing biopolymer and their applications.

Company	Country	Production Capacity	Substrate	Type of Biopolymer Produced and Product name	Application of Product
Novamot	Italy	20000 tons	Cellulose, vegetable oil, Corn, Wheat, and Potato starch	Mater-Bi	Carry bags, containers, Cutlery etc.
Arkema	France	-	Castor oil	Rilsan® PA11 and PA-10 (Polyamides)	Used in automotive industry
Metabolix	USA	-	Corn Sugar	Mirel- (PHA), SoilWraps, Mvera etc.	compost bags, can liners, shopping and retail bags, bottomless biodegradable flowerpots etc.
Riverdia	-	-	Starch	Biosuccinium®- (Succinic acid)	Polybutylene succinate (PBS), Polyester polyols for polyurethanes, coating and composite resins, Phthalate-free plasticizers, and 1,4 Butanediol
Bioamber	Canada	30000 MT	Natural starch and sugars	Succinic acid	personal care products and food additives, bioplastics, pigments, plasticizers, polyurethanes, resins and coatings
Nature works	USA	140000 tons	Corn Starch	Poly-Lactic Acid	Films and Cards, fibers and Nonwoven, Blow modeling, Foam.
Total Corbion PLA	Netherlands	75000 tons	-	Luminy ® PLA and PURALACT (Poly-Lactic Acid)	Used in packaging and food serviceware, in automotive, electronics and textiles
Succinity GmbH	Spain	10000 MT	Starch and Sugars (Basfia succiniciproducens)	Succinic acid	Used widely in bio-plastics, chemical intermediates, solvents, polyurethanes and plasticizers industries
Synvina	Spain	50000 tons	Plant based- sugars	FDCA (2,5-Furandicarboxylic acid) PEF (polyethylenefuranoate)	In the form of bottles and films for packaging of soft drinks, water, alcoholic beverages, fruit juices, food and non-food products
DuPont	USA	-	Glucose extracted from crops like, corn, soybeans, sugar- cane wheat and castor oil	Hytrel ® RS, Zytel ® Sorona ® EP-1,3 Propanediol (PDO), PTT and PA-10	Used mostly in Fabrics, Automotive, Electronics to oil and gas
SIRIM Bioplastics	Malaysia	2000 tons	Crude palm oil kernel and palm oil mill effluents	PHA	packaging, disposable plastic-based products, composites, Carry bags, container, Cutlery etc.
Bio-on	Italy	-	Sugarbeet, Cane-molasses, Fruit and potato waste, Carbohydrate, glycerol and waste frying oil	PHA	Packaging materials and Waste disposables, Garden needs, Food packaging and Industrial packaging
Newco-Lux-on	Italy	-	CO_2	Bioplastic	Will start production in 2019 end
Tate and LYLE	UK	-	Corn starch	STAR*POL ®	Ideal for use in a range of building products and adhesives, wall treatments, adhesives, tile mortar, tile grout, and oil-drilling mud
Genomatica	USA	-	Natural starch and Sugars	Bio-BDO, Brontide™ BG (1,3-butylene glycol), Bio-based Caprolactam	Athletic apparel, running shoes, electronics and automotive uses

Note: Data regarding bioplastic production and companies were taken from website of respective company.

Table 2: Companies producing bioplastics commercially in India.

Company	Year	Location	Production Capacity	Substrate	Product type produced	Cost
True Green	2011	Ahmadabad	5000 tons/year	Corn starch	Packaging materials and Waste disposables	Rs 5-7 for an 14 × 19 inch bag
Plastobag	1968	Bengaluru	-	-	Garden needs, Food packaging and Waste disposables	-
Earth soul India	2006	Mumbai	20000 tons/year	Corn, Wheat and Potato starch	Carrier bags	Rs 8 for an 14 × 19 inch bag
Ecolife	2010	Chennai	-	-	Industrial packaging, Perforation and Lamination films	-
Envigreen	2016	Bengaluru	1000 tons/ year	Potato, Tapioca, organic oil extracted from Banana, Flowers and other vegetables and Natural starch	Carry bags, trash bags, oil and grease sachet, Bin linners, laundry bags	Rs 3 for an 13 × 16 inch bag

Note: Data regarding bioplastic production and companies were taken from website of respective company

Selection of carbon and nitrogen sources for optimum PHA production

The major bottleneck in the production of PHA on a large scale which determines the performance of bacterial fermentation and the cost of the final product is the selection of a carbon source with optimum nitrogen content as PHA accumulation depends on a wider C: N ratio of [30]. Based on the culture conditions required, PHA producers are divided into two groups; Group I require an excess of carbon sources like glucose and a limiting concentration of other essential nutrients in the stationary phase. *Protomonas oleovorans*, *Protomonas extorquens*, and *C. necator* mainly belong to this group. Group II accumulates PHA during the exponential growth phase and does not require any nutrient limitation for its synthesis. Recombinant *E. coli* harbouring *C. necators* PHA biosynthesis operon, the mutant strain of *Alcaligenes latus* and *Azotobacter vinelandii* are examples of group II [31]. Throughout the studies, it is found that nearly all bacterial species produce PHA during the early stages of growth like the lag phase, log and late log phase when the nutrients are available in an ample amount and use during the stationary phase [24]. PHA being a carbon and energy-rich storage granule, is accumulated under nutrient stressed conditions mostly when nitrogen, phosphorus, and other elements are in limiting concentrations, thus different C: N ratios have a varying degree of impact on the level of PHB produced and time taken to start PHB accumulation. Studies indicate that the optimal C:N ratio and C:P ratio for producing PHB by bacteria was at 20.9 and 125, respectively [32,33]. *Rhodobacter sphaeroides* N_2O accumulated the highest PHB content (5.94 ± 0.11 g L^{-1} PHB) at the C: N ratio of 6:1 with a cell dry weight of 73.2% [34]. Furthermore, maintaining a constant C: N ratio throughout fermentation controls both specific rates of PHB production and PHB content. Excessive nitrogen feeding during the PHB accumulation phase can degrade the accumulated PHB and thus reduces PHB synthesis.

Simple sugars are the easiest and best choice of carbon sugars for most PHA producing bacteria. Other substrates like triacylglycerol and hydrocarbons have also been reported but a limited number of bacteria can utilize them. *Pseudomonas* species are versatile in their nutritional requirement and can use most of the natural compounds as carbon and energy source. Because of this versatile nature, *Pseudomonas* species have shown promise in utilizing hydrocarbons as a carbon source for PHA production. Two different bacteria can use similar carbon sources to produce PHA with varying compositions e.g. *Ralstonia eutropha* synthesizes pure P3HB using glucose [15] unlike *Pseudomonas* spp. which accumulates P3HHx using the same substrate [35,36]. Glucose is the preferred carbon source for PHA production in fermentation media for *B. subtilis* (19.51%) [37], *B. megaterium* 12 (19.49%) [24], *B. megaterium* [23], *Alcaligenes eutrophus* (12.5 to 13.0 g L^{-1}) [38]. *Bacillus* sp. JMa5 accumulated the highest PHA 25-35% (w/w) using sucrose [25], while *R. sphaeroides* preferred glucose and fructose over sucrose to produce 61 and 57% PHB of CDW [34]. Halophilic bacterium *Halomonas boliviensis* was able to utilize volatile fatty acids (VFAs), mono and disaccharides, on the other hand, fructose was the carbon source of choice for *A. eutrophus* in the mineral medium [31], whereas xylose was the least preferred C source for PHA accumulation. Unlike simple pure sugars, the mixture of laboratory-grade sugars released after saccharification of lignocellulosic biomass (glucose: xylose: arabinose) in the ratio of 4:2:1 were also shown to support PHA's production employing *Burkholderia sacchari* DSM 17165, resulting in the production of 67 g L^{-1}, 77% CDW with the sugar conversion efficiency of 0.33 g PHB g-1 sugar consumed [39].

Limiting the concentration of nutrients other than carbon is important to initiate intracellular PHB accumulation, nitrogen being the most critical one. The highest PHB accumulation (77-78.69 %) was observed in the media with complex nitrogen source protease peptone, from *B. subtilis* [37] and in *B. megaterium* 12 [24]. Complex nitrogen sources like fish peptone, protease peptone, yeast extract, casitone, phytoene, and tryptone can enhance the PHA yield as evident from *A. vinelandii* UWD strain [40]. Two strains of *Rhizobium sp.* which were grown in different combinations of carbon and nitrogen sources turned up with different results. Yeast extract mannitol (YEM) broth with different carbon (glucose, sucrose, and arabinose) and nitrogen (L-cysteine, L-glycine, DL-tryptophan, protease peptone, potassium nitrate) supported lesser PHB accumulation, but media with L-glycine and L-cysteine supported highest PHB accumulation [32].

The optimal nitrogen source and concentration for *Rhodobacter sphaeroides* was 0.02 gm L^{-1} $(NH_4)2SO_4$, giving the highest PHB concentration (5.98 ± 0.11 g L^{-1}) and PHB content (73.2% of DCW) as well as biomass (8.19 ± 0.23 gm L^{-1}) [34]. In one of the

studies, the effect of several ammonium salts on the growth and PHB production by *A. eutrophus* under the same culture conditions were evaluated and it was found that the growth kinetics were relatively the same when ammonium sulfate, nitrate, phosphate, and chloride salts were used. However, the final biomass was 18% higher in the presence of sulfate than in the presence of chloride salts. With ammonium sulfate, the yields, and productivities for total biomass and PHB were also higher than with the other salts. The nitrate salt gave higher biomass productivity (0.34 gm L^{-1} h^{-1}) than did phosphate (0.32 gm L^{-1} h^{-1}) and chloride (0.30 gm L^{-1} h^{-1}). However, PHB productivity was the same with all three ammonium salts (0.13 gm L^{-1} h^{-1}) [38]. The increased production of biomass and PHA could be partially explained by a higher rate of uptake of ammonium by *A. eutrophus* in the presence of the sulphate anion. Thus, depending upon the utilized sources of carbon and nitrogen, PHB synthesis may be selectively induced in bacterial species.

Types of substrates used for formulating growth media for optimum PHB production

Despite having a large number of applications and advantages, the commercialization of bioplastics is still a farfetched dream with very limited success. Considerable efforts are directed towards reducing the cost of production through finding and developing new efficient bacterial strains, modifying fermentation processes refining recovery processes and finding and selecting relatively cheaper sources of carbon. The overall performance of the fermentation process is dependent on the selection of a suitable carbon source [30]. Accordingly, selection of the easily available, relatively cheaper and inexpensive source of carbon which can support good growth of fermenting bacteria and accumulation of PHA seems to be the simplest way out. Several substrates for PHB production have been reported through various studies; fatty acids [41], complex to plant waste effluents oils [42], alkanes [43] along with various carbohydrates (Figure 1). Considering the availability, price, fermentation technology, PHB yield, and PHB quality, carbohydrates appeared to be the most suitable substrates for PHB production, however, vegetable oils and fatty acids are also promising [41] [44].

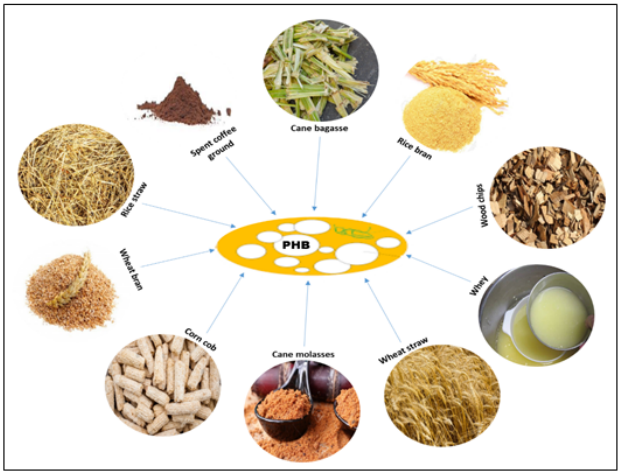

Figure 1: Agro-industrial substrates used for PHB production.

Production of PHB by microbes using lignocellulosic biomass

Lignocellulosic plant biomass comprised of cellulose, hemicellulose, and lignin are tough plant-based materials. They are abundantly available and renewable sources of carbon and energy from the forest and agriculture sector. These can be exploited for cost-effective bioplastic production, although hydrolysis and pretreatments are required for large scale production with detoxification of inhibitors produced during hydrolysis, as reviewed by Obruca [45]. Various pretreatment methods like Ammonia Fiber Expansion (AFEX), dilute acid (Sulphuric, hydrochloric, acetic, nitric acid, etc.) and alkali (sodium hydroxide) treatment either alone or in combination with the steam explosion, were used by a different group of researchers involved. The resultant pretreated material was hydrolyzed enzymatically to release reducing sugars (hexose and pentoses). Different type of lignocellulosic materials was investigated for different PHA production, including wheat and rice straw [46], oil palm empty fruit bunch, wheat bran [47], sugarcane bagasse [48], wood hydrolysates and tequila bagasse [49]. Despite various pretreatments and detoxification, the lignocellulosic materials often result in low levels of cell growth and PHA accumulation. (Supplementary Table 1: Lignocellulosic composition of various agro-residues used as a substrate for PHB production).

Paddy straw

Rice is a staple food for India as well as for many other countries around the world; rice cultivation generates a tremendous amount of straw. On average paddy straw contains 35%-45% cellulose, 25% hemicellulose and 17-19% lignin and thus provides us with an abundant source of cellulose that can be used efficiently for biopolymer production through fermentation of sugars released after pretreatment and saccharification. *Bacillus* firmus NII 0830 was found to grow in a pentose stream from acid pretreated paddy straw hydrolysates medium without any detoxification producing 1.697 g L^{-1} PHB with 89% PHB content in the dry cell [46]. This conveys the ability of the *Bacillus* strain to grow and produce PHAs under stress conditions. Similar results were reported by Sharma and Bajaj using rice straw hydrolysate (RSH) from *B.cereus* PS 10, after optimization using response surface methodology (RSM). 84.19% hydrolysis yield was reported from alkaline pretreated paddy straw [50]. *Ralstonia eutropha* ATCC 17699 produced 15% PHB with the productivity of 11.42 gm L^{-1} with 48 h of fermentation [51]. Belal and Farid evaluated the effect of different substrates and their varying concentration on PHB production by *Bacillus cereus* E6 [52]. Rice straw hydrolysates showed increased PHB productivity with increasing concentration. Acid and alkali combine pretreated and chlorinated paddy straw hydrolysates were used for PHA production using *R. eutropha* MTCC 1472 by Sandhya et al. [53]. In our studies related to PHB production using agricultural residues, paddy straw was treated with 1% sodium hydroxide followed by enzymatic saccharification using commercial fungal cellulase to release 33.29 mg L^{-1} of reducing sugars [54]. Utilizing these sugars two halophilic bacteria *Bacillus cereus* LB7 and *Burkholderia gladioli* 2S4R1 were able to produced 33.21 and 38.35% PHB on CDW basis with productivity of 0.387 and 0.309 g L^{-1} h^{-1} when grown in a novel PMS-NaCl medium [54] A summary of the results using paddy straws and other straws as carbon feedstock is mentioned in Supplementary Table 1.

Wheat straw

Wheat is a major staple food, and it also generates a tremendous amount of residues in the form of straw which can be used economically to produce PHB. The C: N ratio of wheat straw is 80:1 and is composed of 35-38% cellulose, 25-30% hemicellulose, and nearly 15% lignin. PHB production using reducing sugars (hexose and pentoses) released after pretreatment and saccharification with different bacteria ranged from 22.47% to 93% of CDW by *Hydrogenophaga pseudoflava* [55] and *Wautersia eutropha* [56] respectively. The highest PHB yield (105 gm L^{-1}) and CDW 146 gm L^{-1} was produced by *B. sacchari*, the study involved the use of the AFEX process releasing 50 gm L^{-1} of reducing sugars [57]. Along with efficient PHB production, *B. sacchari* DSM 17165 was shown to produce P-(3HB-co-4HB) (poly-(3-hydroxybutyrate-co-4-hydroxybutyrate) when Gamma-butyrolactone was used as a precursor in the fermentation medium. A new ultrasound aided alkaline pretreatment method was used to produce PHA from wheat straw. This new method resulted in 84.5% hydrolysis yield with the production of 74% PHA of dry cell weight with 0.441 g PHB g-1 reducing sugars consumed [58]. Along with the utilization of straw, the wheat-based biorefinery approach is another attractive option for PHB production. *Wautersia eutropha* was used for PHB production in a wheat-based biorefinery approach which led to the final PHB yield of 162.8 gm L^{-1} PHB, with PHB to the total dry mass conversion of 93% w/w. The efficiency of the mixed substrate (wheat hydrolysates and fungal extracts) was evaluated in terms of PHB produced using *C. necator*. The efficiency of bacterial conversion of PHB was found to be surprisingly high i.e. 0.7 gm-1 substrate [59]. This conversion efficiency is the result of the autolysis of cells at the end of fermentation and is very high compared to other wheat straw-based studies. Autolysis of bacterial cells after fermentation makes downstream processing easy as in the case of halophilic bacteria, whose cells get lysed when suspended in distilled water. The summary of PHB production using wheat straw as a substrate is given in Supplementary Table 1.

Corn cob and stover

Corn cob is lignocellulosic waste remaining after the separation of corn grains. Corn cob has a wider C: N ratio and thus takes a longer period for degradation in natural conditions. It has a rich hemicellulosic composition which results in a higher yield of pentoses compared to hexoses, after hydrolysis. Dilute acid hydrolysis of corn cob yielded 35.84 gm L^{-1} of reducing sugars, using which *Bacillus* sp. BM 37 produced 36.16% PHB of dry weight after 48 h of fermentation, which is significantly higher than the amount of PHB produced using glucose i.e. 28.6% [60]. Relatively higher PHB accumulation was reported by Getachew and Woldesenbet, using *Bacillus* sp. isolated from Arba Minch Wastewater. Shruti Patel reported lesser (0.38%) PHB production using corn cob hydrolysates by *Pseudomonas aeruginosa* [61,62]. Like corn cob, corn stover can also be exploited as a renewable resource for economical biopolymer production. A potent PHA producer *Paracoccus sp*. LL1 isolated from Lonar Lake India produced 9.71 gm L^{-1} with 72.4% PHA accumulation of cell dry mass from Corn stover hydrolysates [63]. Studies with corn bran hydrolysates showed reduced accumulation of PHB compared to corn cob and corn stover hydrolysates [64]. These studies highlight the potential of corn cob hydrolysates and related corn wastes as feedstock for PHB production with efficient pretreatment and hydrolysis. The comparative summary of PHB production from corn cob and stover is given in Supplementary Table 1.

Xylose and hemicellulosic hydrolysates

Hemicellulosic fraction mainly xylan or xylose is the second most predominant component after cellulose, but with maturity, hemicellulose content tends to increase in plant wood and also in the agricultural residue. These hemicellulosic hydrolysates rich in pentose sugars be utilized efficiently by various micro-organisms for PHB production. In one such study [55] used hemicellulosic components from wheat straw hydrolysates for PHB production using *Bacillus licheniformis* IMW KHC 3 and *Bacillus megaterium* IMW KnaC2, which produced 46.29% and 45.98% PHB respectively. Though the biopolymer production was higher with cellulosic hydrolysates, production using hemicellulosic hydrolysates was comparable. A recombinant strain of *E. coli* having genes for β-xylosidase and an endoxylanase was evaluated to produce PHAs. Though the polymer yield was low, the culture accumulated nearly 40% PHB of its dry biomass."Therefore accumulation of biomass-derived sugars in the media before their uptake by microbes is an important aspect to enhance PHA production when using plant biomass as a feedstock" [65]. On the other hand, Lopes et al. [66]. Cloned and overexpressed the xylose isomerase gene in *B. sacchari*, which partially restored the growth and PHB production capacity in media containing xylose. Overexpression of this gene does not produce any significant increase in xylose utilization capability, indicating that xylA activity is not limiting in *B. sacchari*. Studies with the catabolite repression mutant of *B. sacchari* showed that the mutant strain *B. sacchari* LFM828 would present released catabolite repression of glucose over xylose and arabinose in the mixture. Mutants showed an increase in growth and specific sugar consumption rate by 10 and 23% respectively, which helped the mutant to consume the sugar mixture in a faster way. On the other hand, the effect on PHB accumulation differs where the wild type strain was able to accumulate a higher amount of PHB using xylose alone and also as a mixture with other sugars (Supplementary Table 1).

Wood hydrolysates

Another inexpensive source of carbon for biopolymer production is hydrolysates of wood in Table 3, but its hydrolysis also leads to the generation of some of the inhibitory compounds like furfural, vanillin, and levulinic acid. In one such attempt, hemicellulosic hydrolysates of sugar maple with xylose concentration of 71.9 gm L^{-1} were used to grow and produce PHB from *Burkholderia cepacia* ATCC 17759, but the productivity was low due to the inhibitory concentration of the above-mentioned compound. Various detoxification methods were used to remove the inhibitory effect, out of which over-liming integrated with low-temperature sterilization resulted in the production of 51.4% PHA with a yield of 8.72 gm L^{-1} [67]. Wood extract hydrolysates of *Paulownia elongate* proved to be a good substrate for PHB production using *B. cepacia*. The hydrolysates contents were mostly pentoses along with a significant concentration of hexoses which were fermented to produce a PHB concentration of 65% [68]. *B. cepacia* also produced 40% PHB of biomass. Besides, levulinic acid is used as a renewable forestry-based co-substrate in the range of 0.25-0.5% (w/v), which resulted in the production of copolymer poly-hydroxyvaleric acid along with PHB [69,124]. In this way, waste wood from the forest and paper industry can find an alternative use as feedstock for biopolymer production after proper detoxification.

Table 3: PHB production using wood hydrolysates as substrate

Organism	Substrate used	Pretreatment method	Total sugars released (g L^{-1})	CDW (g L^{-1})	PHB Productivity (g L^{-1})	% Yield of PHB	Reference
Burkholderia cepacia ATCC 17759	Sugar maple hemicellulosic hydrolysates	Dilute acid pretreatment	71.9g/L	NA	8.72g/L	51.4	[67]
Burkholderia cepacia	Wood extract hydrolysates of *Paulownia elongate*	Hot-water extraction of wood chips Dilute acid hydrolysis of the concentrated wood extract	39.5g/L	8	16.8g/L	42- 43	[68]
Burkholderia cepacia ATCC 17759	Aspen derived xylose through hemicellulosic hydrolysis	NREL Clean Fractionation™	Bioplastic	Bioplastic	Bioplastic	Bioplastic	Bioplastic
(NREL CF)	1.8% (w/v)	NA	5.1 g/L	40	[69]	Bioplastic	Bioplastic
Spingobium scionense WP01T	Pinus radiata wood chip hydrolysates	high-temperature mechanical pretreatment or steam explosion under the presence of sulfur dioxide (3% w/w) and heating with steam	19-25 g/L	1.23	0.22g/g of substrate	32	[98]
Burkholderia cepacia	Spruce sawdust hydrolysates	Sawdust was pretreated with 4% H_2SO_4	15g/L	0.87- 1.57	0.11- 1.39 g/L	9.8 - 74.7	[99]
Burkholderia sacchari	Spruce sawdust hydrolysates	-do-	-do-	1.40- 2.86	0.14- 1.05 g/L	12.2 - 88.7	[99]
Pseudomonas lignicola	Waste wood hydrolysates	Wood extracts processing at 160°C for 120 min, hydrolyzed with 2% H_2SO_4	170.7 and 70.7 g/L	Bioplastic	Bioplastic	Bioplastic	Bioplastic
(85% Xylose)	NA	NA	NA	[100]	Bioplastic	Bioplastic	Bioplastic
Brevindomonas vesicularis	Saw dust hydrolysates	Dilute acid pretreatment with 2% H_2SO_4	112.5 mg/L -18.70%	253 mg/L	162 mg/L	64	[101]
Sphingopyxis macrogoltabida	-Do-	-do-	-do-	320 mg/L	231 mg/L	72	[101]

Wheat bran, rice bran and husk

Wheat bran is a by-product of the wheat milling industry. It is a coarse leftover after the separation of fine wheat flour. It is rich in fibre and cellulosic contents accounting for nearly 50% and 15-20% respectively. Wheat bran can be used as feedstock for commercial production of different types of PHA after pretreatment (Supplementary Table 1). A halophilic bacterium *H. boliviensis* produced 34% PHB of dry biomass using wheat bran hydrolysates, employing indigenous hydrolytic enzymes produced from *Aspergillus oryzae* NM [47]. Halophilic bacteria do not require strict sterile conditions during fermentation as high salt concentration suppresses the growth of other contaminant organisms, and thus can be used for commercial production at a large-scale level. The use of halophilic bacteria together with cheap and renewable substrates like wheat bran can help in downsizing the production cost. Dilute sulfuric acid hydrolysates of wheat bran and wheat bran as such without any hydrolysis were employed for PHB from *Bacillus thuringiensis* IAM12077. The bacterium produced less amount of PHB 7.4% but supported good cellular growth of 12.8 g/L using hydrolyzed wheat bran. A similar kind of result was observed in the case of direct infusion of wheat bran. This may be because of the higher content of protein and other nutrients in the substrate which led to a prolonged growth phase [70]. Hydrolyzed wheat bran was also used for PHB production using *Bacillus amyloliquefaciens* and *Nocardiopsis potent* by Mahitha and Madhuri. Rice husk is a major byproduct of the rice milling industry accounting for nearly 40% of total rice milled. This huge amount of rice husk generated every year is used for different purposes like in the packaging of fruits and vegetables and many others. Likewise hydrolyzed rice husk can also be used for the production of PHA after pretreatment. Shruti Patel employed hydrolyzed rice husk for PHA production using *Pseudomonas aeruginosa*. *Pseudomonas* cells accumulated 0.43% of PHB, but the yield is comparatively low. Similarly, results were obtained by Gowda and Shivakumar who employed *B. thuringiensis* IAM 12077 for PHA production from rice husk and wheat bran. Extremely halophilic archaea *Haloferax mediterraneii* have also been used for PHB production using extruded rice bran and extruded cornstarch in repeated fed-batch operations [14].

Bagasse

Bagasse is rich cellulosic waste generated from the sugarcane industry. A country like India, which is one of the leading countries in sugarcane production, also generates tonnes of bagasse as waste. This waste can be used for biopolymer production in a biorefinery approach including ethanol (Table 4). After proper pretreatment, these bagasse hydrolysates can also be used for PHB production by employing various strains of PHA producing micro-organisms. Yu and Stahl used dilute sulfuric acid for pretreatment of bagasse obtained from a local sugar manufacturer in Hawaii which led to the production of by-products like formic acid, furfural, and acid-soluble lignin in addition to desirable reducing sugars like glucose, xylose etc., which were inhibitory to microbial growth and need to remove or diluted to enhance cell growth in the fermentation medium [71]. Hydrolysis of bagasse released prominently glucose, xylose, arabinose, and other reducing sugars, xylose being produced at the highest concentration, 12 to 18 g L^{-1} under different severity conditions. *R. eutropha* grown in media composed of bagasse hydrolysates 50-75% v/v and mineral medium 25-50% v/v, accumulated 55.6 to 60.2% PHB in respective media with cell dry mass production of 10-11.5 g L^{-1} cell dry mass production and PHB accumulation in media containing 100% bagasse hydrolysates were statistically at par with the results above mentioned. Concentrated pretreated bagasse hydrolysates can also be used as cheap and easily available substrates with measures to reduce the concentration of inhibitors produced, which will lead to higher cellular growth and PHB accumulation. Lopes et al. showed that two strains *B. cepacia* IPT 048 and *B. sacchari* IPT 101 when grown in bagasse hydrolysates medium accumulated a significantly higher amount of PHB, as compared to those grown on laboratory-grade glucose. Treatment of hydrolysates with activated charcoal showed an increase in cell growth and thus PHB production. The choice of treatment for inhibitor removal is important as the better treatment will lead to a better yield of polymer and simultaneously a reduction in the cost involved in the production process. Bacterium *Burkholderia* F 24 isolated from soil was able to remove inhibitors in hemicellulosic hydrolysates of sugarcane bagasse and simultaneously produce PHB [72]. Removal of inhibitors in hydrolysates with simultaneous production of PHB put forward the possibility of developing a large-scale single step process involving simultaneous biological treatment of hydrolysate and PHB production. This strategy has the potential to cut down the production cost incurred on various treatment processes used to reduce the effect of inhibitors on cell growth and thus enhance productivity. Along with bagasse, molasses is the second important byproduct of the sugarcane industry. This low cost easily available concentrated residual sugar syrup can be used directly in the PHA production process as a carbon feedstock along with its other uses in ethanol production.

Table 4: PHB production using Bagasse hydrolysates as a substrate.

Organism	Substrate	Pretreatment, Hydrolysis method	Total sugars released (g L^{-1})	CDW (g L^{-1})	PHB Productivity (g L^{-1})	% yield of PHB	Reference
Ralstonia eutropha	Cane bagasse	Dilute sulfuric acid pretreatment (0.75%)	19-30 (Xylose 12-18)	10- 11.5	NA	56.5- 60.2	[71]
Burkholderia cepacia IPT 048	Cane bagasse	NA	28	4.4	0.29 g/g of substrate	53	[96]
Burkholderia sacchari IPT 101	Cane bagasse	NA	-do-	4.4	0.39 g/g of substrate	62	[96]
Burkholderia sp. F24	Cane bagasse	Dilute sulfuric acid pretreatment (0.5- 4%)	19-23	1.7 to 6.8	0.10 g/L/h	25-53	[102]

Saccharophagus degradanus	Tequila bagasse	Simultaneous degradation of cellulose with PHB production	NA	NA	1.5 mg/ml	NA	[49]
Bacillus cereus E6	Cane bagasse	NA	NA	0.98- 1.3	0.20-0.30	20-23	[52]
Bacillus sp.	Cane bagasse	Zinc chloride (60- 75%) method, hydrolyzed with acid at pH 2)	4715 µg/ml	9	5	55.55	[61]
Bacillus thuringensis IAM 12077	Cane bagasse	Acid hydrolysis + Innate enzymatic potential of Bacillus thuringensis IAM 12077	NA	4.2	NA	46.51; 39.6	[70]

Agro-industrial wastes

Molasses: Sugarcane molasses and corn steep liquor are good renewable sources of carbon and nitrogen which can be exploited as easily available low cost renewable raw materials for PHA production. Chaijamrus and Udpuay used *Bacillus megaterium* ATCC 6748 for PHB production using these raw materials [73]. With increasing concentration of corn steep liquor (6%), cell biomass increased but the total PHB production decreased, which was 43% PHB on CDW when molasses and CSL were 4% each. This indicates that nitrogen starvation leads to more accumulation of PHB. Molasses at the rate of 1% and 2% lead to the accumulation of 37.5 and 47.8% CDW of PHB with a PHB yield of 0.5 and 1.1 g L^{-1}. Beet molasses has been proved to be an excellent feedstock for biopolymer production from *A. vinelandii* UWD. It showed good growth in sugarbeet molasses medium containing nearly 2% sucrose. Biomass growth and polymer production were further enhanced when the fed-batch culture method was used with improved aeration. With the increasing concentration of beet molasses, the viscosity of the medium also increases, resulting in the inhibition of growth and thus polymer accumulation. With vigorous aeration, PHA formation increased from 1 g L^{-1} (9% CDW) to 7 g L^{-1} (70% CDW), which signifies the effect of aeration on high viscosity beet molasses medium. The final yield of PHA obtained was 63% of the biomass. With different n-alkane as precursors added in the medium, it leads to the production of various copolymers. Copolymer 3HB-co-3HV was produced when valerate was used as a precursor material with a total yield of 65% (3HB-co-3HV) of dry biomass [74]. Basnett et al., produced medium chain length PHA a copolymer of 3-hydroxyoctanoate and 3-hydroxydecanoate, P(3HO-co-3HD) from the valorization of cane molasses by *Pseudomonas mendocina* CH_5O, achieving the yield of 14.2% of CDW. Unlike conventional beet and cane molasses, Solaiman et al., used soy molasses for PHA production. *Pseudomonas corrugate* was selected for this purpose. The PHA yield was comparatively lower than beet and cane molasses, with the most prominent monomer units being 3-hydroxydodecanoate (3HDDC), 3-hydroxyoctanoate (3HOC), and 3-hydroxytetradecenoate (3HTDC) [75]. A high polymer yield of 51.37 – 61.07% was reported by Akaraonye et al., using *B. cereus* SPV. Bacterium *Pseudomonas fluorescence* A2a5, isolated from the soils of Alaska of USA, was shown to stockpile a large amount of PHB granules when grown in the sugarcane liquor medium [76]. These results are comparable with results from glucose as a carbon source as reported in various studies with *Pseudomonas* sp. *Pseudomonads* are well known for their versatile nutritional requirements and a good amount of PHB accumulation as per reports in this paper, this property can be efficiently exploited for PHB production using low cost easily available substrates like cane and beet molasses. In various studies, biopolymer production using molasses ranged from 5 to 76% of cell dry mass ranging from 3.9 to 72.6 g L^{-1}.

Whey: Whey is a major byproduct of the dairy industry. About 90% of the initial volume is generated as whey contains nearly 4-4.5% of lactose with other nutrients also. Because of high BOD whey creates severe disposal problems causing environmental pollution. Lactose in the whey can be exploited as cheap and easily available, renewable feedstock for biopolymer PHAs production. The high content of lactose in whey makes it an attractive and economical feedstock for PHB production. Yellore and Desai reported that *Methylobacterium sp*. ZP24 was able to grow on whey solution and produced 20.4% PHB of cell dry weight [77]. The incorporation of ammonium salts in media increased polymer production by up to 44%. A similar type of result was shown by Nath et al., employing cheese whey for PHB production using *Methylobacterium sp*. ZP24 showed a nearly 2.5 fold increase in yield as compared to PHB produced using pure lactose and sucrose [78]. Limited dissolved oxygen in fermenting media led to a further increase in PHB production by 0.8 fold and the most favorable C: N ratio was 5:1 (Lactose and Ammonium sulfate). Ahn et al., studied the effect of highly concentrated whey solution on PHB production by recombinant *E. coli* [79]. A 40% increase in PHB yield by *B. megatherium* CCM 2037 was reported on the introduction of 1% ethanol at beginning of the stationary phase (Table 5) [80]. In addition to major agricultural waste like paddy straw, wheat straw, xylose, hemicellulosic hydrolysates and rice and wheat bran, other agro-industrial waste can also be used for the production of PHA, which may include waste coffee ground, banana peel, walnut shell, cottonseed husk and many others.

Other agro-industrial wastes: In addition to main-stream, agro-industrial waste explained in previous sections other agro-industrial wastes have also been tested successfully as a potential feedstock for biopolymer production by bacteria. The agro-industrial wastes which can be or are being used for PHA production are given in Table 6. All of these wastes contain a significant amount of sugars which can be used economically either without or with varying levels of pretreatment. Spent coffee grounds are the lignocellulosic waste byproduct of the coffee processing industry after extracting oil from it. The viability of using this Spent Coffee Grounds (SCG) for PHB production was checked by Obruca et al. using *B. cepacia*, leading to the production of a good amount of cell biomass with 56% of PHB production on a cell dry weight basis [81]. The same group of authors [82] also used spent coffee ground oil for PHB production with *C. necator* H16 and found that oil is a better feedstock than spent coffee grounds with 70.3% PHB (CDW) production. Shruti Patel used 4 different feedstock for PHB production using *P. aeruginosa*. The highest yield of PHB obtained using rice husk is 0.43% PHB, but the yield is comparatively low.

Table 5: PHB production using molasses and whey as substrate.

Organism	Substrate	Fortification of fermentation medium	CDW (g L^{-1})	PHB Productivity (g L^{-1})	% yield of PHB	Reference
Bacillus megaterium ATCC 6748	Sugarcane molasses	Corn steep liquor	3.9	0.5- 1.1	37.5-47.8	[73]
Azatobacter vinelandii	Sugar beet molasses	NA	12	8.9	60–65/ (23% 3HV)	[74]
Recombinant E. coli	Sugar beet molasses	NA	39.5	1 g/L/h	68–85	[103]
Azatobacter vinelandii UWD	Sugar beet molasses	NA	13.4	33 1.33 g/L/h	76	[25]
Pseudomonas corrugate	Soy molasses	NA	1.5- 3.4	NA	May-17	[75]
Bacillus cereus SPV.	Sugarcane molasses	NA	6.9	1.1	51.37 - 61.07	[76]
Pseudomonas Fluorescence A2a5	Sugarcane molasses	NA	32	31g/L 0.23 g/L/h	70	[48]
Bacillus Jma5	Sugarcane molasses	NA	70	NA	25-35	[25]
Bacillus megaterium	Sugarcane molasses	NA	72.6	1.27 g/L	42.6	[104]
Bacillus subtilis	Sugar beet molasses	1% Ethanol	10.98	5.3	54.1	[105]
E. coli	Sugarcane molasses	1% Ethanol	7.63	2.8	47.16	[105]
Recombinant E. coli	Sugar beet molasses	Ethanol had –ve effect	4.26	NA	NA	[106]
Bacillus sp. CL1	Soy molasses	Anaerobiosis	0.35	0.09 mg/ml	25.4	[107]
Pseudomonas mendocina CH50	Sugarcane molasses	NA	1.9	NA	14.2	[108]
Bacillus cereus E6	Molasses	NA	1.6- 2.3	0.5- 1.1	37.5-48	[52]
Bacillus amyloliquefacience	Molasses	NA	NA	16.5 µg/ml	NA	[29]
Nocardiopsis potens	Molasses	NA	NA	6.1 µg/ml	NA	[29]
Methylobacterium sp. ZP24	Cheese whey	NA	3.8- 7.1	0.4- 2.6	20- 44	[77]
Methylobacterium sp. ZP24	Cheese whey	Limiting the dissolved oxygen supply	NA	0.45- 0.76	64	[78]
Recombinant E. coli	Cheese whey	NA	119.5	96.2 and 2.57g/L/h	77.5	[79]
Bacillus megaterium CCM 2037	Cheese whey	1% Ethanol	2.51	0.79	51.56	[80]
Bacillus cereus S3	Cheese whey	NA	1.13	0.614	54.3	[109]

Table 6: PHB production using other complex Agro-industrial waste as substrate.

Organism	Substrate	Total sugars released (g L^{-1})	CDW (g L^{-1})	PHB Productivity (g L^{-1})	% Yield of PHB	Reference
Pseudomonas aeruginosa	Cottonseed husk	NA	0.95 g/10ml	0.0018 g/10ml	0.26	[62]
Pseudomonas aeruginosa	Walnut shell	NA	0.83 g/10ml	0.0022 g/10ml	0.36	[62]
Bacillus cereus sp.	Pea shells	NA	1230	5.6	68	[83]
Bacillus thuringensis	Pea shells	NA	1035	5.6	58	[83]
Bacillus sp.	Teff straw	NA	8.3	3.2	37.4	[61]

Bacillus sp.	Banana peel	NA	7.8	2.1	25	[61]
Bacillus sphericus	Cassava bagasse	NA	2.5	0.161	6.4	[17]
Bacillus sphericus	Sesame oil cake	NA	1	0.146	14.6	[17]
Bacillus sphericus	Groundnut oil cake	NA	1.5	0.28	187	[17]
Bacillus sphericus	Jackfruit seed powder	NA	1.5	0.69	46	[17]
Bacillus sphericus	Potato Starch hydrolysates	NA	1.5	0.71	47	[17]
Bacillus sphericus	Corn flour	NA	1.5	0.049	3.3	[17]
Bacillus thuringensis IAM 12077	Mango peel	NA	7.86	3.3; 4.03	51.3; 45.6	[70]
Bacillus thuringensis IAM 12077	Jackfruit seed powder	NA	13.4	8.03; 3.93	29.32; 51.7	[70]
Halomonas boliviensis NM1	Anaerobic digest of potato peel + wheat bran hydrolysates	NA	6.6	NA	43	[47]
Haloferax mediterraneii	Extruded corn starch	NA	62.6	24.2	38.7	[14]
Haloferax mediterraneii	Vinasse	NA	NA	19.7 g/L and 0.21 g/l/h	70	[110]
Azotobacter beijerinkii	Coir pitch	30	0.498 g/100ml	2.4	48.19	[85]
Bacillus megaterium R11	Oil palm empty fruit brunch	45/60		9.32/ 12.48	51.6/ 58.5	[111]
Ralstonia eutropha	Water hyacinth hydrolysates	NA	12	4.3/ 2.0	58.3	[112]
Ralstonia eutropha	Pulp fibre hydrolysate	30	3.22/ 8.78	2.5/ 2.8	31.9/ 77.8	[113]
Recombinant E. coli	Soya hydrolysates, cottonseed hydrolysates	NA	5.95	0.226g/g of xylose	73.9	[97]
Alcaligens latus DSM 1124	Soya waste	NA	18.42	6	32.57	[114]
Alcaligens latus DSM 1124	Malt waste	NA	32	22.68	70	[114]
Comomonas sp.	Sugarcane tops hydrolysates	NA	NA	0.195	55.85	[115]
Bacillus amyloliquefacience	Orange peel	NA	NA	NA	11 µg/ml	[29]
Bacillus amyloliquefacience	Jambul seed powder	NA	NA	NA	12.8 µg/ml	[29]
Bacillus amyloliquefacience	Ragi bran	NA	NA	NA	13.6 µg/ml	[29]
Nocardiopsis potens	Orange peel	NA	NA	NA	13.8 µg/ml	[29]
Nocardiopsis potens	Jambul seed powder	NA	NA	NA	11.6 µg/ml	[29]
Nocardiopsis potens	Ragi bran	NA	NA	NA	6.6 µg/ml	[29]
Cupriavidus necator H16	Orange peel	NA	9.01	7.34	81.5	[116]
Cupriavidus necator H16	Date seed	NA	6.8	4.6	73	[117]
Cupriavidus necator NCIMB 11599	Oil Palm fround juice	54	40	30.5	75	[118]
Activated sludge	Rice grain distillery water	5.4	6.6	2.7/ 0.028g/L/h	40	[86]
Activated sludge	Jowar grain-based distillery water	0.225	NA	0.021 g/L/h	42.3	[86]
Escherichia coli LS5218	Cellulose hydrolysates	NA	5.6	3.3	59	[119]
Cupriavidus necator	Jerusalem artichoke hydrolysates	NA	NA	NA	70	[120]
Alcaligenes eutrophus	Tapioca hydrolysates	NA	106	61	58	[121]
Alcaligens latus	Sugar Maple sap	NA	4.4	3.41	77.6	[122]

Alcaligens latus	Sugarbeet juice	NA	9.23-	0.12 g/L/h	66	[111]
Bacillus sp. SV13	Pineapple juice	112.47	4.2	1.621/ 0.0604 g/L/h	56	[123]
Burkholderia cepacia	Spent coffee ground hydrolysates	50.1	4.91	2.69	56	[82]
Cupriavidus necator H16	Spent coffee ground oil	15.1% coffee oil	14.2	10	70.3	[81]
Cupriavidus necator DSM 428	Spent coffee grounds	90% oil extraction yield	16.7	Batch mode-6	78.4	[124]
Recombinant E. coli	linerboard recycling waste	127.3	NA	6.88- 7.65	NA	[87]
Cupriavidus necator	volatile fatty acids from anaerobic digest of shredded office papers	521.50 mg L^{-1}	1.71	0.20 g g-1 of VFA	53.5	[88]

Other substrates with decreasing PHB yield are cottonseed husk 0.26%, walnut shell 0.36% and corn cob meal produced 0.89 gm 10 mL^{-1} of cell biomass with 0.38% of PHB accumulation in 24 h. A significant level of PHB accumulation was reported from *Bacillus sp*. and *Enterobacter aerogenes* supplemented with pea shells [83]. Arba Minch wastewater isolate, *Bacillus* sp., was tested for PHB accumulation by [61], it produced a significant amount of PHB using, teff straw at 37.4%, corn cob hydrolysates at 51.6% and banana peel with 25%. Ramadas et al., used seven different agro-waste as a substrate which showed significant PHB production. The highest yield 46% of dry cell weight was obtained with Jackfruit seed powder. A similar type of result was obtained with potato starch hydrolysates. Other substrates with decreasing yield are groundnut oil cake 18.7%, sesame oil cake 14.6% and wheat bran, cassava bagasse and corn flour with less than 6% PHB production.

RESULTS

In addition to PHB production using starch, a strain of *B. thuringiensis* IAM 12077 has also shown encouraging results in producing PHB from nine different agro-industrial waste viz. rice husk, wheat bran, ragi husk, Jowar husk, jackfruit seed powder, mango peel, potato peel, bagasse and straw. Mango peel supported the highest PHB accumulation [70]. Van-Thuoc et al. used *H. boliviensis* to produce 43% PHB using anaerobic digest of potato peel in combination with wheat bran hydrolysates (1%w/v+1%w/v) [47]. Vinasse is effluent waste from the ethanol industry, which creates serious disposal problems. Activated charcoal pretreated was used to detoxify vinasse before fermentation using *H. mediterraneii* which accumulated 70% of PHA (max 19.7 g L^{-1}) [84] Coir pitch is a by-product of coconut fibres and waste material from the coir pitch industry. The presence of high lignin content provides high stability and resistance to degradation by microorganisms. Degradation of coir generally takes decades and lignin also contains a major proportion of celluloses and hemicelluloses, which can be utilized as substrate for PHB production following chemical pretreatment and enzymatic hydrolysis. Sathesh Prabu and Murugesan employed *Azotobacter beijerinkii* for PHB production from delignified coir pitch, resulting in the production of 2.4 g L^{-1} of PHB from 3% coir pitch hydrolysates. Growth associated PHB accumulation in *Methylobacterium sp* [85]. ZP24 from disaccharides like lactose, sucrose, and cheese whey was reported by Nath et al. Studies using unrefined *Mahua* flowers as a sole carbon source have shown PHB accumulation up to 51%, 31%, and 22% by *Bacillus* sp-256, *Rhizobium meliloti* and *Spingomonas* respectively [86]. Scheel et al., used sugars enzymatically hydrolyzed from linerboard recycling waste for the biosynthesis of (PHA) using Recombinant *Escherichia coli* harbouring PHA biosynthesis genes [87]. PHB synthesis using crude hydrolysates showed a two-fold increase over pure sugars. The use of volatile fatty acids from an anaerobic digest of shredded office papers showed enhancing effect on PHA production using *C. necator*. Almost 2.24 fold increased PHA yield in the nutrient-limited medium over nutrient content medium was achieved with PHA content of 53.50% of dry cell weight [88-124]. The use of such and many other easily available and cheaper substrates can lead to a cut down in production costs and commercialization of bioplastics.

DISCUSSION AND CONCLUSION

The major challenge in the commercial production of PHB is its high production cost, out of which a major portion is incurred by carbon sources. Finding the alternative relatively cheaper and renewable sources of carbon is of paramount importance to downsize the production cost. Agro-industrial residues have come up as potential feedstocks for PHB production but not without limitations. Releasing of sugars from the lignocellulosic complex involves a series of pretreatment and saccharification steps, which need to be taken care of. The severity of acidic and alkaline pretreatment results in the production of inhibitory compounds along with the sugars, which interferes with growth and fermentation by the bacterial cultures resulting in slower growth, longer fermentation periods, and reduced production of PHB. There is a need to find suitable pretreatment methods producing a lesser number of inhibitory compounds and improved ways of treating these inhibitory compounds to neutralize their effect on fermenting bacteria. Though there is a lot of work published in this area, still we have to go a long way toward achieving the economy in bioplastic production and bringing down petrochemical plastic production. The development of PHA as a potential substitute material for some conventional plastics has drawn much attention due to its biodegradable and biocompatible properties of PHA. Though the higher production cost of PHA is a major bottleneck, it has got potential applications in various industries. Constant efforts are being taken up to reduce the cost of production and achieve the goal of economical production of various biopolymers worldwide by developing new recombinant strains of good PHA accumulators, engineering various kinds of PHAs, use of easily available and renewable feedstocks and searching for novel strains of microorganisms which can accumulate an even higher concentration of PHAs. The ongoing commercialization activities

in several countries are expected to make PHA available for applications in various areas in the immediate future.

Lignocellulosic biomass can be exploited as a cheaper and renewable substrate for biopolymer as its being used in the production of bioethanol (second-generation bioethanol production). The concept of converting biomass into varied valuable products through a biorefinery approach by various industries is gaining importance and PHA's can become the dominant product of these bio-refineries, helping the polymer compete with petrochemical-based plastics thus bringing environmental sustainability. Along with agro-industrial residues weed and algal biomass can come up as alternative feedstock for PHB production. Carbon dioxide concentration in the environment has increased tremendously following the post-industrialization period. An Italy based firm Newco-Lux-on has shown promise in exploiting the CO_2 present in the environment for biopolymer production. Along with finding alternative sources of carbon, searching, and engineering microorganisms for the higher accumulation of PHA, higher carbon utilization efficiency should also go side by side. It would be desirable if we can engineer the bacterium for cell lysis at the end of fermentation, which will facilitate easy extraction of polymer excluding the involvement of the costlier chemical, thus further economizing commercial bioplastic production.

ETHICAL APPROVAL

Not applicable.

CONSENT TO PARTICIPATE

Not applicable.

CONSENT TO PUBLISH

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AUTHOR'S CONTRIBUTION

Dr Rajeev Kaushik and Dr Surender Singh substantially contributed to the conception and design of the article and the interpretation of the relevant literature. Mr. Mayur Naitam compiled the literature and drafted the article. Mr. Govind Singh Tomar helped with data collection and literature review. Dr Lata revised it critically for important intellectual content.

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DECLARATION OF COMPETING INTEREST

The authors hereby declare that there is no conflict of interest for authorship of the manuscript in the subject matter or materials discussed in this manuscript.

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