ISGC 2022

N°156 / OC
TOPIC(s) : Biomass conversion / Polymers or composites

Polyhydroxyalkanoates (PHAs) as a platform for producing bio-based chemicals, solvents and biopolymers

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PURPOSE OF THE ABSTRACT

Polyhydroxyalkanoates (PHAs) are bio-based polyesters produced by a variety of organisms able to accumulate PHA granules inside the cells as energy and carbon storage. Thanks to their biodegradability under aerobic and anaerobic conditions, PHAs could meet the demand for bio-based plastics from renewable resources in the next future. The aim of the present work is to demonstrate that PHAs could also be intended as a polymeric platform and give building blocks that can be converted again into PHAs or other bio-based chemicals/solvents (Figure 1). To this purpose, herein we proposed four conversion pathways (a-d) that can convert intracellular or isolated PHB (the homopolymer of the PHA family) into:

a) two bio-based solvents, methyl 3-hydroxybutyrate (MHB) and methyl 3-methoxytbutyrate (MMB), usable to extract PHB from bacteria.1 The synthetic approaches were optimized in terms of yield, solvent/chemical consumption, and E-factor, while the PHB recovery was optimal independently from the bacterial biomass (freeze-dried biomass or microbial slurry; single strain bacteria or mixed microbial populations) and PHB content;

b) crotonic acid (CA) through a novel thermolytic distillation process at mild conditions (170 °C and 150 mbar), and without the need of any catalyst that selectively breaks PHB bonds and gives high yield (92% from isolated PHB) and purity (> 98%) of CA.2 Such a drop-in approach has a carbon footprint of 4.8 kgCO2eq/kgCA, while the fossil-based production of CA has a carbon footprint of 13.5 kgCO2eq/kgCA; moreover, a preliminary evaluation of the energy consumption of various depolymerization approaches indicated that the thermolytic distillation consumes 20-25% less energy than previously reported methods.3 Bio-based CA can replace fossil-based CA in several applications (e.g. the synthesis of co-polymers with vinyl acetate) or be exploited in other ways, like pathway C and pathway D described below;

c) ?-keto acids through a photochemical approach applied on bio-based CA.2 The photocatalytic addition (promoted by tetrabutylammonium decatungstate - TBADT) of aliphatic and aromatic aldehydes to CA has been explored under solar-simulated light irradiation. TBADT triggered the in-situ formation of valuable acyl radicals from the corresponding aldehydes, thus inducing the desired hydroacylation via radical conjugate addition;

d) renewed PHB through the use of bio-based CA as a substrate for microbial fermentation, giving complete recycling of PHB via a ?depolymerization-polymerization? tandem approach.3 The yield of PHB (0.6 g PHB per g of CA), final PHB content (63%), and PHB-molecular weight (1.5 MDa) confirmed the technical feasibility of this tandem approach, with a 55% overall yield. Moreover, the energy demand of the entire process applied to waste containing PHB resulted comparable to the energy required for obtaining fermentable sugars to be used for feeding bacteria that accumulate PHB.

FIGURES

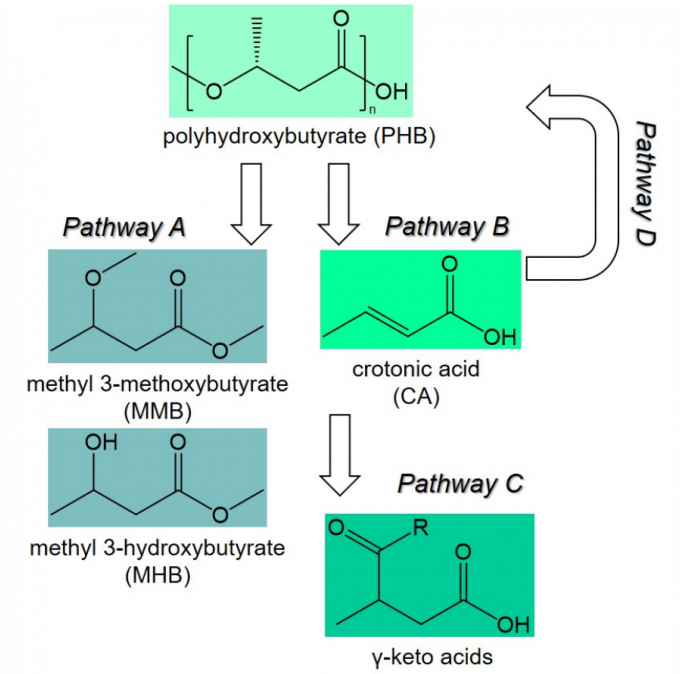

FIGURE 1

FIGURE 1

Polyhydroxybutyrate (PHB) platform to produce bio-based solvents (pathway A), drop-in crotonic acid (pathway B), gamma-keto acids under solar-light irradiation (pathway C), and renewed PHB (pathway D).

FIGURE 2

KEYWORDS

polyhdroxybutyrate | crotonic acid | photocatalysis | bio-based solvents

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