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Techno-economic assessment of poly-3-hydroxybutyrate (PHB) production from methane—The case for thermophilic bioprocessing

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ABSTRACT

A major obstacle preventing the large scale production of polyhydroxyalkanoates (PHAs) has been the lack of a reliable, low cost, large volume feedstock. The abundance and relatively low price of methane therefore marks it as a substrate of interest. This paper presents a techno-economic assessment of the production of poly-3-hydroxybutyrate (PHB) from methane. ASPEN Plus was used for process design and simulation. The design and economic evaluation is presented for production of 100,000 t/a PHB through methanotrophic fermentation and acetone-water solvent extraction. Production costs were estimated at \$4.1–\$6.8/kg PHA, which compares against a median price of \$7.5/kg from other studies. Raw material costs are reduced from 30 to 50% of production for sugar feedstocks, to 22% of production for methane. A feature of the work is the revelation that heat removal from the two-stage bioreactor process contributes 28% of the operating cost. Thermophilic methanotrophs could allow the use of cooling water instead of refrigerant, reducing production costs to \$3.2–5.4/kg PHA; it is noted that PHB producing thermophilic methanotrophs are yet to be isolated. Energy consumption for air compression and biomass drying were also identified as significant capital and operating costs and therefore optimisation of bioreactor height and pressure and biomass moisture content should be considered in future research.

1. Introduction

Polyhydroxyalkanoate (PHA) bioplastics are widely recognised as outstanding candidates to replace conventional plastics. Their mechanical properties are good, they are biodegradable, and unlike many alternatives, they don't rely on oil-based feedstocks. Further, they are the only commodity polymer that can be synthesised intracellularly, ensuring stereoregularity. However, despite offering enormous potential for many years, they are still not making a significant impact. This is broadly because commercial uptake has been limited by variable performance (inconsistent polymer properties) and high production costs of the raw polymer. The cost of the raw polymer is strongly impacted by the feedstock used [1]. With the world currently experiencing a natural gas boom, there is growing interest in utilising methane for synthesis of higher value products.

This paper presents the first techno-economic assessment of large scale production of poly-3-hydroxybutyrate (PHB) from methane. The specific objectives of the work are to:

- Design a full process for utilising methane as a feedstock for large scale PHB production, incorporating biotechnology specific for utilising gas substrates as well as state-of-the-art non-chlorinated solvent extraction based downstream processing.
- Perform a techno-economic assessment on the design, with the view to evaluating process viability, and to identifying challenges regarding (i) utilising methane as a feedstock and (ii) biotechnology for PHB production more generally.

Industrial production of PHB, the simplest form of PHA, typically involves accumulation of polymer in pure cultures using plant-derived carbon sources as the feedstock. Table 1 summarises current large-volume commercial PHA production from pure cultures. DaniMer Scientific and Meredian Inc. opened the doors to the world's largest PHA manufacturing plant in October 2012 [2].

Pure culture production using plant-derived feedstocks can compete with food supply, and potentially have indirect adverse impact on natural environments; such processes require expensive

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Table 1
Current industrial production of polyhydroxyalkanoates.

Company name	Carbon Substrate	Product name	Production (t/a)	Ref.
DaniMer Scientific and Meredian Inc.	Canola oil	Seluma^{TM}	15,000	[2]
Metabolix/Antibióticos	Switchgrass, camelina, sugar cane	Mirel, Mvera^{TM}	10,000	[3]
TianAn Biologic Material Co	Corn/cassava starch	ENMAT	10,000	[4]
Tianjin GreenBio	Corn starch	SoGreen^{TM}	10,000	[5]
Bio-on	Beet or sugar cane	Bio-on^{TM}	10,000	[6]
Shenzhen Ecomann Biotech. Co	Corn starch		5000	[7]
PHB Industrial	Sugar cane	Biocycle^{TM}	2000	[8]
Kaneka	Vegetable oil	AONILEX^{TM}	1000	[6]
Biomer	Sugar (sucrose)	Biomer P^{TM}	1000	[9]
Newlight Technologies	Waste methane	AirCarbon^{TM}	>500	[10]

refined substrates and need sterilization, limiting widespread commercialisation [11]. Techno-economic studies have shown that a major cost of pure culture production is the carbon feedstock, estimated to be up to 40% of the product cost [1,12,13]. Consequently many research groups are investigating the potential of using waste streams for PHA production, such as dairy whey waste, waste lipids, sugar industry waste streams, agricultural crop residues, petrochemical waste, syngas and glycerol [14].

The problems with waste streams, however, are their limited abundance and distributed nature. In contrast, methane is a cheap, abundant and widely available carbon source. Also, the robust, self-regulating nature of mixed methanotrophic cultures [15] offers the opportunity to operate under non-sterile conditions, thereby reducing operating costs on an industrial scale. Over 300 bacterial strains, including the methanotrophs: *Methylocystis paravus, Methylosinus trichosporium, Methylosinus sporium, Methylocystis* spp. GB25, MTS, and *Methylocella tundra* [1], have shown potential to synthesise and store PHB.

The economic feasibility of PHB production from methane was first reported by Listewnik, et al. [16]. They studied relatively small-scale production (500 t/a) and found biosynthesis of PHB from methane to cost \$8.5/kg. This was extrapolated to \$15.1–18.3/kg when accounting for downstream processing costs. It was estimated expansion to 5000 t/a could enable a 30–35% price reduction, but considering PHB can be produced for \$2.00–6.50/kg and bio-alternatives are in the order of \$2–5/kg (Table 2), the cost would still be relatively high. Still, Newlight Technologies have commercialised proprietary greenhouse gas-to-plastic technology, ramping up from pilot scale to 500+ t/a production in 2013 (Table 1) [10]. This is the first technology to utilise methanotrophs for industrial scale PHA production, converting waste methane from wastewater treatment facilities, anaerobic digesters, landfills and energy facilities [17]. Other companies, like Mango Materials, are now following, albeit at relatively small scale.

For large scale production (in the order of 100,000 t/a), a readily accessible and reliable feedstock is needed. Here the feasibility of using methane for the production of PHB is investigated. A process is proposed for production of 100,000 t/a of PHB with at least 98% purity. Capital and operating costs were estimated.

A feature of the work is analysing the energetics for large scale PHB production. At the scale investigated, very large bioreactors are required, which reduces the surface area to volume ratio, limiting the potential for heat removal. The benefit of operating the bioreactors at higher temperatures is considered, highlighting the potential for thermophilic methanotrophs to reduce production costs. For PHB production from methane, this is the first investigation into the energy requirements for maintaining bioreactor operating temperature and for downstream processing.

Table 2
Price comparison for biodegradable polymers.

Plastic	Price Range (US2014\$/kg)	Reference
Starch-derived bioplastics	2.60–5.80	[18]
Poly(lactic acid) (PLA)	2.00–3.45	[19,20]
Poly(3-hydroxybutyrate) (PHB)	2.00–6.50	[19,21,22,23]

2. Methods

2.1. Process development

A simplified process flow diagram (PFD) for PHB production from methane is shown in Fig. 1 with detailed PFDs and mass balance tables available in the Supplementary material. A list of the key model assumptions in given in Table 3.

The process can be broken down into the following steps: (i) bioreactors: for biomass growth and for accumulation of PHB, (ii) biomass treatment: to harvest and dry PHB rich biomass, (iii) solvent extraction: to release PHA from the PHB rich biomass, and (iv) PHB precipitation and purification: to recover and dry the PHB product.

2.1.1. Bioreactors

A two stage growth and accumulation strategy for PHB production by a mixed methanotrophic culture was selected. Mixed methanotrophic cultures have been found to self-regulate, giving stable populations under non-sterile conditions [15], thereby offering significant savings in capital and operating cost. The bioreactors for both growth and accumulation were assumed to operate under an elevated pressure of 5 bar in the head space to improve gas-liquid mass transfer efficiency [15]. Operating temperature was set at 38 °C. Due to high volumetric gas requirements air-lift bioreactors with a concentric internal draft tube were selected to reduce mixing costs [26]. The flue gas from both growth and accumulation was set at 2% (v/v) methane. The gas was assumed to be sent to a catalytic converter for heat recovery and low pressure steam generation. This step has not been explicitly considered in the design. It is expected to be approximately cost neutral compared with purchasing the heating that the catalytic converter could have offset.

Stage one of the two stage growth and accumulation strategy involves continuous biomass growth. At the large scale considered here, operating the bioreactors at the dilution rate of 0.17/h reported by Wendlandt et al. [24,25] may be unrealistic due to mass transfer limitations, so a conservative value of 0.085/h was assumed. The bacteria will store low levels of PHB in the growth phase (assumed PHA content in biomass of 3 wt%).

Stage two refers to the accumulation phase. Biomass is semi-continuously harvested from the growth reactors for 24 h batch accumulations. Methane and air are supplied to the accumulation