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Research article

Life cycle assessments of bio-based sustainable polylimonene carbonate production processes

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ABSTRACT

Biomass is a promising feedstock for the production of sustainable biopolymers, which could offer a significant reduction of the adverse environmental impacts associated with conventional petroleum-based polymers. To further evaluate their potential, this study investigated the environmental impacts associated with the production of the newly proposed biopolymer polylimonene carbonate. Different feedstocks (citrus waste and microalgae) were selected and a conceptual process design from limonene oxidation to polymer synthesis was completed. Using life cycle assessment, the potential for energy integration and the contributions of individual process sections on the overall process environmental impacts were thoroughly analysed. The results showed, that sustainable polylimonene carbonate synthesis was limited by the use of tert-butyl hydroperoxide as the limonene oxidation agent and consequently, a more environmentally-friendly and energy-efficient limonene oxidation method should be developed. Based on the economic analysis, the polymer cost was estimated to range from \$1.36 to \$1.51 kg^{-1}, comparable to the costs of petrol-based polystyrene (\$1.2 to \$1.6 kg^{-1}). Moreover, this study found that both feedstock selection and the biowaste treatment method have significant effects on the process environmental impacts, and a carbon negative process was achieved when applying the waste biomass for electricity generation. Therefore, it was concluded that future process designs should combine polymer production with the co-generation of energy from waste biomass.

1. Introduction

Polymers, such as polylactic acid (PLA), polyethylene terephthalate (PET) or polystyrene, represent an important global commodity, both industrially and domestically. They can adopt a large variety of configurations, with highly specialised properties, making them applicable to a wide range of areas including electronics, healthcare products, toys, packaging materials, and coatings (Hottle et al., 2013; Zhu et al., 2016). The annual consumption of polymers in the US alone has been estimated at around 31 million tonnes whilst the global production of polymers has exceeded 260 million tonnes since 2009 (Zhang et al., 2017; Thompson et al., 2009). In addition, global polymer production between 2009 and 2015 was reported to have increased by up to 20%, indicating a huge potential global market in the future (Han, 2017).

To improve the sustainability of the polymer production processes, the last two decades have seen increasing efforts to identify renewable and more environmentally friendly raw materials, particularly biomass, to replace the fossil carbon resources used in traditional polymer synthesis (Zhu et al., 2016; Miller, 2013). These include agricultural biomass, citrus wastes, and microorganisms, *e.g.* microalgae and cyanobacteria (Darensbourg et al., 2014; Winkler et al., 2015; Isikgor and Becer, 2015; Gandini et al., 2016; Wang et al., 2015; Paggiola et al., 2016), which have been used for the synthesis of bio-based polymers such as polycarbonates, polyesters, and polyurethane (Winkler et al., 2015; Hauenstein et al., 2016b; von der Assen and Bardow, 2014). To improve the usability of these sustainable feedstocks, new reaction routes have been proposed and compared to the traditional fossil based methods (Darensbourg et al., 2014; Ellis et al., 2014; Peña Carrodeguas et al., 2015).

Amongst the newly proposed biopolymer candidates, particular attention has been given to polylimonene carbonate (PLC), produced by the reaction of limonene with carbon dioxide (Hauenstein et al., 2016b; Peña Carrodeguas et al., 2015; Ciriminna et al., 2014). PLC has similar properties to polystyrene (Dalaeli et al., 2005), one of the major fossil based polymers with a predicted global production of 700,000 tonnes $year^{-1}$ by 2020 and annual sales volume of \$28.7 billion (Wood, 2016). As polystyrene is

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predominantly made from hydrofluorocarbons (HFC-134a), with global warming potentials around 1000 times that of CO_2 (U.S. Environmental Protection Agency, 2016), there is a great drive to identify more environmentally friendly alternatives. Limonene, required for PLC synthesis, can be obtained from a range of biomass sources, including orange peels, microalgae and other citrus wastes, with an estimated global production of 70,000 to 100,000 tonnes year^{-1} (Ciriminna et al., 2014; Dalaeli et al., 2005; Davies et al., 2014), indicating a stable supply for industrial PLC production. Furthermore, as PLC synthesis directly consumes CO_2, the overall process has the potential to actively sequester carbon, and therefore be carbon negative (*i.e.* avoiding greenhouse gas (GHG) emission) (Hauenstein et al., 2016b; Dalaeli et al., 2005). Consequently, PLC has great potential to replace polystyrene in the near future.

Previous studies employed life cycle assessments to investigate the potential environmental impacts of limonene production from citrus wastes (Roberts, 2012) and microalgae (Jahandideh et al., 2017), whilst a process design for the oxidation of limonene to PLC was published recently (Dalaeli et al., 2005). Moreover, optimal reaction conditions for PLC precursor oxidation and monomer polymerisation have been proposed by different studies (Hauenstein et al., 2016b; Peña Carrodeguas et al., 2015; Hauenstein et al., 2016a). In spite of these achievements, the environmental impacts of the entire PLC production process, ranging from feedstock selection (algae *vs.* citrus) to downstream PLC synthesis, have not yet been explored, and therefore the process sustainability, economic viability, and industrialisation feasibility are unknown.

To address this open challenge, the current study aimed to design a conceptual PLC production process and conduct a high-level life cycle assessment, facilitating the industrialisation of PLC production at an early stage of the research. In addition, a preliminary economic analysis was carried out to estimate and compare the potential cost of PLC against the price of polystyrene. The next sections will provide a detailed explanation of the design and life cycle assessment of the PLC production process, followed by the results and conclusions discovered in the current research.

2. Methodology

2.1. Process description

The overall polylimonene carbonate (PLC) production process can be divided into four distinct operating stages: (1) Production of limonene, (2) Production of the oxidant tert-butyl hydroperoxide (TBHP), (3) Limonene oxidation and (4) PLC synthesis (Fig. 1). Moreover, limonene can be produced either from citrus waste or engineered microalgae, and each of these sources will be considered in turn.

2.1.1. Limonene production from citrus waste

Limonene is an important component of all citrus fruits (Dalaeli et al., 2005), and particularly abundant in wastes from the orange juice industry (3.8 wt%) (Ciriminna et al., 2014). Consequently current limonene production is mostly focused on these wastes and is usually conducted in two stages. Initially, citrus oils (also called 'cold press orange oil') are extracted from the orange juice during the juicing process, before additional citrus oils ('expressed orange oil') are recovered from the orange peels using steam extraction. Together, the collected citrus oils contain ~95% limonene, which is further purified using either vacuum distillation or winterisation (freezing oils) (Dalaeli et al., 2005; Roberts, 2012). As this process has already been analysed in detail in the literature, including orange collection and use of the extracted orange peels as cattle feed (Roberts, 2012), it was chosen as the standard route for the production of citrus-based limonene in the current research.

2.1.2. Limonene production from algae

An alternative to the conventional, citrus-based limonene production route, is the use of microalgae and cyanobacteria, genetically engineered to produce limonene (Davies et al., 2014; Jahandideh et al., 2017). This route promises substantial advantages (*e.g.* high growth rate and solar energy utilisation efficiency) over other solar energy and CO_2 derived biomass (del Rio-Chanona et al., 2016; Zhang et al., 2015). Recently, a detailed process design for algal limonene and energy co-production was proposed, and the critical limonene productivity, at which the process starts to break even, was identified through process economic analysis (Johnson et al., 2016). The process considers limonene as the major product, whilst algal biomass waste is anaerobically digested for the production of hydrogen and methane, which are subsequently combusted in gas turbines for electricity generation. This configuration was adapted as the standard route for the production of algal limonene in the present work, to allow comparison against the citrus-based process.

To model algal limonene production, the process was split into five stages (detailed introduction in Supplementary): (1) Algae cultivation in a photobioreactor, (2) limonene recovery via absorption and distillation, (3) algae biomass recovery (including settling, floatation, and electrocoagulation), (4) anaerobic digestion (used for biogas and electricity generation), and (5) wastewater treatment (for water recycle) (Jahandideh et al., 2017; Johnson et al., 2016). Previous work tested two different algal limonene productivities; a real-case limonene productivity of 1.8 mg L^{-1} h^{-1} and a much higher productivity value of 55.5 mg L^{-1} h^{-1} (Jahandideh et al., 2017). In contrast, the present study adapted a limonene productivity value of 4.5 mg L^{-1} h^{-1}, consistent with the highest algal limonene productivity reported in the literature (Davies et al., 2014).

2.1.3. Limonene oxide production

Prior to converting limonene into PLC, it must be oxidised into limonene oxide. This can be achieved using a variety of oxidants such as molecular oxygen gas, hydrogen peroxide and epoxides under specific conditions (Bonon et al., 2014; Pena et al., 2012; Casuscelli et al., 2004). However, most available data stem from laboratory scale experiments, requiring numerous assumptions to correlate the reaction selectivity and conversion efficiency to large scale systems (linear scale-up) (Montazeri and Eckelman, 2016). A particularly promising oxidant is tert-butyl hydroperoxide (TBHP), due to its mild operating conditions (room temperature, 1 bar), high single-pass conversion (75%) and selectivity (88%) Eq. (1) (Dalaeli et al., 2005). Therefore, TBHP was selected as the oxidant for limonene oxide synthesis in the current study.

$$C_{10}H_{16} + C_4H_{10}O_2 \xrightarrow{\text{rt. 1 bar}} C_{10}H_{16}O + C_4H_{10}O \quad (1)$$

Initially, limonene and TBHP are fed to the reactor at a molar ratio of 1:1. The reaction is conducted at room temperature and atmospheric pressure in the presence of catalyst (silica dissolved in solvent) (Dalaeli et al., 2005). The resulting product mixture containing limonene oxide, tert-butyl alcohol (TBA), and unreacted limonene and TBHP (side reaction is neglected) is sent to a distillation column (MIDSEP) for the separation of TBA and TBHP from limonene and limonene oxide. Further separation of limonene and limonene oxide and of TBA and TBHP is achieved in two additional columns. Eventually, unreacted TBHP and limonene are recycled back to the reactor, limonene oxide is sent to the PLC production stage, and TBA is returned to the TBHP regeneration stage. Heat exchangers are used to pre-heat the product mixture and cool the outlets from the distillation columns.

2.1.4. Tert-butyl hydroperoxide regeneration

Although tert-butyl hydroperoxide (TBHP) is a commercially available chemical commodity, the environmental and life cycle

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