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Sustainability metrics for a fossil- and renewable-based route for 1,2-propanediol production: A comparison

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ABSTRACT

Historically, 1,2-PDO had always been exclusively produced from fossil resources and many routes have been industrially commercialized. More recently, new strategies based on renewable resources have allowed for the development of technology for the commercial production of 1,2-PDO from glycerol. In the present study the fossil-based chlorhydrin process is taken as a reference and compared to the catalytic hydrogenolysis of glycerol route to evaluate which one is the most advantageous in terms of sustainability. To this extent, a concise and practical approach is employed that allows for an early stage comparison based on four preselected green metrics that estimate material and energy efficiency, economic added value and land use. The evaluation shows that the renewable-based routes can provide a viable alternative to the petrochemical route and both approaches must therefore be considered in a global process. Importantly, the production of valuable co-products needs to be included in such an assessment as these strongly influence its outcome.

1. Introduction

Diols, including ethylene glycol, propylene glycol, 1,3-propanediol, neopentyl glycol, 1,3-butanediol, to name a few, are commercially important polyols and find application in the polymer industry or as platform molecules, for instance. Of these diols, 1,2-propanediol (1,2-PDO) or propylene glycol is a particularly important chemical feedstock with an annual global demand exceeding the 1 million tons [1]. It is a non-toxic chemical intermediate approved as food additive that is extensively used for the production of polyester resins (34%), and as a solvent or additive in cosmetics and pharmaceuticals (18%), liquid detergents (11%), functional fluids (21%) and others (fragrances, tobacco humectants, paints) [2–4]. The use of 1,2-PDO in functional fluids (antifreeze, de-icing and heat transfer) is growing because of concerns over the toxicity associated with ethylene glycol-based products for humans as well as for animals [5]. In contrast, 1,2-PDO is biodegradable and easily metabolized by the human body; moreover, it has a low irritating capacity even at high concentrations [6].

The current industrial production of racemic 1,2-PDO involves two different routes: (i) a petrochemical route, starting from propylene through propylene oxide (PO) and, to a lesser extent, (ii) a bio-based route using glycerol (Gly) as the starting raw material. Both these routes produce racemic 1,2-PDO. Examples of 1,2-PDO production from other renewable feeds, e.g. by hydrogenolysis under alkaline conditions directly from cellulose or hemicelluloses or from polyols obtained from these polysaccharides, have been reported but have, to the best of our knowledge, not yet been commercialized [7]. Indeed, as with many other potential renewable platform molecules, various different chemo- and biocatalytic production routes are often being proposed and studied [8,9]. To judge the sustainability and feasibility of these routes with respect to the petrochemical ones that they propose to replace, metrics are needed to allow an early sustainability assessment. Many methods have been developed, varying in the considered criteria and in the extent to which these approaches aim to be comprehensive [10]. Such comprehensive sustainability assessments often require a considerable investment of resources and access to large amounts of detailed information, data that are not always available depending on the stage of development of the new route that is being assessed. In this paper, we have applied a more concise, practical approach to assess sustainability metrics, which is based on the criteria discussed by Sanders and Sheldon, to

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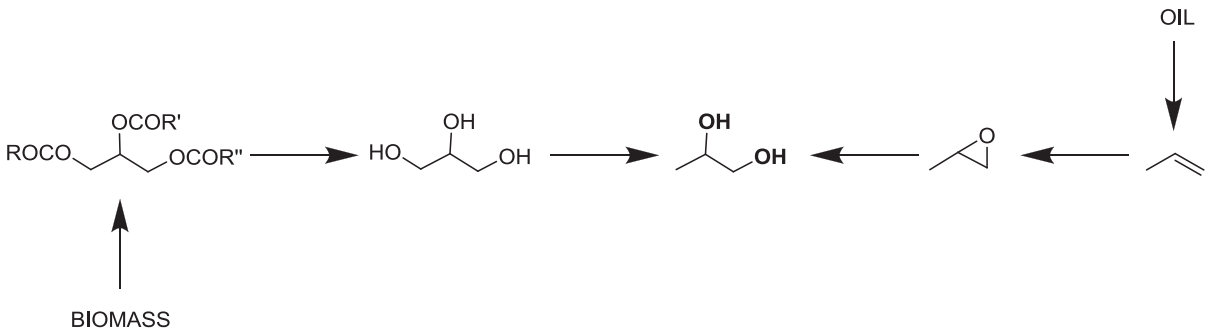

Scheme 1. The petrochemical and bio-based routes to 1,2-PDO that are compared in this study.

the renewables-based production of 1,2-PDO. More particularly, a petrochemical and renewable-based route to 1,2-PDO (Scheme 1), are assessed in terms of efficiency, environmental and economic impact using four metrics, i.e. material and energy efficiencies, economic added value and land use, as defined previously [11].

2. Production

2.1. Petrochemical processes

Nowadays, the commercial production of 1,2-PDO is achieved mainly by the hydration of propylene oxide (PO), which is in turn derived from propylene. The key step in the petrochemical route is the synthesis of the PO, for which there are five main technologies, which are commercially operational at different scales: (i) the cumene hydroperoxide process (CHP, Sumitomo Chemical Company); (ii) epoxidation with hydrogen peroxide (HPPO, Dow-BASF); (iii) the propylene oxide/styrene monomer process (PO/SM, LyondellBasel and Shell Company); (iv) the propylene oxide/t-butyl alcohol process (PO/TBA, LyondellBasel and Huntsman Corporation) and, finally, (v) the chlorhydrin process (CHPO, Dow) (Schemes 2 and 3). The use of silver and gold catalysts for the direct epoxidation of propene with molecular oxygen is also under study, but these alternative approaches are not yet viable and require improvements in selectivity and catalyst stability [12].

Currently, the PO/SM and the chlorhydrin processes are the dominant ones in terms of production volume (Fig. 1) [13]. A major drawback of the CHPO process is that it requires the use of chlorine, which is an expensive, toxic and corrosive reagent. On the other hand, the PO/SM process yields to the production of one equivalent of styrene. This chemical is not considered as waste since it finds application in bulk chemistry. Similarly, the PO/TBA process produces an equimolar amount of tert-butanol that can be used directly or dehydrated to isobutene, which in turn is mainly converted to MTBE [12].

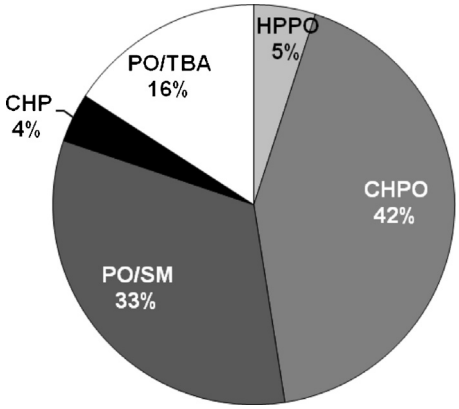

Fig. 1. Different technologies used to obtain propylene oxide (PO) using the petrochemical route. CHPO: chlorhydrin process; PO/SM: propylene oxide/styrene monomer process; CHP: cumene hydroperoxide process; PO/TBA: propylene oxide/t-butyl alcohol process; HPPO: hydrogen peroxide oxidation process.

To reduce the footprint and environmental impact of PO production, alternative, more environmentally friendly routes have been developed, including the direct catalytic epoxidation of propylene by hydrogen peroxide (produced via the anthraquinone process) under mild reaction conditions (HPPO process). Epoxidation catalysts include titanium-silicalites or methyltrioxorhenium/pyridine N-oxide catalytic systems [14]. The overall efficiency of this approach is directly linked to effective recycling of the anthraquinone required for the hydrogen peroxide synthesis step, for which significant improvements have been reported [15]. A comparative LCA analysis of the HPPO and PO/TBA processes has been recently reported, suggesting that the HPPO and PO/TBA processes are actually comparable in terms of production costs and environmental impact [13]. As the CHPO process continues to be the main route that is practiced at the industrial scale, this particular process was chosen as the benchmark petrochemical route for this comparative study (Fig. 1) [16–18].

The production of 1,2-PDO via the chlorydrin process takes place in three main steps (Scheme 3). First, propylene reacts at a temperature between 35 and 50 °C and a pressure of 2–3 bar with an aqueous chlorine solution. The resulting mixture of α- and β-propylene chlorohydrin (C_3H_7OCl; ratio 9:1) is then dehydrochlorinated at 25 °C (step 2) under highly alkaline conditions (using NaOH or $Ca(OH)_2$). The propylene oxide formed is driven out of the reaction mixture with steam to avoid its hydration and subsequently purified by distillation. While high yields are claimed for this process (90–95%), a significant drawback of this route is the large amount of brine effluent that is produced, estimated to be in the range of 30–60 kg/kg of propylene oxide [17]. The chlorine products obtained are obtained as economically non-usable solutions and to prevent this loss, a strategy is typically adopted to recycle the chlorine from this effluent via electrolysis [14].

In the third and last step, the obtained propylene oxide is combined with water in a molar ratio of 1:15 at 125 °C under a pressure of ~20 bar. Under these experimental conditions, a mixture of propylene glycol, di-propylene glycol and tri-propylene glycol is obtained in a ratio of 100:10:1, respectively. A higher selectivity to the desired product (propylene glycol) can be obtained with higher ratios of water/propylene oxide, but such a modification has an impact on the energy costs and final price of propylene glycol.

2.2. The bio-based route

Several routes for the production of propylene glycol from renewable feedstock are being explored. Most studied is the hydrogenolysis of sugars or sugar alcohols at high temperature