



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



Alberto Marinas<sup>a</sup>, Pieter Bruijninx<sup>b</sup>, Jamal Ftouni<sup>c</sup>, Francisco J. Urbano<sup>a</sup>, Catherine Pinel<sup>c,\*</sup>

<sup>a</sup> Faculty of Sciences, University of Córdoba, Campus de Rabanales, Marie Curie Building, E-14014 Córdoba, Spain

<sup>b</sup> Inorganic Chemistry & Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

<sup>c</sup> IRCELYON, UMR 5256 CNRS/UCBL, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

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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.

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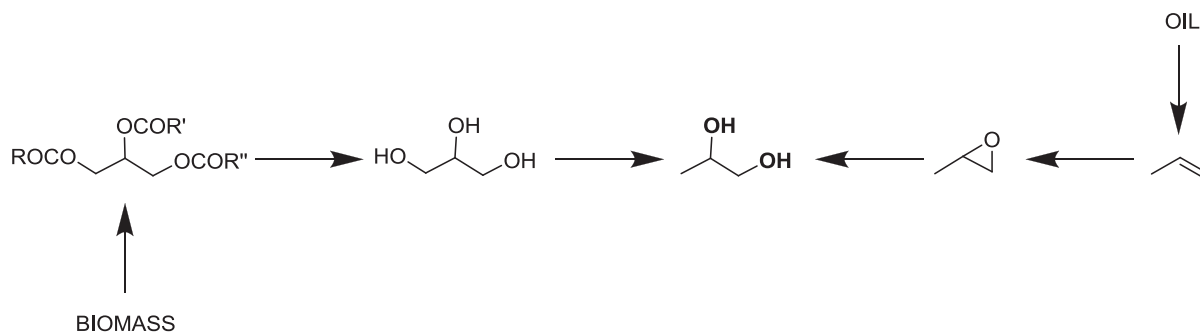
## 1. Introduction

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

\* Corresponding author. Tel.: +33 04 7244 5478.

E-mail address: [catherine.pinel@ircelyon.univ-lyon1.fr](mailto:catherine.pinel@ircelyon.univ-lyon1.fr) (C. Pinel).



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

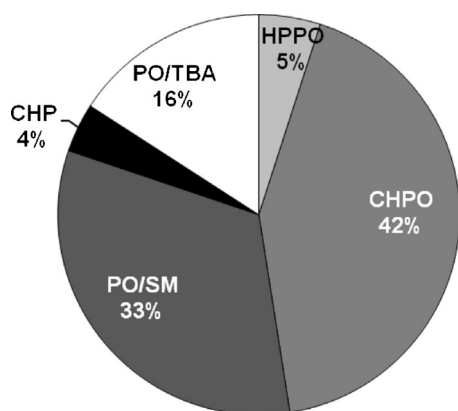
the renewables-based production of 1,2-PDO. More particularly, a petrochemical and renewable-based route to 1,2-PDO (Scheme 1), are assessed in terms of efficiency, environmental and economic impact using four metrics, i.e. material and energy efficiencies, economic added value and land use, as defined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



**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.

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].

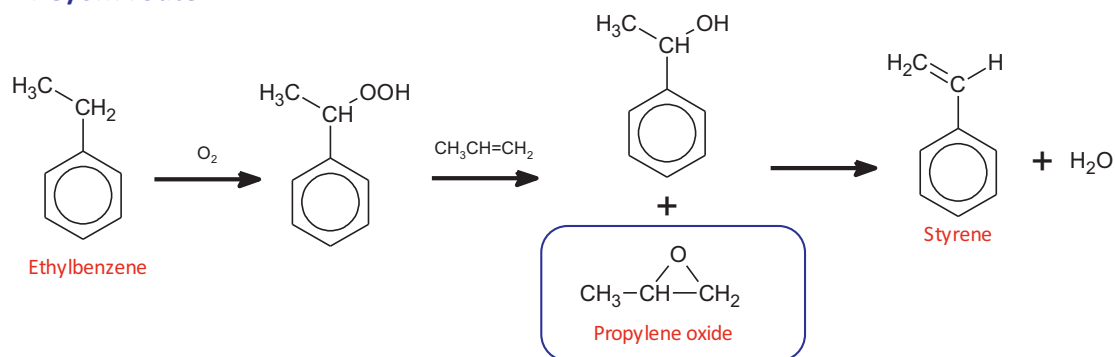
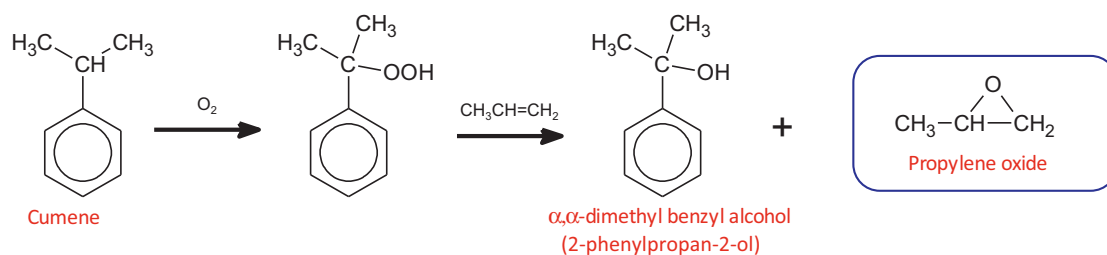
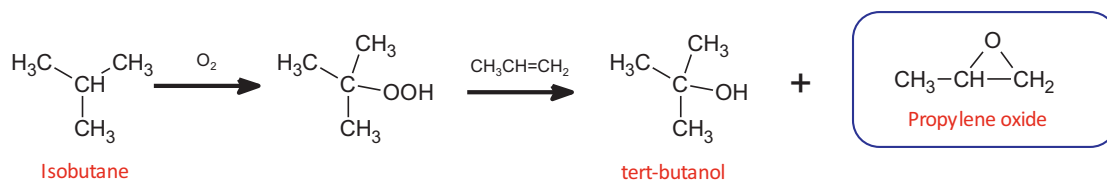
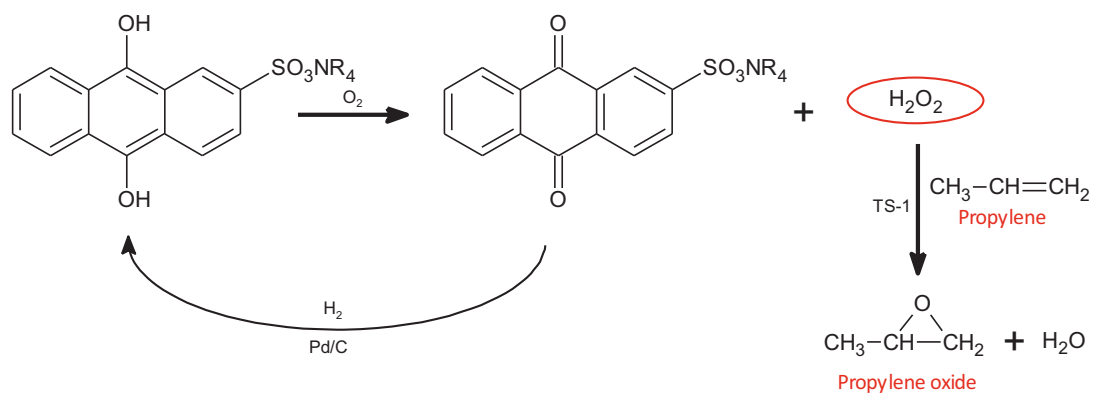
To reduce the footprint and environmental impact of PO production, alternative, more environmentally friendly routes have been developed, including the direct catalytic epoxidation of propylene by hydrogen peroxide (produced via the anthraquinone process) under mild reaction conditions (HPPO process). 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 chlorhydrin 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  $\alpha$ - and  $\beta$ -propylene chlorohydrin (C<sub>3</sub>H<sub>7</sub>OCl; ratio 9:1) is then dehydrochlorinated at 25 °C (step 2) under highly alkaline conditions (using NaOH or Ca(OH)<sub>2</sub>). 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 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.

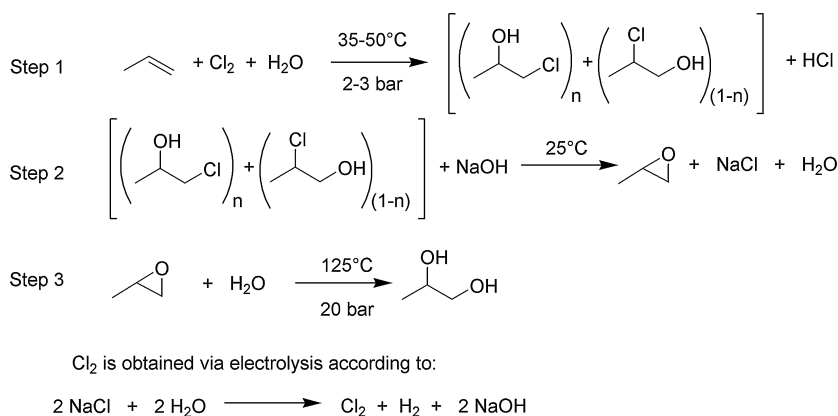
### 2.2. The bio-based route

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

**PO/SM route****CHP route****PO/TBA route****HPPO route****Scheme 2.** Petrochemical alternatives to the chlorhydrin process for the production of 1,2-PDO.

and pressure in the presence of supported metal catalysts and under alkaline conditions [19,20]. Such processes typically yield a mixture of propylene glycol, ethylene glycol and glycerol as the main products, which can be separated by distillation. Starting

from sorbitol, 1,2-PDO yields of up to 62% have been reported while direct hydrogenolysis of cellulose yielded mainly ethylene glycol [21,22]. These polysaccharide or higher sugar alcohol-based routes are currently still in an early stage of development.



**Scheme 3.** The three-step route to 1,2-PDO from propylene involving the chlorohydrin process for propylene oxide formation (steps 1 and 2), followed by a final epoxide hydrolysis step.

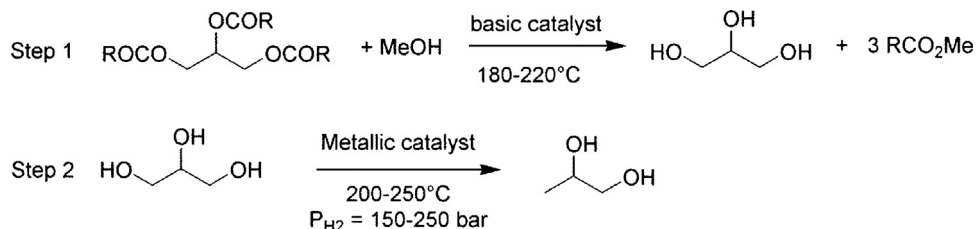
On the other hand, the alternative, bio-based route that uses glycerol as a raw material has become a serious alternative to the petrochemical routes. The production of glycerol is directly associated with the biodiesel industry, as it accounts for about 10 wt.% of the output of a triglyceride-based biodiesel production process. Glycerol can be obtained in different purities depending on the process adopted for its production. Using classic transesterification technology, a crude glycerol product of about 85% purity can be achieved (Scheme 4). Many energy-intensive purification steps are needed (3–4) to eliminate salts and other impurities from this crude glycerol to finally obtain technical or even reagent-grade (USP) glycerol. These additional purification steps obviously directly influence the final price of glycerol. Since many of the impurities are derived from the homogeneous catalysts used in the transesterification process and neutralization steps required during workup, many efforts have been devoted to the development of alternative, heterogeneous processes. For instance, the Esterip process, developed by Axens, uses heterogeneous catalysts to obtain technical glycerol directly. This technology yields salt-free pure glycerol of higher purity (>98%) while generating practically no waste products. The transesterification step is typically carried out at 180–220 °C in the presence of a zinc alumina catalyst in this process [23].

According to the European Biodiesel Board, total European production of biodiesel reached 8.6 Mt in 2011, mainly from Germany and France, corresponding to 0.8 Mt of glycerol production. Nowadays, many outlets exist for glycerol, which is used either directly or serves as a raw material for a large number of industrial applications, including food, pharmaceuticals, fuel additives, adhesives, explosives, etc. The large amounts of glycerol produced by the biodiesel industry cannot be accommodated, however, by these existing outlets and new routes for glycerol valorization are therefore required [24,25]. Valorization into 1,2-PDO by a selective hydrogenolysis process would turn the oversupply of glycerol into an “advantage for the biodiesel industry” [17]. Many catalytic

systems and operating conditions are reported for this transformation, a topic that has been recently comprehensively reviewed [8,9,26,27]. Already in 1932, a process based on a copper-chromite catalyst (CuO·Cr<sub>2</sub>O<sub>3</sub>) was reported to yield 1,2-PDO from glycerol [24]. More recent examples of catalysts used for this conversion include supported and bulk copper catalysts (e.g. CuZnO), supported ruthenium catalysts, and even homogeneous complexes were reported to be efficient and selective at 200–250 °C and under 150–250 bar. As an optimized process, the reaction pathway involves the dehydration of crude glycerol to give an acetal intermediate (1st step), followed by the hydrogenation of the acetal to propylene glycol under 10 bar of H<sub>2</sub> at a reaction temperature of 200 °C. This two-step process affords propylene glycol in high yields (>70%) [28]. The hydrogenolysis process has been commercialized by Archer Daniels Midland (ADM), for instance, producing biobased propylene glycol either at industrial-grade or at USP-specifications-grade. In 2012, BASF and Oleon have started up a new manufacturing plant in Belgium for the production of propylene glycol from glycerol, with an annual production of 20 kT. These recent developments show the potential and economic viability of the glycerol-based route.

### 3. Metrics analysis

A metrics analysis has been carried out in order to compare the fossil-based CHPO and renewables-based glycerol hydrogenolysis route for the production of 1,2-PDO. For a comprehensive comparison, a large number of parameters need to be assessed in the calculations, but here we aim for a more crude, but rather quick, first assessment of sustainability and competitiveness. Four metrics were selected for this, as these are considered essential to give a first estimation of how the potential routes compare. We therefore focused on material efficiency (E factor), energy efficiency, land use and economic added value.



**Scheme 4.** A bio-based route to 1,2-PDO, based on oils and fats, involves the production of glycerol via transesterification and its subsequent conversion by hydrogenolysis.

### 3.1. E factor

The E factor, as defined by Sheldon [29], allows for a quick assessment of the environmental footprint of a specific manufacturing process by expressing the amount of waste produced per kilogram of product. The E factor for both bio-based routes to 1,2-PDO has been determined, taking the overall reaction stoichiometries for the petrochemical (1) and bio-based (2) routes into account (Scheme 5). The different variables used for the E factor calculations are presented in Tables 1 and 2.

Given the overall stoichiometry of the reaction (Scheme 5) and assuming a 100% yield, the E factor (calculated as the weight amount of waste per weight amount of desired product) is 1.01 for the petrochemical process (1). From a conceptual point of view, H<sub>2</sub> should not be considered as waste, leaving only NaOH and HCl to be considered. It should be noted though that the inclusion of the hydrogen as waste would not change the calculation much, given its low molecular weight. If we assume a propylene oxide (PO) yield of 95%, an 80% yield of 1,2-PDO starting from PO, as well as a 100% yield of Cl<sub>2</sub> formation via electrolysis, then the E factor would increase to 1.33.

Biodiesel in Europe is mainly derived from rapeseed oil, of which the triglycerides in turn are composed mainly of oleic acid (>60%) and linoleic acid (ca. 20%). In order to simplify calculations for the bio-based route, all triglycerides were assumed to be esters of oleic acid (Table 2). The biodiesel, being the main product of the transesterification reaction, cannot be considered as waste. Therefore, again assuming a 100% yield, the E factor of the bio-based route would be 0.24. This value is 4 times smaller than the one obtained for the petrochemical route (1.01), indicating that the former is more sustainable at least from the point of view of avoiding waste formation. Moreover, the main “waste” product in the glycerol route would be water (Scheme 5). The material efficiency, defined as 1/(E + 1), is 0.81 for the renewables-based route, while it is 0.50 for the petrochemical technology.

### 3.2. Energy efficiency and total energy input

The energy efficiency of the two processes has been calculated as proposed by Sanders and Sheldon [11]: Energy efficiency =  $\frac{\text{combustion energy of products}}{\text{combustion energy of reactants} + \text{energy requirements of the process}} \times 100$

Heats of combustion of reactants and products can be found in Tables 1 and 2 for the petrochemical and the bio-based route, respectively.

For the petrochemical route, the combustion energy of products and reactants is 2114 and 2058 kJ/mol, respectively (Table 1). Estimating the energy requirements of the process, literature values for the production of propene range from 7.0 to 13.5 GJ/ton (depending on the method being deep catalytic cracking of vacuum gasoil (VGO), propane dehydrogenation, etc.) [31]. The production of propylene oxide from propene via the chlorhydrin process has been estimated to require 25.2–31.8 GJ/ton [32]. Finally, the last step of the process, the transformation of propylene oxide into 1,2-PDO, requires ca. 2.0 GJ/ton [33]. When all these values are considered, the energy efficiency of the petrochemical process would be in the range of 45.8–53.3%.

As mentioned above, one of the drawbacks of the chlorhydrin process is that it requires chlorine, the production of which via electrolysis being one of the most energy demanding processes. It is estimated to consume ca. 3000 kWh/t Cl<sub>2</sub>, which would result in 767 kJ/mol 1,2-PDO [34]. In fact, a reduction in energy consumption of 35% has been claimed for the HPPO technology as compared to the CHPO process [16]. This would result in a 52.3–61.2% energy efficiency for that particular route. As for the energy efficiency of

the bio-based route, the data in Table 2 shows combustion energies of products and reactants of 37,291 and 37,530 kJ/mol, respectively.

To estimate the energy requirements of the process, calculations were performed again taking rapeseed oil as the starting point. Energy requirements for the production of biodiesel involve cultivation (16.78 GJ/ha), transportation (0.18 GJ/ha), electric power for transesterification and oil extraction (6.45 GJ/ha) [35]. Nevertheless, we should emphasize that glycerol is in fact not the desired product of the transesterification reaction but the ineluctable co-product of biodiesel production and the energy required for the esterification step should be weighted to the respective amounts of biodiesel and glycerol produced. We should also take into account that the production of 1 ton glycerol requires 7.1 Ha (see land use section below). This would result in an energy requirement of 166.2 GJ/ton glycerol or 15,308 kJ/mol. Considering that the hydrogenolysis step can be performed with crude glycerol (85%), no purification step is needed. Finally, glycerol must be reacted with hydrogen to yield 1,2-PDO; considering the heat capacities (C<sub>p</sub>) of glycerol (221.9 J/mol °C) and C<sub>v</sub> hydrogen (20.32 J/mol °C), a reaction temperature of 250 °C, heating from 25 °C up to 250 °C and assuming a H<sub>2</sub>/glycerol molar ratio of 75, the process would involve a total energy of 393 kJ/mol glycerol or 4.3 GJ/t. All in all, the estimated energy efficiency would be ca. 70%. This value is in any case greater than the one obtained for the petrochemical route.

### 3.3. Land use

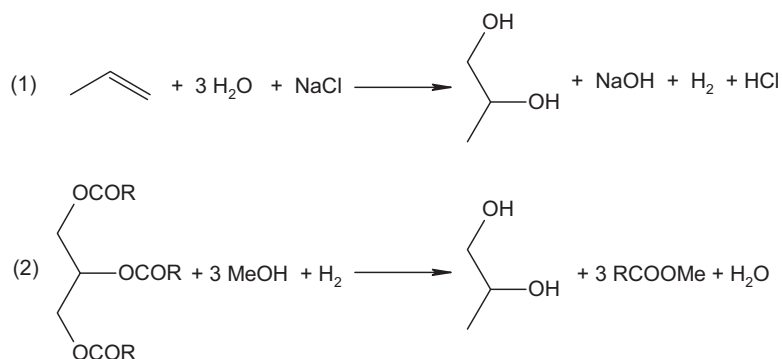
As stated above, biodiesel is mainly produced from rapeseed in Europe. According to the 2011 report of the Food and Agriculture Organization of the United Nations (FAOSTAT) [36], the yield for the production of rapeseed in France (adopted by consensus as a reference in the series of sustainability metrics assessments that this contribution is part of) is 3.45 ton/Ha. Assuming an average 41% fat content in rapeseed, this would equate to 1.41 ton oil/Ha rapeseed. As the biodiesel/glycerol ratio is 90/10 by weight, this would mean that 0.141 ton glycerol/Ha can be obtained, resulting in a land use of 7.1 Ha/ton. As already mentioned, the first use of this land is for biodiesel production and glycerol is the co-product that must be co-valorized.

For the petrochemical route, the land use is considered 0 Ha/ton. Actually, the petrochemical plant itself occupies some space, but this should be more or less equal to the space occupied by the biomass plant. The land use for the petrochemical route was therefore set to 0 Ha/ton, again by consensus.

### 3.4. Cost investment

Estimation of the costs of the 1,2-PDO production processes is complicated by the many factors involved (e.g. variable feedstock price, country of production, etc.) and the fact that some of this information is not readily available in the public domain. Based on the few reports that are available, the estimations show, however, that it can be inferred that the bio-route can be competitive.

An additional point that needs to be taken into account is the impact of selling the co-products of the process on the overall costs. This idea is well illustrated in a recent paper by Ghanta et al. [16]. Indeed, the authors compared different petrochemical PO production technologies and concluded that the PO/TBA process was the most profitable technology. An estimated profit of ca. 1450 euro/t was reported, despite the fact that production costs (2484 euro/t) were above the estimated market price of PO (2000 euro/t). This is because TBA, which is obtained as a stoichiometric co-product (ca. 2.4 t TBA/t PO) can be sold for a price of ca. 680 euro/t mainly as feedstock for MTBE production [16,37]. This again emphasizes the fact that in the calculation of the E factors for the petrochemical alternatives to the CHPO process,



**Scheme 5.** Overall stoichiometric reactions for the production of 1,2-PDO.

**Table 1**

Molecular weight and heat of combustion of the different compounds involved in the preparation of 1,2-PDO via the petrochemical route.

	$\text{C}_3\text{H}_6(\text{g})$	$\text{H}_2\text{O}(\text{l})$	$\text{NaCl}(\text{s})$	$\text{NaOH}(\text{s})$	$\text{C}_3\text{H}_8\text{O}_2(\text{l})$	$\text{H}_2(\text{g})$	$\text{HCl}(\text{g})$
Molecular weight (g/mol)	42.0	18.0	58.5	40.0	76.0	2.0	36.5
$\Delta H_c^\circ$ (kJ/mol)	-2058	0	0	0	-1828	-286	0

**Table 2**

Molecular weight and heat of combustion of the different compounds involved in the preparation of 1,2-PDO using the bio-based route. Rapeseed was assumed as the starting material and for simplicity it was considered to contain 100% oleic acid triglyceride ( $\text{C}_{57}\text{H}_{104}\text{O}_6$ ) [30].

	$\text{C}_6\text{H}_5\text{O}_6\text{R}_3(\text{g})$	$\text{CH}_3\text{OH}(\text{l})$	$\text{H}_2(\text{g})$	$\text{C}_3\text{H}_8\text{O}_2(\text{l})$	$\text{RCOOCH}_3(\text{l})$	$\text{H}_2\text{O}(\text{l})$
Molecular weight (g/mol)	885.5	32.0	2.0	76.1	296.5	18.0
$\Delta H_c^\circ$ (kJ/mol)	-35,066	-726	-286	-1828	-11,821	0

styrene and *t*-butanol can obviously not be considered as waste; in fact, it is their added value that makes the process profitable.

A recent report by SCI in China compares production costs of several PO production technologies based on feedstock prices in 2012 [38]. The study concluded that the lowest production costs for the MTBE/PO technology (ca. 700 euro/t) were the lowest, whereas for CHPO, the technology considered as the benchmark for our calculations, production costs were estimated to be ca. 1316 euro/t. Assuming that the bio-based route can make use of technical-grade glycerol (>97%, market price below 700 euro/t) or even crude-grade glycerol (85%, 400 euro/t), it seems there is a reasonable margin to consider the bio-based route cost-competitive compared to the petrochemical route [39].

The energy required for the last step is ca. 2.0 GJ/t and 4.3 GJ/t for the propylene oxide and glycerol route, respectively. The related costs, with an average price of energy (gas) of 12.5 euro/GJ, are thus estimated to 25 euro/t and 54 euro/t for the fossil and bio-based route, respectively. Again, although these calculations are highly dependent on feedstock prices, they do give an estimation of the potential of the bio-based alternative.

### 3.5. Comparison

The data calculated for fossil and renewable-sources are compared in Table 3.

It is clear from Table 3 that the bio-based route allows for a more efficient use of material and energy. This is mainly due to the fact that the chlorhydrin process produces a large amount of

**Table 3**

Comparative metrics evaluated for fossil and renewables-routes.

	Material efficiency (E-factor)	Energy efficiency	Land use
PO route	50% (1.01)	52–61%	0
Glycerol route	81% (0.24)	ca. 70%	7 Ha/t

salts and that it requires the production of  $\text{Cl}_2$ . Alternative fossil routes produce other co-products (e.g. styrene, *t*-butanol), which should not be considered as waste and will thus have significantly improved E factors (and thus material efficiency). Concerning the land use, as expected, the glycerol route requires a significant area of arable land, but it should be stressed that the glycerol is in fact a “waste” fraction of the biodiesel industry, representing 10 wt.% of the production volume of this industry. In other words, in as far as the biodiesel is produced from rapeseed, the concomitant formation of glycerol is ineluctable and the total use of the land should not only be dedicated to 1,2-PDO. Indeed, the biorefinery approach should be aimed at maximum valorization of the selected biomass and should ideally use the entire plant both for food and chemical applications. Alternatively, lignocellulosic biomass could be used for the production of 1,2-PDO within an integrated biorefinery; this route is promising, but the technology is still in its infancy. Finally, also the cost estimations show that the bio-based route should be considered as a real alternative to the petrochemical-based production of 1,2-PDO. However, it is clear that the final costs will strongly depend on the market price of the starting materials which will in turn be influenced by the global development in fossil fuel (including shale gas) and biofuel production [40].

## 4. Conclusion

The presented metrics allow for a concise and practical comparison of the synthesis of 1,2-PDO via a fossil or bio-based route. The comparison between the chlorhydrin process and glycerol hydrogenolysis route indicates that both approaches are competitive considering the four selected metrics (E factor, energy efficiency, land use and economic added value). The calculations demonstrate that the glycerol route gives better material and atom efficiency, but needs more arable land. The final costs and economics of the process will strongly depend on the price of

starting material, which can fluctuate considerable and is market-dependent, as well as on the value of any co-products obtained.

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